THE DIFFUSION OF GASES THROUGH GRAPHITES

by

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SUMMARY

The general aim of the project was to collect low pressure gas diffusion data for samples of graphite donated by the Australian Atomic Energy Commission, and to use these data to elucidate further the mechanism of gas transport in graphites.

The particular aim of the experimental work described in this thesis was to establish an explicit relation between the effective diffusion coefficient D_{eff} and the determining variates, viz. pressure, concentration, and molecular weight of the diffusing gases using Morgan EY9-166 graphite as the diffusion diaphragm.

Transient-state measurements of the diffusion of the radio-active isotopes Kr^{85} and Xe^{133} through their respective inactive isotopes and through equilibrium binary mixtures of the inactive isotope and another rare gas were performed in five two-compartment cells. A graphite specimen provided the diffusion path between the two compartments of a cell.

A statistically designed set of 150 runs yielded a set of values of α (the effective diffusion coefficient multiplied by a cell constant) from which a regression model of the form

$$\log\alpha = m + c + g_1 + g_2 + s + b\left[\log(p + 60) - P\right]$$

was derived.

In this expression m is the mean of all values of α, c_j the deviation from the mean due to the j^{th} cell; g_1, g_2 and s deviations due to the active gas, the inactive gas and the relative proportions of each; p (torr.) the pressure; P the mean value of log (p + 60) and b the pressure regression coefficient which, for these experiments, had a mean value of −0.47 indicating that the pressure dependence of α was not a simple reciprocal one as predicted by an earlier model. Further, the value of b was dependent on the gases used and their relative concentrations.

It was also found that the regression model

(1) fitted samples of published data,

(2) predicted that the effective self diffusion coefficients of Kr and Xe were inversely proportional to the square-roots of their molecular weights at low pressures, confirming earlier work, and

(3) showed that D_{eff} is concentration-dependent.

This is the first experiment to use more than one gas pair per specimen. However, the ranges of gases, compositions and pressures were not sufficiently large to form adequate regressions of α on molecular weight or molar concentrations. Nevertheless, significant variations in α were recorded.

The effects of pore structure and surface properties on the diffusion rates could not be quantitatively assessed because only one type of graphite was used and because no comparative model for diffusion in capillaries exists.

I certify that this Thesis contains no material which has been accepted for the award of any other Degree or Diploma in any University and that, to the best of my knowledge and belief, this Thesis contains no material previously published or written by any other person except when due reference is made in the text of the Thesis.

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1. INTRODUCTION

Graphite is one of the few materials with good moderating properties (1,2), i.e. the ability to slow down the fast neutrons liberated in a nuclear reactor without capturing many of them. This property, coupled with its high strength at high temperatures and its good thermal conductivity, makes graphite a very attractive material for the construction of nuclear reactors.

Research work done by the Australian Atomic Energy Commission has shown that one of the most suitable atomic power reactors for Australian conditions would be the high-temperature gas-cooled graphite-moderated reactor. Fuel elements for this reactor would be enclosed in a graphite can, which would provide the heat transfer surface for the cooling gas. The use of graphite would enable the reactor to be run at a much higher temperature than is possible using metal-clad fuel elements. However the greatest problem associated with the use of graphite as a fuel can is its high permeability. If commercial graphites were used, gaseous fission products could readily diffuse through the can walls, and contaminate the cooling gas. For successful operation, a millionfold reduction in the permeability of commercial reactor-grade graphites would need to be achieved (3,4).

In considering the flow of gas mixtures through porous media, the rate of flow of any one species is governed by

(1) the nature and magnitude of the driving forces,
(2) the other gases present in the mixture,
(3) the pore structure of the porous medium,
(4) the manner in which each gas interacts with the pore walls,
(5) the mean pressure of the system, and
(6) the mean temperature of the system.

In the present project, the general aims were:

(1) to develop an apparatus suitable for measuring the diffusion of gases through graphite at pressures less than one atmosphere,
(2) to provide diffusion data for the graphites supplied by the A.A.E.C.,
(3) to study the effects of pressure and different gas mixtures on the diffusion coefficient, and
(4) if possible, to elucidate further the mechanism of gas transport in porous materials.

The thesis commences with a review of the literature, which comprises Chapters 2, 3 and 4. In Chapter 2, the theory of diffusion in gases is summarised, the lack of experimental work in the transition region between Knudsen and bulk-phase diffusion noted, and conclusions relevant to the study of gaseous diffusion in porous media listed. A summary of the properties of porous media which are likely to influence diffusion rates, is presented in Chapter 3. In Chapter 4, the theoretical and experimental work on the diffusion of gases in porous media is reviewed. In particular, some of the basic concepts are clarified, previous assumptions stated, the contribution of previous work assessed, and scope for future work delineated.

A discussion of the alternative experimental methods is presented in Chapter 5. Here also, the preliminary experiments are described and the results obtained from them evaluated.

An assessment of the results of the preliminary experiments coupled with the findings of the literature survey led to the decision to limit the investigations to Morgan EY9-166 graphite and to design a set of experiments in such a way that the resulting data could be used to establish an explicit empirical correlation between the measured diffusion coefficients and the pressure and various gas mixtures. The final apparatus and the experimental plans and procedure necessary to carry out this investigation are described in Chapter 6.

The method of deriving the final results from the recorded data, the analysis of these results and a discussion of the experimental work follow in logical sequence. Finally, the conclusions drawn from the results, together with recommendations for future work, are listed in Chapter 10.

2. DIFFUSION IN GASES

When internal or external forces act on a multicomponent multiphase fluid system, a rearrangement of the chemical species occurs until the forces are reduced to zero, i.e. until thermodynamic equilibrium is reached. This rearrangement is termed mass transfer. It may be accompanied by momentum and energy fluxes, depending on the nature of the forces involved. In the chemical engineering literature, the terms "diffusion" and "mass transfer" are used more or less interchangeably. Here, "mass transfer" is used as a general term embracing all mechanisms of transport of chemical species relative to each other in a given system, and "diffusion" describes mass transfer by molecular motion within a single phase.

2.1 Relation between Fluxes and Forces

For each force acting on a given system, a relation linking it to the flux it produces can be found. It is known that such relationships are linear over a wide range of experimental conditions (5, p.31), and that where two or more transport processes occur simultaneously, they may interact to produce cross effects which are also linear. These observations are expressed by the relation

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \qquad j=1,n \qquad \ldots\ldots (2.1\text{-}1)$$

where J_i is the i^{th} flux, X_j the j^{th} force and L_{ij} the "phenomenological coefficient" connecting them.

Onsager (10) was able to show that, by carefully defining the fluxes and forces, the coefficients controlling the cross fluxes would be equal, i.e.

$$L_{ij} = L_{ji} \qquad \text{.....} \; (2.1-2)$$

Very complete discussions of Eq. 2.1-1 and Eq. 2.1-2 have been given in recent texts on non-equilibrium thermodynamics (5,6). It is sufficient to state here that the definition of the L_{ij} depends on the units chosen for J_i and X_j and on the reference frame to which the various J_i are referred. If consistent units are chosen for J_i and X_j, the L_{ij} have the dimensions (length^2/time), and are referred to the same frame as J_i. In general, however, the reference frames for both J_i and L_{ij} must be specified. For the particular case of molecular diffusion coefficients, the X_j have been defined in terms of molar or mass concentration gradients, partial pressure or chemical potential gradients, and J_i and L_{ij} have been referred to coordinates with origins at the centre of mass, the centre of volume or some fixed point in the apparatus. Eq. 2.1-2 is not true for all such definitions. Both texts mentioned above have discussed the conditions for which Eq. 2.1-2 applies.

2.1.1 Ordinary Diffusion in Multicomponent Mixtures

Bird (7), in an excellent review article, stated that mass transfer can occur by one or more of eight distinct processes, of which four are diffusion processes. Thus for diffusion only, he pointed out that the total flux of a diffusing component was equal to the sum of the fluxes due to concentration gradients (ordinary diffusion), pressure gradients (pressure diffusion), external forces (forced diffusion) and temperature gradients (thermal diffusion). For Eq. 2.1-2 to hold, it would be necessary to define separate diffusion coefficients for the direct and cross effects. Using results from the kinetic theory of gases, Bird (9) was able to define a system of fluxes and forces such that only two types of coefficient, each referred to the molar average velocity ($\underset{\sim}{v}^{*}$) were necessary, viz. D_{ij}, a multicomponent diffusion coefficient, and D_i^T a multicomponent thermal diffusion coefficient. His expression[†] for the mass flux (referred to the mass-average velocity) for ordinary diffusion acting alone in a multicomponent single phase system is

$$\underset{\sim}{j}_i = (C^2/\rho RT) \sum_{j=1}^{n} M_i\, M_j\, D_{ij} \left[x_j \sum_{\substack{k=1 \\ k \neq j}}^{n} (\partial \bar{G}_j/\partial x_k)_{T,p,x_s \atop s \neq j,k} \underset{\sim}{\nabla} x_k \right] \qquad \ldots.(2.1\text{-}3)$$

[†] The notation in this thesis follows ref. 9 as closely as practicable.

where C is the concentration of the mixture,

ρ its density,

M_i, M_j the molecular weights of i and j,

x_j the mole fraction of j, and

$\bar{G}_j$ its partial molal free energy.

For the special case of binary diffusion Eq. 2.1-3 simplifies to

$$\underset{\sim}{j}_A = -(C^2/\rho)\, M_A\, M_B\, D_{AB}\, (\partial \ln a_A / \partial \ln x_A)\, \underset{\sim}{\nabla} x_A \quad \ldots\ (2.1\text{-}4)$$

where a_A is the activity of A. The driving force is expressed as a chemical potential gradient.

In experimental work, the driving forces normally measured are concentration gradients, so, for binary diffusion, Fick's first law, viz.

$$\underset{\sim}{J}_A^{*} = -\mathcal{D}_{AB}\, \underset{\sim}{\nabla} C_A \quad \ldots\ldots\ldots\ (2.1\text{-}5)$$

where $\underset{\sim}{J}_A^{*}$ is the molar flux referred to the mean molar velocity, and C_A is the molar concentration of A, has been the starting point for the evaluation of most experimental results.[†]

[†] This definition of Fick's first law follows ref. 9 where a table of the equivalent forms of Eq. 2.1-5 is given on p. 502.

The expression equivalent to Eq. 2.1-5 for the molar flux referred to stationary coordinates is

$$\underset{\sim}{N}_A = - C \mathcal{D}_{AB} \underset{\sim}{\nabla} x_A + x_A (\underset{\sim}{N}_A + \underset{\sim}{N}_B) \quad \ldots\ldots\ldots (2.1\text{-}6)$$

and for the mass flux referred to the centre of mass velocity is

$$\underset{\sim}{j}_A = - \mathcal{D}_{AB} \underset{\sim}{\nabla} \rho_A = - (C^2/\rho)\ M_A\ M_B \mathcal{D}_{AB} \underset{\sim}{\nabla} x_A \quad \ldots (2.1\text{-}7)$$

whence, by comparison with Eq. 2.1-4

$$\mathcal{D}_{AB} = D_{AB} (\partial \ln a_A / \partial \ln x_A) \quad \ldots\ldots\ldots (2.1\text{-}8)$$

In all these expressions $\mathcal{D}_{AB}$ is referred to the molar-average velocity. For ideal binary mixtures (e.g. low density gas mixtures such as those used in the present experimental work) where the chemical potential and concentration gradients are equal, then

$$\mathcal{D}_{AB} = D_{AB} \quad \ldots\ldots\ldots (2.1\text{-}9)$$

however, Eq. 2.1-9 does not hold for mixtures of more than two components as D_{AB} is a multicomponent coefficient but $\mathcal{D}_{AB}$ a binary diffusion coefficient. To make this distinction clear, Eq. 2.1-3 has been written in the form (9)

$$\underset{\sim}{\nabla} x_i = \sum_{j=1}^{n} (1/C \mathcal{D}_{ij})(x_i \underset{\sim}{N}_j - x_j \underset{\sim}{N}_i) \quad \ldots\ldots\ldots (2.1\text{-}10)$$

where N_i and N_j are molar fluxes referred to stationary coordinates.

For the special case of an ideal ternary mixture, it can be shown that

$$D_{12} = \mathcal{D}_{12}\left[1 + \left(x_3(M_3\,{}_{13}/M_2 - \mathcal{D}_{12})/(x_1\mathcal{D}_{23} + x_2\mathcal{D}_{13} + x_3\mathcal{D}_{12})\right)\right] \qquad \text{.......} \; (2.1\text{-}11)$$

The $\mathcal{D}_{ij}$ defined by Eq. 2.1-10 are preferred for measurements of diffusion in multicomponent systems as they are almost independent of concentration in ideal mixtures whereas the D_{ij} are strongly concentration dependent as evidenced by Eq. 2.1-11.

Frequently it is convenient to define an effective binary diffusion coefficient $\mathcal{D}_{im}$ by analogy with Eq. 2.1-6 for the diffusion of i in a mixture, thus

$$\underset{\sim}{N}_i = -C\mathcal{D}_{im}\underset{\sim}{\nabla}x_i + x_i\sum_{j=1}^{n}\underset{\sim}{N}_j \qquad \text{.......} \; (2.1\text{-}12)$$

whence

$$1/C\mathcal{D}_{im} = \left[\sum_{j=1}^{n}(1/C\mathcal{D}_{ij})(x_j\underset{\sim}{N}_i - x_i\underset{\sim}{N}_j)/(\underset{\sim}{N}_i - x_i\sum_{j=1}^{n}\underset{\sim}{N}_j)\right] \qquad \text{.......} \; (2.1\text{-}13)$$

2.2 The Continuity Equation

In any fluid system undergoing change, the principles of conservation of mass, momentum and energy must be obeyed. The equations describing them have been discussed in detail for multicomponent systems by Bird (7,9). For ordinary diffusion, only the principle of conservation of mass is required. The equation describing it is called the equation of continuity.

In a binary mixture, the equation of continuity, referred to stationary axes and expressed in terms of moles of component A, is

$$\partial C_A / \partial t + (\underset{\sim}{\nabla} \cdot \underset{\sim}{N}_A) = R_A \qquad \ldots\ldots\ldots (2.2\text{-}1)$$

where R_A is the molar rate of production of A by chemical reaction.

If Eq. 2.2-1 is combined with the corresponding form of Fick's first law (Eq. 2.1-6) then

$$\partial C_A / \partial t + (\underset{\sim}{\nabla} \cdot C_A \underset{\sim}{v}^{*}) = (\underset{\sim}{\nabla} \cdot C \mathcal{D}_{AB} \underset{\sim}{\nabla} x_A) + R_A \qquad \ldots\ldots\ldots (2.2\text{-}2)$$

where $\underset{\sim}{v}^{*}$ is the mean molar velocity of the system. Eq. 2.2-2 is quite general and therefore cumbersome. However, for low-density non-reacting gases at constant temperature and pressure, C and $\mathcal{D}_{AB}$ are constant, and $R_A = R_B = 0$. If, in addition, the experimental conditions are so arranged that either $\underset{\sim}{v}^{*} = 0$ (equi-molar counter-diffusion) or x_A is only a trace (9, p. 593) then Eq. 2.2-2 reduces to

$$\partial C_A / \partial t = \mathcal{D}_{AB} \nabla^2 C_A \qquad \text{..... (2.2-3)}$$

which is often termed Fick's second law of diffusion.

The derivations of the equations of change from a molecular viewpoint indicate that they are only applicable where the local density, velocity and temperature do not change over distances of the order of a mean free path, consequently Eq. 2.2-1 does not describe changes in a "Knudsen" gas, i.e. a gas which is so dilute that constituent molecules collide only with the walls of the containing vessel and not each other.

2.3 <u>Theory of Ordinary Diffusion in Dilute Gases</u>

2.3.1 <u>Diffusion Expressions based on the Kinetic Theory of Gases</u>

Chapman and Enskog (11) derived highly sophisticated expressions for $\mathcal{D}_{AB}$ from the kinetic theory of gases. An exhaustive discussion of their work has been given in a comprehensive text by Hirschfelder et al (8). According to their theory, the first approximation for $\mathcal{D}_{AB}$ is given by

$$C\,\mathcal{D}_{AB} = 2.2646 \times 10^{-5}\, T^{\frac{1}{2}}\, (1/M_A + 1/M_B)^{\frac{1}{2}} / \sigma_{AB}{}^{2}\, \Omega_{\mathcal{D},AB} \qquad \text{..... (2.3-1)}$$

where $\Omega_{\mathcal{D},AB}$, the collision integral, is a dimensionless function of temperature and the inter-molecular potential field between A and B, and σ_{AB} measured in Ångstrom units, is the distance of separation for a minimum in the potential field. If the ideal-gas law holds, C may be replaced by p/RT, whence

$$\mathcal{D}_{AB} = 0.0018583\ T^{3/2}\ (1/M_A + 1/M_B)^{\frac{1}{2}} / p\ \sigma_{AB}{}^2\ \Omega_{\mathcal{D},AB} \qquad \text{.......}\ (2.3\text{-}2)$$

Higher approximations have the form

$$(\mathcal{D}_{AB})_k = (\mathcal{D}_{AB})_1\ f^{(k)}_{\mathcal{D}_{AB}} \qquad \text{.......}\ (2.3\text{-}3)$$

where $f^{(k)}_{\mathcal{D}_{AB}}$ is a complex factor taking into account the dependence of $\mathcal{D}_{AB}$ on concentration (8, p. 539,12).

If self diffusion is considered as a special case of binary diffusion (e.g. the diffusion of the isotopic pair A and A^* where $M_A \simeq M_A{}^*$), Eq. 2.3-1 becomes

$$C\mathcal{D}_{AA^*} = 3.2027 \times 10^{-5}\ T^{\frac{1}{2}} / M_A{}^{\frac{1}{2}}\ \sigma_A{}^2\ \Omega_{\mathcal{D}A} \qquad \text{.......}\ (2.3\text{-}4)$$

The intermolecular potential function $\Omega_{\mathcal{D}}$ allows for the forces of attraction and repulsion between molecules. Currently it must be evaluated by assuming arbitrary potential functions. Bird (7) has discussed the use of two such functions. The parameters in σ and $\Omega_{\mathcal{D}}$ can be estimated from diffusion measurements or from viscosity data. Because viscosity data provide more accurate estimates of σ_A than σ_{AB}, self rather than binary diffusion measurements have been preferred for comparing potential functions (8, p. 540 and 580; 14, p. 426).

Summarising, the kinetic theory predicts

(1) that $\mathcal{D}_{AB} \propto T^{3/2} p^{-1}$,

(2) that as $p \to 0$, ${}_{AB} \to \infty$, and

(3) that $\mathcal{D}_{AB}$ is a complex function of the molecular properties, i.e. the effects of M_A and M_B cannot be separated from σ_{AB} and $\Omega_{\mathcal{D},AB}$.

2.3.2 Empirical Relationships

Reid and Sherwood (13) have summarised the empirical methods for estimating $\mathcal{D}_{AB}$ and compared values calculated by them with those obtained from the kinetic theory and from experimental data. They concluded that the most accurate empirical equation developed to date is that of Slattery and Bird (15), viz.

$$p\,\mathcal{D}_{AB}/(p_{cA}p_{cB})^{1/3}(T_{cA}T_{cB})^{5/12}\,(1/M_A + 1/M_B)^{\frac{1}{2}} = a(T/T_{cA}^{\frac{1}{2}}T_{cB}^{\frac{1}{2}})^b \qquad \text{.......}\ (2.3\text{-}5)$$

where the subscript c indicates critical values, and a and b are experimentally determined constants.

2.3.3 Other Theories

On the basis of a "phenomenological" theory of diffusion proposed by Hartley and Crank (16), Carman and Stein (17) postulated that

$$\mathcal{D}_{AB} = x_B D_A^* + x_A D_B^* \qquad \ldots\ldots\ldots (2.3\text{-}3)$$

where D_A^* represents the diffusion of a labelled trace (A^*) of A in an equilibrium mixture of A and B.

If D_A^* is referred to $\underset{\sim}{v}^*$, the kinetic theory predicts

$$1/D_A^* = x_A/\ {}_{AA^*} + x_B/\mathcal{D}_{AB} \qquad \ldots\ldots\ldots (2.3\text{-}4)$$

where D_A^* has been written instead of $\mathcal{D}_{A^*m}$ in Eq. 2.1-13 and where it is assumed $x_{A^*} \simeq 0$.

Eq. 2.3-3 cannot be reconciled with Eq. 2.3-4. Several authors (18-21) have shown experimentally that Eq. 2.3-4 holds for gases. Miller and Carman (18) claimed Eq. 2.3-4 held because of the particular mechanism of diffusion in gases as distinct from that in liquids and solids, but other authors (22,23) have shown that Eq. 2.3-3 was derived without clear definitions of the reference frames for $\mathcal{D}_{AB}$, D_A^* or D_B^*. Thus, at least for gases, Eq. 2.3-3 is quite misleading.

The concept of measuring the diffusion of a trace of A^* in an equilibrium mixture of A and B, however, is a valuable one, because if $M_{A^*} \simeq M_A$ and $x_{A^*} \simeq 0$, $\underset{\sim}{v}^* = 0$, hence the molar and stationary (apparatus) reference frames become identical and Fick's second law is applicable. Diffusion coefficients measured with respect to the stationary frame are then equal to the diffusion coefficients referred to the molar frame (i.e. those predicted by the kinetic theory).

2.4 Knudsen Diffusion

Knudsen diffusion occurs when the gas pressure in a system is so low that the mean free path of the gas molecules is many times greater than the dimensions of the containing vessel. Under these conditions, gas molecules collide almost exclusively with the walls of the vessel and not with each other. If the simple case of transport in a straight circular capillary is considered, then the ratio of the gaseous mean free path (λ) to the capillary diameter (d) is equal to the ratio of the wall and gas collision frequencies (25), and is termed the Knudsen number (N_{Ku}).

Knudsen diffusion in a single gas species represents the limiting case of either self diffusion or slip flow under a total pressure gradient. Rutz and Kammermeyer (26), in a comprehensive review, discussed diffusion and flow processes in the Knudsen and transition regions. Timofeev (27) and Carman (28, p. 62) were content to review Knudsen diffusion as a flow process. In this work it is regarded more as the limiting case of self diffusion.

2.4.1 The Infinitely Long Capillary

A coefficient for Knudsen diffusion in circular capillaries is defined by the relation

$$N_{Az} = - D \; \partial C_A / \partial z \qquad \ldots\ldots\ (2.4\text{-}1)$$

where D is the Knudsen diffusion coefficient based on a driving force measured in terms of a concentration difference. It is referred to stationary coordinates. The early work of Knudsen (29) and Smoluchowski (30) showed that as $N_{Ku} \rightarrow \infty$ a limiting value (D_K) of D was reached. They showed

$$D_K = \bar{v}d/3 = d(8RT/\pi M)^{\frac{1}{2}} /3 \qquad \ldots\ldots\ (2.4\text{-}2)$$

where d is the capillary diameter, $\bar{v}$ the mean molecular velocity and M the molecular weight of the gas.

In their study of self diffusion in long capillaries, Pollard and Present (25) used the mean-free-path concept of the simple kinetic theory to describe the variation of D in the pressure region where both wall and gas collisions occur. They showed that the resultant mathematical expression for D was a complex function of the Knudsen number. It could be readily evaluated only for very small and very large values of N_{Ku}.

Their limiting expressions are

$$D = (\bar{v}d/3)\left[1 - d(1.2264 + 0.75\ \ln(\lambda/\gamma d))/2\lambda + \ldots\right],$$

$$\lambda >> d \qquad \ldots\ldots. \ (2.4\text{-}3)$$

and

$$D = (\bar{v}\lambda/3)(1-3\lambda/4d) \qquad \lambda << d \qquad \ldots\ldots. \ (2.4\text{-}4)$$

where γ is Euler's constant. It is easily seen that, in the extreme limit, Eq. 2.4-3 reduces to Eq. 2.4-2, and Eq. 2.4-4 reduces to

$$D = \lambda\bar{v}/3 \qquad \ldots\ldots. \ (2.4\text{-}5)$$

Eq. 2.4-5 is equivalent to $\mathcal{D}_{AA}$ based on the simple kinetic theory, i.e.

$$\lim_{N_{Ku}\to 0} D = \mathcal{D}_{AA} \qquad \ldots\ldots. \ (2.4\text{-}6)$$

For self diffusion, the molar and fixed reference frames coincide, so it is mathematically possible for D_{KA} to be the limit of D at low pressures and $\mathcal{D}_{AA}$ to be its limit at high pressures. Pollard and Present stated that Eq. 2.4-2 and Eq. 2.4-6 would also be obtained, but with different numberical constants, when the more complex Chapman-Enskog theory is used. The Chapman-Enskog constants would include the fact that the nature of a gas-wall collision is different from a gas-gas collision. Remembering that D, as defined by Eq. 2.4-1, is a function of the capillary, it is seen that D_{KA} and $\mathcal{D}_{AA}$ are true physical limits of D, but the Chapman-Enskog theory indicate that D_{KA} cannot be regarded physically as a limiting case of $\mathcal{D}_{AA}$ because D_{kA} is a function of only gas-wall collisions, whereas $\mathcal{D}_{AA}$ is a function only of gas-gas collisions. Both the simple kinetic theory and the Chapman-Enskog theory lead to limiting expressions for D (e.g. Eq. 2.4-3 and Eq. 2.4-4) which, in turn, have D_{kA} and $\mathcal{D}_{AA}$ as their limits at low and high pressures respectively. In this sense, D_{kA} and $\mathcal{D}_{AA}$ may be said to be related physically. It does not seem possible, for the reasons stated in Section 2.5, to so relate the binary coefficient $\mathcal{D}_{AB}$ to D_{kA} or D_{kB}.

Using the "Random Walk Theory" Bosanquet (31) produced an interpolation formula for calculating D from small to large values of N_{Kn}. He showed

$$D = \bar{v}d/3\ (1 + d/\lambda) \qquad \text{.......} \ (2.4\text{-}7)$$

Pollard and Present showed that Eq. 2.4-7 differed but slightly from their more rigorous analysis, indicating that for most practical purposes the two approaches give identical results.

In the derivation of Eq. 2.4-3 and Eq. 2.4-4 it was assumed that the molecular emission from the surface of the capillary obeyed the laws of diffuse reflection. To account for any specular reflection that might occur, Smoluchowski (30) introduced a factor f which represented the fraction of molecules undergoing diffuse reflection, thus:

$$D_k = (\bar{v}d/3)\left[(2-f)/f\right] \qquad \ldots\ldots\ (2.4\text{-}8)$$

However, DeMarcus (32) has since shown that this correction factor gives approximately the correct result for long capillaries only ($L/d > 100$) and is hopelessly inexact for short capillaries ($L/d \simeq 2$). For short capillaries he claimed it would be better to use no correction factor at all.

2.4.2 Short Capillaries

In the derivation of the formulae for long capillaries, the concentration gradient in the tube is assumed to be constant, but this is not quite true for short capillaries because end effects become important (25,26).

Using their kinetic theory approach, Pollard and Present showed that

(i) the slope of a plot of D against $1/N_{Kn}$ for an infinitely long tube approached a negatively infinite value as $N_{Kn} \to \infty$ but approached a finite limit for a tube of finite length, and

(ii) $$\lim_{\lambda \to \infty} D/D_\infty = 1 - 3d/8L \qquad \ldots\ldots\ (2.4\text{-}9)$$

where D_∞ is the value of D_k for a long tube.

Rutz and Kammermeyer (26) have reviewed other approaches to the short tube problem.

2.4.3 Non-Circular and Bent Capillaries

Smoluchowski (30) pointed out that it was necessary to introduce a shape factor k_1 into the expression for D_k for long capillaries. Thus, if the hydraulic radius (m) is used as the characteristic dimension of the capillary, Eq. 2.4-8 becomes

$$D_k = 4m\bar{v}(2-f)/3k_1 f \qquad \ldots\ldots\ldots (2.4\text{-}10)$$

(For circular capillaries $m = d/4$).

Clausing (33) used k_1 to correct D_k for both the length and the shape of capillary. He calculated values of k_1 for various regular shapes and L/m ratios.

The effects of bends or irregularities in capillaries were investigated mathematically by DeMarcus and Lang (34). They showed that bends or irregularities in capillary shape markedly reduced the value of D_k.

2.5 The Transition from Knudsen to Binary Diffusion

Very few flow or diffusion experiments have been carried out in long capillaries in the pressure region where the number of collisions between gas molecules begins to become significant.

Flow experiments have been performed by Knudsen (29), Gaede (35) and Adzumi (36). Knudsen reported a minimum flow as the mean pressure was increased from zero to the range where slip flow occurred. Knudsen's data as reported by Carman (28, p. 65) are shown in Fig. 2.5-1. No quantitative theoretical explanation has been put forward to explain this minimum. Pollard and Present (25) pointed out that a quantitative theoretical expression for flow could not be developed from the kinetic theory, however they did present a qualitative explanation for the observed minimum. They suggested that the increasing number of gas phase collisions would first reduce the flow by shortening the mean free path, then increase it by causing more molecules to move with a net drift velocity to the low pressure end.

In summarising previous approaches to the flow problem, Carman (28, p.64) replaced the term for specular reflection in Eq. 2.4-8 by a dimensionless factor δ in an attempt to make the one equation cover the range from Knudsen to slip flow. He claimed that for a given surface and gas, f had a constant value f_o for Knudsen flow and a different but constant value f_1 for slip flow. Also, as the slip flow term in the total flow equation differed by a factor of $3\pi/16$ from the limiting Knudsen diffusion term, he proposed that δ should vary in a somewhat arbitary fashion in the transition zone to cover changes in f and the numerical

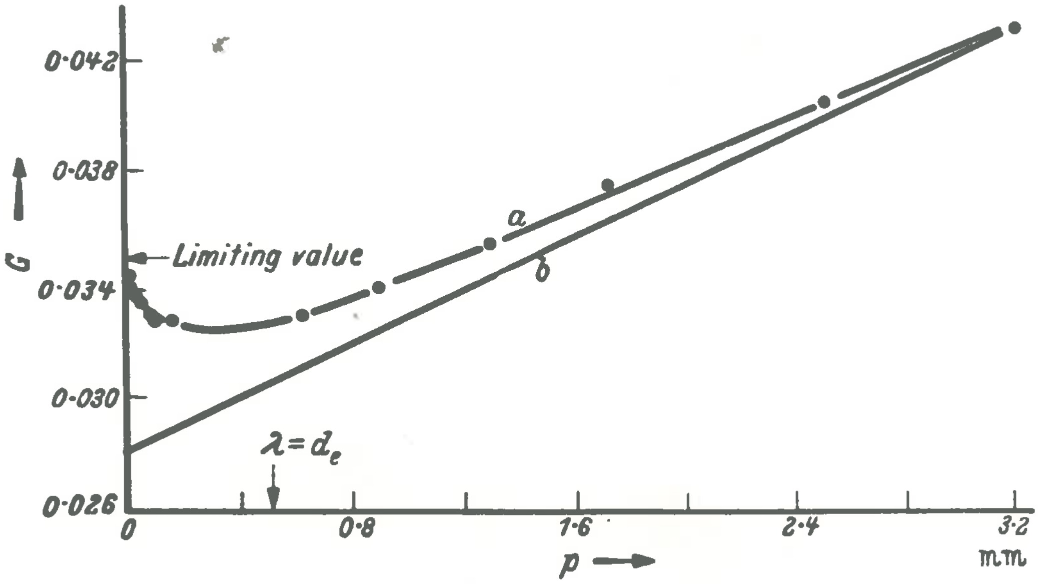

Fig. 2.5-1 Knudsen's Data as presented by Carman (28, p.65)

constant, thus he wrote Eq. 2.4-8 in the form

$$D = 4m\bar{v}\delta/3k_1 \qquad \ldots\ldots\ldots (2.5\text{-}1)$$

After comparing the mathematical approach of DeMarcus (32) and Pollard and Present with Carman's empirical approach it would seem better to regard D as a complex function of N_{Ku}, rather than to assume most of the variability to be in f.

Visner (37) has measured self diffusion and flow in capillaries of various lengths at low pressures.† No other diffusion measurements in the transition region have been carried out to the present author's knowledge.

The theoretical approaches of Bosanquet (31), and Pollard and Present were discussed in Section 2.4. It is sufficient to emphasize that, for all practical purposes, their results are identical.

Bosanquet's formula (Eq. 2.4-7) may also be written thus:

$$1/D = 1/D_K + 1/\mathcal{D}_{AA} \qquad \ldots\ldots\ldots (2.5\text{-}2)$$

Wheeler (38) has suggested the semi-empirical formula

$$D = \mathcal{D}_{AA}\left[1 - \exp(-D_K/\mathcal{D}_{AA})\right] \qquad \ldots\ldots\ldots (2.5\text{-}3)$$

---

† Visner's work has been reported by Rutz and Kammermeyer (26). The original reference is not available in Australia.

as an alternative to Eq. 2.5-2. In terms of λ and d, Eq. 2.5-3 becomes

$$D = \bar{\bar{v}} \lambda \left[1 - \exp(-d/\lambda) \right] /3 \qquad \ldots\ldots\ldots (2.5\text{-}4)$$

Eq. 2.4-7 and Eq. 2.5-4 are compared below by plotting $D/d\bar{\bar{v}}$ (Fig. 2.5-2) and its reciprocal (Fig. 2.5-3) against $1/N_{Ku}$. It is interesting to note that

(1) if Bosanquet's formula is correct, D_k may be estimated by the extrapolation of high pressure values of D to zero pressure, thus enabling correct values of $\mathcal{D}_{AA}$ to be determined, but

(2) if Wheeler's formula is correct, high pressure values of D are equal to $\mathcal{D}_{AA}$ and D_k cannot be determined from them with any precision because D_k is the point of inflection on a curve that tends to zero on a 1/D plot against pressure.

Insufficient low pressure diffusion data suitable for testing these formulae are available.

In order to provide a theoretical background for measurements of diffusion in porous media, it has been assumed that a simple relation between $\mathcal{D}_{AB}$ and D_{kA} can be derived from the kinetic theory, but no such relation can exist because

(1) $\mathcal{D}_{AB}$ is defined for the molar and D_{kA} the fixed reference frame, and

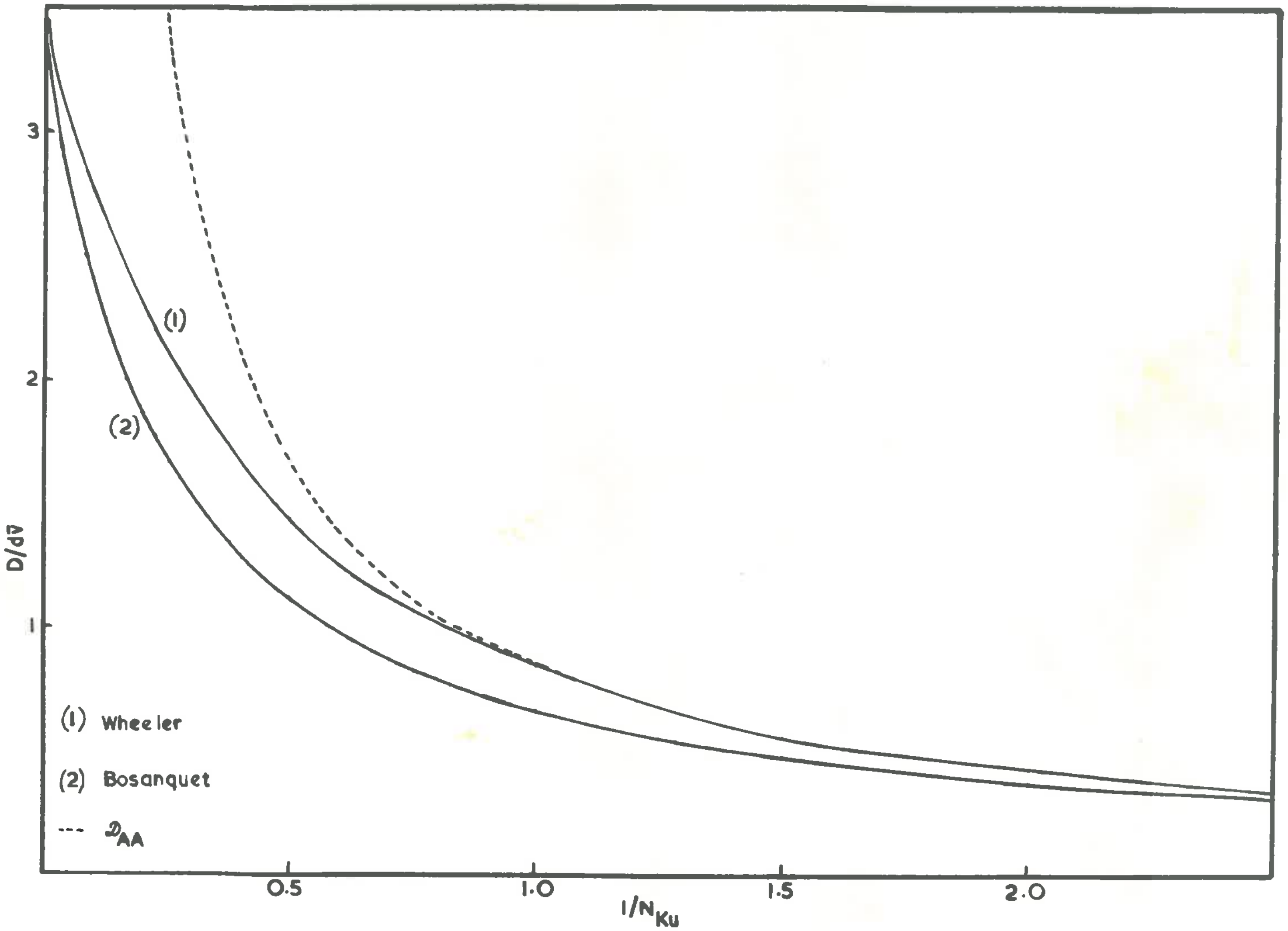

Fig. 2.5-2 A Comparison of Diffusion Models

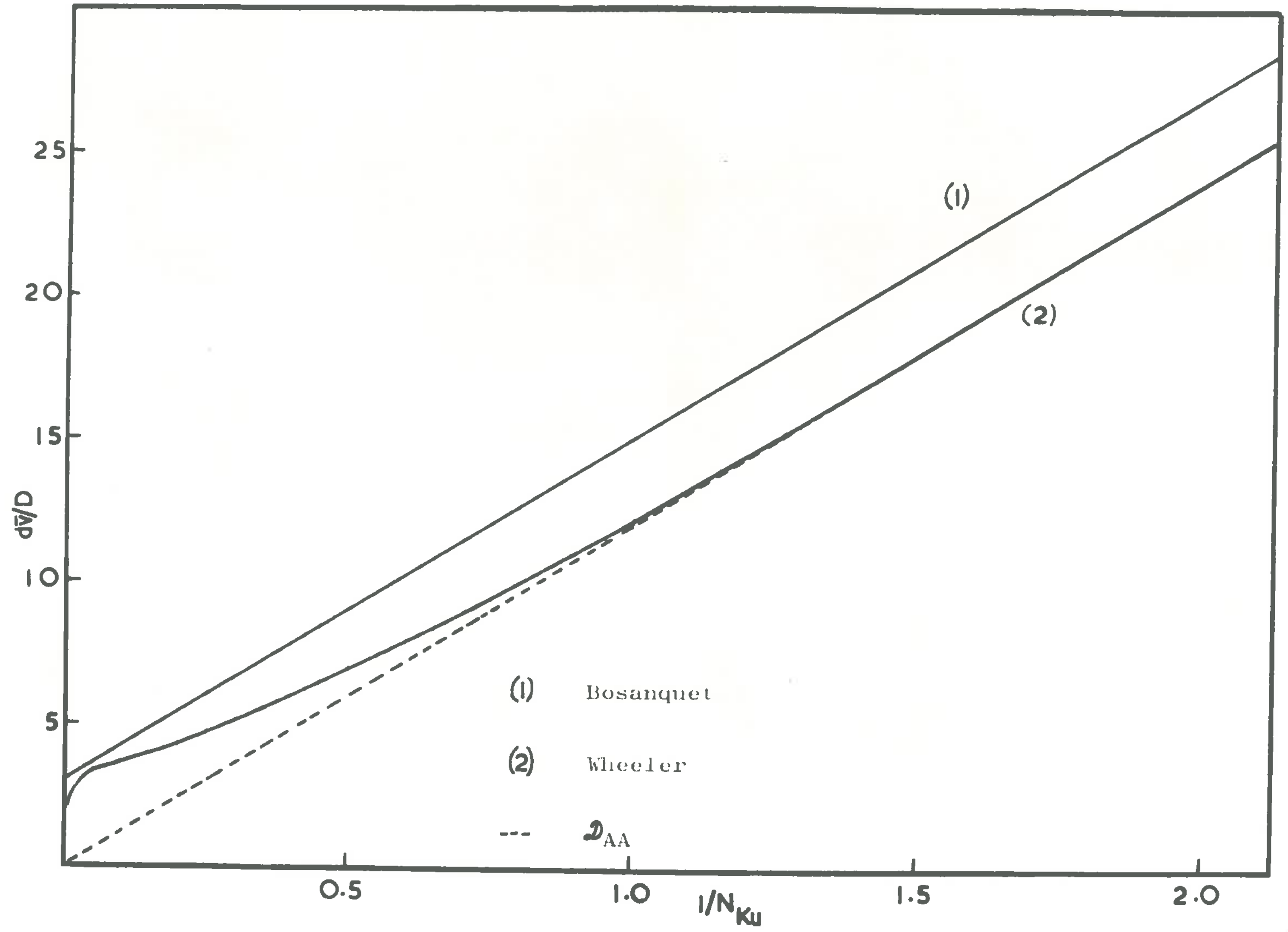

Fig. 2.5-3 A Comparison of Diffusion Models.

(2) $\mathscr{D}_{AB}$ depends only on collisions between molecules of A and B, whereas D_{kA} depends only on collisions between A and the wall,

thus a kinetic theory treatment (or any other treatment based on the physics of the system) cannot justify the substitution of $\mathscr{D}_{AB}$ for $\mathscr{D}_{AA}$ in Eq. 2.5-2, Eq. 2.5-3, or any other similar equation. (Dimensional similarity provides no guarantee of the same physical basis for observed phenomena). It is true to say, however, that $\mathscr{D}_{AB}$, D_{kA} and D_{kB} do characterise the system in that they collectively account for all the collisions, i.e. they are all conductances, hence the overall flux of A, for example, does depend on $\mathscr{D}_{AB}$ and D_{kA}, but the only type of relation possible between $\mathscr{D}_{AB}$ and D_{kA} is an empirical one based on experiment.

One can write

$$\underset{\sim}{J}_A^* = - g(\mathscr{D}_{AB}, D_{kA}) \underset{\sim}{\nabla} C_A \qquad \ldots\ldots\ (2.5\text{-}5)$$

where $g(\mathscr{D}_{AB}, D_{kA})$ referred to the molar frame, is a function of $\mathscr{D}_{AB}$ and D_{kA}, the nature of which not only depends on the variables that affect $\mathscr{D}_{AB}$ and D_{kA} individually, but also may depend on the arrangement of a particular experiment (e.g. transient or steady-state measurements, or the geometry of the diffusing system). An overall diffusion coefficient D_o can be substituted for g in Eq. 2.5-5 to obtain

$$D_o = g(\mathcal{D}_{AB}, D_{KA}) \qquad \text{.......} \ (2.5\text{-}6)$$

where D_o is similarly referred to the molar frame. Bearing in mind the empirical nature of g, two approaches are possible.

(1) An overall diffusion coefficient referred to a convenient frame is defined for a given set of experimental conditions, then the conditions are varied in a predetermined fashion to yield a set of such coefficients. The total variability within the set may then be divided into parts ascribable to each of the controlled variates and a regression model in terms of them developed thus:

$$D_o = g' \ (p, M_A, M_B, T, x_A, x_B, d, \ldots \ ) \qquad \text{.......} \ (2.5\text{-}7)$$

If sufficient data are available, it may be possible to group the determining variates in such a fashion that D_o can be expressed as an explicit function of $\mathcal{D}_{AB}$ and D_{KA}.

(2) An explicit form of g is proposed and substituted directly in Eq. 2.5-5. Experiments are then performed to test the precision of the proposed model. An overall diffusion coefficient need not be defined as the data are used to evaluate $\mathcal{D}_{AB}$ and D_{KA} explicitly.

The first approach yields more information about the diffusion process, in that the data are free to express themselves fully, but it requires a large experimental programme. The second is essentially a cut-and-try technique useful for establishing a design equation over a small range of the predetermined variates. However, the total variability in a set of data obtained to check the adequacy of a proposed model can only be divided into two parts - one ascribable to the model, the other to deviations from it. Consequently such data cannot be made to yield any new information about the diffusion process.

No experimental work based on the first approach has been published.

Scott and Dullien (39) used the second approach. They presented an elementary kinetic theory proof for Eq. 2.5-2 with $\mathcal{D}_{AB}$ substituted for $\mathcal{D}_{AA}$. Their proof contained the assumptions that the bulk and Knudsen diffusion resistances acted in series and that reference frame difficulties could be overlooked. Their expression for the total flux N_A in a steady-state counter-diffusion experiment, viz.,

$$\underset{\sim}{N}_A = -(p/RT)\left[(1-\beta x_A)/\mathcal{D}_{AB} + 1/D_{kA}\right]^{-1} \underset{\sim}{\nabla} x_A \qquad \text{.......} \; (2.5\text{-}8)$$

where

$$\beta = 1 + \underset{\sim}{N}_A/\underset{\sim}{N}_B \qquad \text{.......} \; (2.5\text{-}9)$$

does not follow from their initial equations[*], but can easily be derived by combining Eq. 2.1-10 and Eq. 2.4-1 in accordance with the above assumptions to give

$$\underset{\sim}{\nabla} x_A = (x_A \underset{\sim}{N}_B - x_B \underset{\sim}{N}_A)/C\mathcal{D}_{AB} - \underset{\sim}{N}_A/CD_{kA} \qquad \ldots\ldots\ldots (2.5\text{-}10)$$

Eq. 2.5-8 follows on rearrangement.

This model may be expressed in the form of Eq. 2.5-5 by writing

$$\begin{aligned} g(\mathcal{D}_{AB}, D_{kA}) &= 1/\left[1/\mathcal{D}_{AB} + 1/D_{kA}\,(1-\beta x_A)\right] \\ &= D_o \qquad \ldots\ldots\ldots (2.5\text{-}11) \end{aligned}$$

or, if a fixed reference frame is preferred

$$\begin{aligned} g^f(\mathcal{D}_{AB}, D_{kA}) &= 1/\left[(1-\beta x_A)/\mathcal{D}_{AB} + 1/D_{kA}\right] \\ &= D_o^f \qquad \ldots\ldots\ldots (2.5\text{-}12) \end{aligned}$$

where the superscript refers to the reference frame. In either case D_o is concentration dependent hence the explicit form of g must be used in the integration step. Scott and Dullien derived the correct integral expression for D_o^f by equating the integrated form of Eq. 2.5-8 to the integrated form of

$$\underset{\sim}{N}_A = - C\,D_o^f\,\underset{\sim}{\nabla} x_A \qquad \ldots\ldots\ldots (2.5\text{-}13)$$

---

[*] There may be a misprint in one of their equations.

to obtain

$$D_o^f = \mathcal{D}_{AB}/X_{1m} \qquad \ldots\ldots\ldots (2.5\text{-}14)$$

where $X_{1m} = (X_2 - X_1)/\ln(X_2/X_1)$

and $X_2 = 1 - \beta x_{A2} + \mathcal{D}_{AB}/D_{kA}$

Their experimental work was performed with porous media so their data are discussed in Section 4.4.

No other empirical relations for the transition region have been developed.

2.6 Conclusions

The diffusion theory outlined above provides the basis for a study of the diffusion gases in porous media. The following conclusions are listed as being of particular relevance to the present work.

1. The units and reference frame implicit in the definition of all diffusion coefficients must be specified. In this work all diffusion coefficients are defined in relation to molar fluxes and forces, and are either referred to the mean molar velocity $\underset{\sim}{v}^*$, or to apparatus-fixed axes.
2. The theory of diffusion in dilute gas mixtures is highly developed. Values of self, binary and multicomponent diffusion coefficients can be estimated quite accurately from the theoretical and empirical expressions available.

3. The theoretical approach suggested by Carman and Stein (17) does not lead to any useful result, but their idea of measuring "self-diffusion" in a binary mixture is worth investigating.

4. It is seen empirically that Knudsen diffusion is the limiting case of either slip flow or self diffusion. Knudsen diffusion coefficients can only be referred to apparatus-fixed axes. For self diffusion, the fixed and molar reference frames are identical thus Knudsen diffusion can be investigated theoretically as a limiting case of self diffusion.

5. Both the approach to and the limiting value of D itself are markedly affected by the geometry of the diffusion channel.

6. The Bosanquet interpolation formula provides an adequate description of self diffusion in the transition zone for long circular capillaries. Its relative accuracy for capillaries of different shapes and lengths has not been investigated.

7. Only an empirical relationship can exist between Knudsen and binary diffusion coefficients. Two methods of establishing it are suggested. In the first, an explicit relationship is deduced from the data, whereas in the second, it is postulated first then its adequacy is experimentally tested. The first method, as yet untried, may require more experiments but provides a more fundamental approach.

3. PROPERTIES OF POROUS MATERIALS

3.1 Properties of Porous Media in General

Porous media can be classified as consolidated or unconsolidated (28, p.7), and the pore spaces within them can be qualitatively described as voids, capillaries or force spaces according to the effect they have on hydrodynamic phenomena occurring in them (40, pt. 1).

The pore structure of an unconsolidated medium depends on

(1) the shape, size and porosity of the individual particles,
(2) the resistance that these particles have to deformation and fracture under the bed pressure, and
(3) the mode of packing of the particles.

In all unconsolidated media the primary pore structure is made up of the spaces between the particles. If the particles themselves are porous, then a secondary pore structure will be present, which may have a significant effect on hydrodynamic phenomena occurring within the bed of particles as a whole. In general, the pore structure of unconsolidated media is uniform and isotropic, and exhibits a high degree of reproducibility.

The pore structure of a consolidated medium such as graphite depends on

1. the crystal structure and chemical homogeneity of the solid matrix, and
2. the method by which the porous matrix was formed, e.g. it may have been formed by the sintering or cementing together of discrete particles, or it may have been formed by the removal of part of the solid.

In general such pore structures are non-uniform and anisotropic; even specimens cut from the one piece of porous material may have different pore properties.

In order to characterise fully a porous medium, the following "ideal" properties must be known,

1. the size and shape of individual pores,
2. the way each pore varies in size and shape along its length,
3. the total number of pores, and
4. the manner in which they are interconnected.

Even supposing these properties could be found accurately, the problem of analysing fluid flow or diffusion in the complicated network of channels found in a porous medium would still be exceedingly complex.

The only quantitative measurements that have been devised to determine pore geometry are porosity, surface area, pore-size distribution and tortuosity measurements (28,40).

Porosity and surface area measurements are fairly precise, and their physical meaning is quite clear, but no relationship exists between porosity or surface area and the four quantities listed above as necessary for proper pore characterisation. Pore-size distribution and tortuosity data even lack a clear physical meaning.

The determining parameter in pore-size distribution measurements is the cross-sectional area of the neck of a pore. If this neck leads to a pore of larger diameter, then the volume of the larger pore is recorded as having the same diameter as the neck, consequently data from these measurements can never represent a true pore-size distribution.

Tortuosity is defined as the ratio of the fluid path length to the geometric length of the specimen, but in practice it amounts to little more than a factor of ignorance (41,42). Sensible values are obtained for unconsolidated media ($q \underline{\Omega} 1.4$) but, for very fine-pored impregnated graphites, values of up to 1000 have been obtained (43). Such values make the concept of tortuosity quite meaningless.

In order to interpret the actual physical measurements in terms of definable geometric properties of the medium, a pore model must be assumed. Various models have been proposed (40, pt. 6). Of these, the simplest and most widely used is the parallel capillary model (44), but it is so unrealistic that it is quite inadequate for describing consolidated media. It does however give a useful approximation for unconsolidated media. Scheidegger's suggestion (40, pt.6) that models based on the statistics of disorder should provide the best basis for the description of hydrodynamic phenomena in porous media, seems to be the most logical so far.

Summarising then, quantitative measurements of pore geometry are limited to porosity, surface area, pore size distribution and tortuosity measurements. However, they must be related to the "ideal" properties of a porous medium by a pore model before they can be used in the evaluation of fluid transport data.

An accurate mathematical description of a porous medium, which does not employ a pore model, is only conceivable for a uniform isotropic unconsolidated medium.

3.2 Graphite

Several comprehensive reviews of the manufacturing processes, and the pore structures and properties of artificial graphites have appeared in recent years (45-52). As a result, only the salient features of the manufacturing processes are discussed in this thesis. A brief description of the relevant physical properties of graphite is also included.

3.2.1 Graphite Manufacture

Natural graphite, because of its high percentage of impurities, is quite unsuitable as a reactor material, so artificial graphite has been used exclusively for developing nuclear-grade graphite.

Artificial graphite is produced by mixing crushed and screened petroleum coke with coal tar pitch at 160°C and extruding the product into bars, which are stacked in an electric furnace and graphitised at temperatures ranging from 2500-3000°C (45-49). Graphite produced by this process has a density of 1.60 to 1.70 g/ml compared with a theoretical density of 2.25 g/ml.

Many impregnation processes have been developed to reduce the porosity and increase the density (4,48,53-55). Of these, the process involving the continuous cracking of CH_4 in a graphite specimen (53) and the process involving repeated impregnations with furfural alcohol (54,55) appear to be the most satisfactory (4,56).

In a recent graphite moulding process announced by the United States Atomic Energy Commission (57), petroleum coke is mixed with furfural alcohol and the moulded mixture is heated straight to graphitisation temperature. No details of the properties of the graphite produced by this process have been released.

3.2.2 Pore Structures and Properties

The pore structures and properties of artificial and natural graphites have been reviewed by several authors (45,46,48-52).

Graphite crystals are composed of thin hexagonal flakes (49,52). In non-impregnated artificial graphites, these flakes are very small and do not affect the pore structure to any marked extent (48). The shape, size and distribution of the pores are governed by the disposition of the original coke particles prior to graphitisation. The crushed coke consists largely of small splintery particles. When the coke-pitch mixture is extruded into bars these particles tend to align themselves parallel to the extrusion axis giving the final graphite a pronounced anisotropic pore structure (48) which is demonstrated by the fact that gases flow (58) and diffuse (59) more rapidly in the direction parallel to the extrusion axis than perpendicular to it.

A lot of work has been published on the crystal and ultra-fine capillary structure of graphite (60-63). However these ultra-fine capillaries have little effect on flow or diffusional phenomena in non-impregnated graphites. Few accurate permeability or pore size data have been published for the near-impermeable graphites that are now being produced, but it is anticipated that the ultra-fine capillary structure of the original coke particles would play a significant part in gas transport in such graphites.

In a recent comprehensive review, Culver and Watts (64) discussed the interaction of gases with carbon surfaces. They pointed out that structural changes in very porous graphites can be brought about by the penetration of adsorbate between crystallites and the intercalation of adsorbate molecules between graphitic layers. Further, Dawe and Stevens (65) have shown that the surface characteristics of graphite powders can be appreciably altered by the type of gases adsorbed on them. Although no adsorption data are available for fine-pored graphites, it is likely that adsorbed gases would have a marked effect on their gas transport properties. Further investigations of adsorption phenomena are needed for a complete understanding of the mechanism of gas diffusion in graphite.

3.2.3 Summary

The raw materials, for making nuclear-grade graphite by the standard (Acheson) process are petroleum coke and coal tar pitch. The final product is too porous for immediate use, so several impregnation processes have been developed. Furfural alcohol and methane have proved to be the two most successful impregnating materials tested to date. A new process for making graphite from coke and furfural alcohol has been announced, but no details are available.

Artificial graphite is an anisotropic porous material, whose structure and gas transport properties depend largely on the disposition of the coke particles prior to graphitisation.

The structural properties of impregnated graphites have not been well characterised but it is expected that the micro-pore structure of the original coke particles could make a significant contribution to transport phenomena. It also seems likely that adsorbed gases could markedly affect gas transport. The effects of adsorbed gases and the micro-pore structure of the original coke particles on gas transport within impregnated graphites have not been established.

4. DIFFUSION OF GASES IN POROUS MEDIA

The same driving forces that cause mass transfer to occur in bulk samples of gas mixtures are responsible for mass transfer in gas mixtures that permeate a porous medium. The porous medium acts as an extra resistance to mass transfer, and hence modifies the fluxes produced by these driving forces. Thus the rate of transfer of any one species of a gas mixture through a porous medium is governed by,

(1) the nature and magnitude of the driving forces,
(2) the other gases present in the mixture,
(3) the pore structure of the porous medium,
(4) the manner in which each gas interacts with the solid surface,
(5) the mean pressure of the system, and
(6) the mean temperature of the system.

Research workers are confronted with the problem of adequately defining each of the above factors, and of discovering how these factors individually affect the net flux observed.

Unfortunately it is not always possible to devise experiments in which one independent variable alone acts on the flux produced by a given driving force. Experimental methods have been developed to measure permeability coefficients, diffusion coefficients and adsorption isotherms, but little work has been done towards correlating them.

Since they each involve the combination of different variables affecting the flow, it may be possible to find some relationship between them, and thus identify the effects of the variables mentioned above.

In the present research project, the aim is to find out how the flux produced by one driving force only, viz. a concentration gradient, is modified by the presence of a porous medium, i.e. it is concerned with the measurement of ordinary gaseous diffusion. Consequently the following discussion is largely limited to a survey of the literature on this aspect of gas transport in porous media.

4.1 Description of Diffusive Processes

It is generally agreed that the diffusion of a component of a gas mixture which permeates a porous medium may proceed in whole or in part by one of three distinct mechanisms (66);

(1) ordinary or free-gas diffusion, in which transfer takes place wholly through the intercollision of gas molecules,

(2) Knudsen diffusion, in which the gas molecules collide only with the pore walls, and

(3) surface diffusion, in which adsorbed molecules undergo a process of activated surface migration.

Following Scheidegger's classification of porous media

(40, pt. 1), ordinary or free-gas diffusion occurs in porous media containing voids. For gases at atmospheric pressure, the term "voids" would include all pores greater than about 1 μ diameter (38). Knudsen diffusion occurs in capillaries (40, pt. 1) where the mean free path of the gas molecule is many times greater than the pore diameter (38). For gases at atmospheric pressure the term "capillaries" would include all pores less than about 500 Å diameter. Surface diffusion seems to occur in capillaries and force spaces. Gases which are strongly adsorbed exhibit this phenomena most markedly. However surface diffusion only becomes noticeable under conditions in which Knudsen diffusion predominates. The flux due to surface diffusion is normally defined as the observed flux which is in excess of that expected for Knudsen diffusion alone (67). It is shown later that this definition is inadequate and could be quite misleading.

Although Scheidegger's classification is helpful in picturing how diffusion occurs in porous media, it does not provide an adequate quantitative basis for the analysis of these diffusive processes because:

(1) all types of pores occur in most porous media,
(2) the actual number of each type of pore and how they are connected is unknown, and
(3) the nature of the diffusion process in a given pore depends on the mean pressure and the mean

temperature of the gas in that pore.

In order to assess the effect that a porous medium has on a diffusion flux, it is necessary to define a pore model which will relate the pore space of a medium to the same volume of free space, thus enabling the diffusion coefficients of gases in porous media to be calculated in terms of the gas phase concentration and the cross-sectional area actually occupied by the gas phase.

In studying diffusion phenomena in porous media, three quantities have been measured;

(1) the rate of diffusion of a gaseous species in a binary gas mixture at a constant total pressure,

(2) the rate of flow of a single gas species through a porous medium under such conditions that Knudsen flow occurs, and

(3) the rate of flow of a single adsorbable gas species through a porous medium under Knudsen flow conditions with considerable adsorption taking place as well.

Diffusion data for binary gas mixtures are few. Those that are recorded have been obtained largely for their own intrinsic value, and little attempt has been made to correlate them with other recorded flow data. Knudsen and surface flow measurements have been carried out in conjunction with permeability measurements because, in theory, there is no difference between Knudsen flow and Knudsen diffusion, and because the experimental techniques are similar to those employed for permeability measurements.

4.2 Binary Gas Diffusion in Porous Media

4.2.1 Scope of Previous Work

Measurements of self diffusion in gases that permeate porous media are completely non-existent to the present author's knowledge although some workers have used very porous discs as diffusion barriers for high pressure bulk phase measurements (68,69).

Measurements of diffusion in binary gas mixtures, although few in number, have been carried out for a variety of reasons. Most of the work has been published by chemists (38,66,70-75), who have tried to find an overall or effective diffusion coefficient which can be used to describe mass transfer effects in gas-solid reactions.

Agricultural scientists have studied the diffusion of gases and vapours through air in soils of varying porosity and moisture content in an attempt to discover some relation between diffusion rates and soil porosity. In general their techniques have been too crude, and their systems too complex, to provide fundamental data. Currie (76) has recently provided a clear summary of their work.

More recently, engineers have been concerned with the transport of fluids through porous media, particularly in relation to the separation of isotopes by gaseous diffusion and the design of nuclear reactors. As a result, they have published several papers discussing the nature of porous media in relation to diffusion processes (77-79) and have measured effective diffusion coefficients (39, 80-88).

4.2.2 Effective Diffusion Coefficients

Most authors have defined an effective binary diffusion coefficient (D_{eff}) by the relation

$$\underset{\sim}{J}_A^* = - D_{eff} \underset{\sim}{\nabla} C_A \qquad \text{.......} \; (4.2\text{-}1)$$

where D_{eff} is referred to $\underset{\sim}{v}^*$.
In most experimental systems the flux and concentration gradient occur in one dimension only so Eq. 4.2-1 becomes

$$\underset{\sim}{J}_A^* = - D_{eff} \; \partial C_A / \partial z \qquad \text{.......} \; (4.2\text{-}2)$$

where J_{Az}^* is the flux in moles/sec per unit cross-sectional area of the porous medium, and z is measured along the length of the medium. However, if Eq. 4.2-2 is to be consistent, the concentration C_A should be measured in moles/total volume of porous medium. This definition of concentration is discussed below.

Let us consider a right cylindrical porous specimen, and imagine that one component of a gaseous mixture is diffusing parallel to the axis of the cylinder. If the pores are so fine and so numerous that the gas can be considered to have dissolved in the medium (e.g. H_2 in Pd), then, in any slice of the cylinder, the concentration will be uniform, i.e. if the disc is divided into segments of equal area, each segment will contain the same quantity of gas evenly dispersed in it. Under these conditions the above definition of concentration has an exact physical meaning, and further, the concentration of gas in the solid phase is generally proportional to the gas-phase concentration, i.e.

$$(C_A)_S = \beta (C_A)_g \qquad \ldots\ldots\ldots (4.2\text{-}3)$$

where the subscripts refer to the solid and gaseous phases respectively. Diffusion in such systems is called structure-insensitive diffusion, and will not be considered further here.

If, however, the pores cannot be regarded as molecular interstices, i.e. there is a pronounced pore structure in our porous cylinder, then the gas distribution will no longer be uniform. Let us consider the end slice of the cylinder. It will be made up of areas of solid, in which the gas concentration is zero, and void areas in which the gas concentration is equal to the gas phase concentration in the free space outside the solid. A definition of the gas concentration in terms of the total volume of the porous medium then has no physical meaning. Also, while it is correct to assume that the gas concentration in the pores at both ends of the cylinder is equal to the gas phase concentration at each end (unless marked adsorption occurs), it is an over simplification to assume that the concentration in any particular pore at any other section will be equal to the concentration in other pores at that section or that the concentration gradient will be a linear function of the geometric length of the specimen. Nevertheless, in the absence of an adequate pore model, this assumption must be made. Consequently the most meaningful concentration is the gas phase concentration. This definition is the one most commonly used in previous work.

Several authors (28, 76, 87) have tried to define the concentration in terms of the porosity (ϵ) of the specimen. They write

$$(C_A)_S = \epsilon (C_A)_g \qquad \ldots\ldots\ (4.2\text{-}4)$$

whereupon Eq. 4.2-2 becomes

$$J^{\equiv}_{Az} = -\,\epsilon D_{eff}\ \partial (C_A)_g / \partial z \qquad \ldots\ldots\ (4.2\text{-}5)$$

However, Currie (76) and Dye and Dallevalle (87) arranged their experiments so that Fick's second law was applicable.

If Eq. 4.2-5 is used to define D_{eff}, Fick's second law becomes

$$\partial(C_A)_g/\partial t = D_{eff}\,\partial^2(C_A)_g/\partial z^2 \qquad \ldots\ldots\ldots (4.2\text{-}6)$$

which is indistinguishable from that obtained using Eq. 4.2-2 as the defining equation. However, these authors claimed that Eq. 4.2-6 is correctly written

$$\partial(C_A)_g/\partial t = (D'_{eff}/\epsilon)\,\partial^2(C_A)_g/\partial z^2 \qquad \ldots\ldots\ldots (4.2\text{-}7)$$

but Currie (76) used an incorrect form of the continuity equation in his derivation of Eq. 4.2-7. To be consistent, the continuity equation should also contain a porosity term which would vanish in the subsequent derivation. In effect, Eq. 4.2-7 defines a new effective diffusion coefficient

$$D'_{eff} = \epsilon\, D_{eff} \qquad \ldots\ldots\ldots (4.28)$$

4.2.3 Experimental Methods for Determining D_{eff}

1. Steady-State Methods

Wicke and Kallenbach (70) were the first to study the counter-diffusion of two gases separated by a porous medium. They measured the counter-diffusion of CO_2 and N_2 through glass frits, clay pellets and tablets of activated carbon. In their experiments a mixture of N_2 and CO_2 flowed past one face of the porous medium, and a stream of pure N_2 at the same total pressure flowed past the other. Their studies were carried out from 100 to 700 torr. pressure, and from 0°C to 300°C. They concluded that, in the porous glass, bulk diffusion predominated, but, in the active carbon specimen, both bulk and Knudsen diffusion occurred. Further, they claimed that considerable surface diffusion occurred in the activated carbon, and explained their anomalous results for the pressure and temperature dependence of D_{eff} in terms of surface diffusion.

A method similar to that described by Wicke and Kallenbach was used by Weisz (71,74) to measure D_{eff} for H_2-N_2 mixtures in various catalyst pellets and by Walker et al (59,75) for H_2-N_2 mixtures in extruded carbon rods. Neither Weisz nor Walker made any attempt to relate his results to the pore structure or to $\mathcal{D}_{AB}$, the free gas binary diffusion coefficient, although Walker (59) did show that D_{eff} was highly anisotropic in extruded carbon rods and attributed this anisotropy to a preferential alignment of the carbon particles in the extrusion direction.

All the above authors measured the concentration change in only one sweep stream and calculated D_{eff} from Eq. 4.2-2. However, as later authors have pointed out (83,85,90), equimolar counter-diffusion does not occur in steady-state experiments thus, as N_A not J_A^* is the flux measured, the correct form of Fick's first law is

$$N_{Az} = x_A\,(N_{Az} + N_{Bz}) - D_{eff}\,\partial C_A/\partial z \quad \ldots\ldots\ldots \; (4.2\text{-}9)$$

so the values of D_{eff} published by earlier workers are in fact referred to stationary axes and thus cannot be compared with subsequent values of D_{eff}.

Hoogschagen (66) and co-workers (72) were the first to use Eq. 4.2-9. They described a very simple method of determining D_{eff} for catalyst pellets, using air as the binary gas mixture. One side of their pellet was open to the air; the other formed part of a closed circulation system in which the O_2 was continually removed by hot activated copper tablets, thus keeping the O_2 concentration effectively zero in the closed tube. If the volume of the circulating tube was kept constant, the total pressure inside it dropped well below atmospheric pressure indicating that there was a net flow (N_{N_2}) of nitrogen out of the tube. In subsequent experiments they kept the pressure inside the tube constant at 1 atm. by continuously reducing the volume throughout the experiment.

Hoogschagen (66) assumed that, for his constant pressure experiments, the oxygen and nitrogen fluxes were related by the expression:

$$\underset{\sim}{N}_A M_A^{\frac{1}{2}} + \underset{\sim}{N}_B M_B^{\frac{1}{2}} = 0 \quad \ldots\ldots\ldots \; (4.2\text{-}10)$$

where M is the molecular weight. He offered a tentative derivation of Eq. 4.2-10 and some experimental evidence for its validity. Dullien and Scott (89) showed theoretically that

$$M_B/M_A < \left| N_A/N_B \right| < (M_B/M_A)^{\frac{1}{2}} \qquad \ldots\ldots\ldots (4.2\text{-}11)$$

where $M_B/M_A < 1$,

and that N_A/N_B approached these limits asymptotically. Further, they showed that N_A/N_B remained very close to the upper limit for all reasonable diameters of diffusion channels. It was only when the diameter became infinitely large that $N_A/N_B \rightarrow M_B/M_A$. The inequalities 4.2-11 held from the Knudsen to the normal region. Evans et al (107) also derived Eq. 4.2-10 but their derivation did not include the possibility of a lower limit for N_A/N_B.

Scott et al (85,89) and Evans et al (83,84) used apparatuses similar to the one described by Weisz to measure effective binary diffusion coefficients. Both these groups measured the composition of both sweep streams. Scott measured the counter-diffusion of N_2 and H_2, and O_2 and Ar through various porcelains and catalyst-support materials in the pressure range 20 torr. to 1 atm. Evans made similar measurements of He and Ar diffusion rates through two grades of nuclear graphite in the pressure range 1 to 7 atm.
As both groups developed equations for D_{eff} in the transition region between Knudsen and bulk diffusion, their results are

discussed in detail in Section 4.4.

Smith et al (88) have presented values of D_{eff} for the counter-diffusion of He and N_2 through several types of pelleted silver catalysts. All their runs were performed at 1 atm. In other papers (91-93) they did not calculate D_{eff} from their measurements at all, but developed rather complex pore models to relate diffusion fluxes directly to their pore structure parameters.

2. Unsteady-State Methods

In general, unsteady-state methods have been preferred by soil scientists. Currie (76) has described their apparatuses and methods. Apart from these workers, Fleming et al (82) and Dye and Dallevalle (87) have measured D_{eff} using unsteady-state methods.

Dye and Dallevalle (87) compressed powdered potassium perchlorate into cylinders of varying length and porosity, and mounted them between two geometrically similar gas-circulating systems. Initially pure N_2 was circulated past one face of the specimen and pure CO_2 past the other face. Diffusion of both gases took place through the specimen until equilibrium mixtures of N_2 and CO_2 were obtained on both sides of the specimen. Gas concentrations were continuously measured in thermal conductivity gas analysers. They calculated D_{eff}[†] from Eq. 4.2-6 (Fick's second law), however,

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[†] Although they reported their results in terms of D'_{eff} (Eq. 4.2-8), their numerical values in fact correspond to D_{eff}.

Fick's second law is only valid for equimolar counter-diffusion. Now it is known that pressure gradients are set up in the usual two-bulb diffusion experiment (94) (q.v. section 5.2) but, provided the connecting capillary offers little resistance to viscous flow, they are quickly reduced by a bulk flow of the mixture such that, for all practical purposes,

$$\underset{\sim}{N}_A + \underset{\sim}{N}_B = 0 \; ; \; t \geq 0 \qquad \text{.......} \; (4.2\text{-}12)$$

However, a porous medium offers considerable resistance to a relieving bulk flow, thus the pressure gradient could be expected to pass through a maximum as the system approached equilibrium. Under such conditions it is not intuitively obvious that Eq. 4.2-12 holds for all or even any of the time. The correct differential equation for the unsteady-state porous-medium system has yet to be established. Dye and Dallevalle did not monitor pressure changes across their specimens, so their values of D_{eff} cannot be accepted with any confidence until the above problem is solved.

Fleming et al (82) overcame the problem of pressure gradients by using a trace of radio-active Kr^{85} to measure D_{eff}, thus reducing Eq. 2.2-2 to Fick's second law. They clamped a sample of porous slipcast fused silica between two Pyrex glass pipe crosses. Counting tubes were fixed to the opposite ends of both crosses. The diffusion of Kr^{85}

in air was measured, and the appropriate solution of Fick's second law presented. To remove the active gases between runs they flushed the system out with water. They were concerned with demonstrating the utility of the method rather than reporting any extensive investigations. They quoted only one value for D_{eff}.

4.3 Knudsen Diffusion in Porous Media

Only flow methods have been used to measure Knudsen diffusion in porous media. Timofeev (27), Carman (28), Rutz and Kammermeyer (26), and Field (58) have described them and summarised the results, so it is sufficient to establish the theory here.

If Eq. 2.4-1 is used as the defining equation for Knudsen diffusion the difficulties of unknown flow areas and concentration gradients arise in exactly the same way as they do for bulk diffusion, so an effective diffusion coefficient referred to a stationary frame is defined by analogy with Eq. 2.4-1. One writes

$$N_{Az} = - D^{f}_{eff} \partial C_A / \partial z \qquad \ldots\ldots\ldots (4.3\text{-}1)$$

where the superscript denotes the fixed reference frame. This coefficient must be clearly distinguished from D_{eff} defined by Eq. 4.2-1. No previous authors have made this distinction clear. As in bulk diffusion, D^{f}_{eff} can only be quantitatively related to D_k by means of a pore model.

4.3.1 Analysis of Flow Data

Because Knudsen diffusion has been treated as a flow problem, experimental results have been presented in terms of permeability coefficients. The permeability coefficient most commonly used is defined by the relation

$$N = - K\partial C/\partial z \qquad \ldots\ldots\ldots (4.3\text{-}2)$$

where N is the total flow through the medium measured in moles/cm^2, sec, thus K has the same units and reference frame as D^f_{eff}. Many authors (28,58,95) have shown that a plot of K against p_m, where p_m is the mean pressure, is linear to very low pressures. Carman (28, p. 68) defined specific permeability coefficients B_o and K_o, which he claimed were functions of the pore properties of the medium only. They are related by the expression

$$K = B_o\, p_m/\eta \; + 4\, K_o\, \bar{v}/3 \qquad \ldots\ldots\ldots (4.3\text{-}3)$$

in which the first term represents viscous and the second slip flow. Both K_o and B_o can be evaluated from a plot of K against p_m, by assuming that Eq. 4.3-3 holds to zero mean pressure and that K is unaffected by the magnitude of the pressure drop across the specimen (c.f. Section 4.4).

4.3.2 Use of Pore Models

Most workers have used their K_o values in conjunction with a pore model to evaluate pore properties. Rigden (44), Arnell (96,97) and Lea and Nurse (98) assumed their media to be equivalent to a bundle of parallel capillaries with dimensions such that the ratio of the effective flow area to the total specimen cross-section was equal to the porosity, and that the length of flow path (L_p) was longer than the specimen by the ratio L_p/L. Using Rigden's model Eq. 4.3-1 becomes

$$N_{Az} = -(D\epsilon/q^2)\partial C_A/\partial z \qquad \ldots\ldots. \quad (4.3\text{-}4)$$

where D is defined by Eq. 2.4-1 and the tortuosity $q = L_p/L$. If it is assumed that flow and diffusion processes are equivalent in the Knudsen region then,

$$D^f_{eff} = K = 4K_o\bar{v}/3 \qquad \ldots\ldots. \quad (4.3\text{-}5)$$

whence, from Eq. 2.5-1

$$K_o = \delta\epsilon m/k_1 q^2 \qquad \ldots\ldots. \quad (4.3\text{-}6)$$

The hydraulic radius m can be determined from porosity and surface area measurements hence δ/k_1q^2 can be determined from Eq. 4.3-5, but it is hard to separate q from k_1 because they are both shape factors. Various methods have been devised for measuring q (58) but the definition of q is not precise and the range of reported values is so large that it can be regarded as little more than a factor of ignorance (41,42). Thus Barrer's approach (99) of combining these shape factors into one structure factor

$$\kappa = k_1 q^2/\delta \qquad \ldots\ldots. \quad (4.3\text{-}7)$$

would appear to be the most logical. Carman (28,p.77) attempted to calculate values of q assuming $\delta/k_1 = 0.8$ for consolidated media. Since he made no attempt to separate these factors when summarising results for unconsolidated media (28,p.70) it is hard to see the basis for his statements on consolidated media.

Deryagin (100) applied a statistical pore model to his Knudsen flow results and arrived at the equation

$$K = D^f_{eff} = 12\epsilon m\bar{v}/13 \qquad \ldots\ldots\ (4.3\text{-}7)$$

which he claimed was only valid in the Knudsen diffusion region. In a later paper (101) he produced a more sophisticated solution to the same problem.

4.3.3 Specular Reflection

By analogy with Knudsen diffusion in capillaries, the factor in Eq. 4.3-5 allows for specular reflection effects. However, no method for separating the variability due to specular reflection from that due to the other pore structure factors in Eq. 4.3-6 has been proposed. Until methods for measuring or estimating specular reflection effects are developed, the usual assumption of no specular reflection is not likely to lead to serious errors provided very little adsorption takes place.

4.3.4 The Continuity Equation

In Section 2.2 it was stated that the equation of continuity does not hold for a Knudsen gas, but in porous media systems where the gas outside the specimen is not a Knudsen gas and where overall concentration changes across the specimen are measured, the use of the continuity equation (implicit in Fick's second law) for unsteady-state experiments should not give values of D^f_{eff} that differ significantly from steady-state values provided changes in adsorption equilibria are negligible.

The distinction between flow and diffusion experiments must be emphasized here. Diffusion coefficients calculated from steady and unsteady flow experiments differ markedly because the flow measured in the latter case includes that required to fill the dead-end pore space (102). (Barrer (103) considered that the latter diffusion coefficients were time-dependent.) Whether such a difference exists for constant pressure diffusion experiments is unknown. If it does, it would be difficult to separate the variability due to pore effects and that due to the breakdown of the continuity equation.

4.4 Diffusion in the Transition Region

4.4.1 Low Pressure Permeability Measurements

The analysis of low pressure permeability experiments has been based largely on the twin assumptions that Eq. 4.3-3 holds over the pressure range from Knudsen to viscous flow and that in the Knudsen region $K = D^f_{eff}$.

The factors that affect flow in the Knudsen and transition region have not been well defined. Pollard and Present (25) predicted that there would be no observable minimum in plots of K against p_m because the tortuous nature of the flow paths in porous media would make long molecular "flights" improbable. To date the experimental evidence is conflicting. Whereas Grove and Ford (104), and Field (58, p.249) have observed marked minima, Carman (105) found only a slight and gradual decrease in the gradient of the curve in the transition region with no evidence for a minimum K value. In contrast to Carman's work, Monroe and Gaffee (106) found that the gradient increased in the transition region for H_2 and He, but decreased for air and freon. Maidanik (108) developed a semi-empirical theory predicting minima in K-p_m plots, and Deryagin and Bakanov (101) showed theoretically that K-p_m plots for highly porous materials ($\epsilon > 0.7$) must have a minimum. A wide range of pore sizes (104), variations in the value of δ(101), and faulty experimental techniques have all been suggested as possible sources of the variability noted at low pressure.

Summarising, it is not yet clear whether the observed variations from Eq. 4.3-2 are real or whether they depend on measuring techniques. If they are real, the determining variates have yet to be isolated.

4.4.2 Diffusion Measurements

Wheeler (38) suggested that models developed for diffusion in capillaries would describe diffusion in porous media equally well. Thus he expected that Eq. 2.5-2 or 2.5-3 would be adequate but no experimental data existed to test his suggestion.

Scott and Cox (85) did not recognise the difference between D^f_{eff} and D_{eff}. They assumed that, when the total pressure was low enough for the mean free path of H_2 (λ_H) to be greater than the equivalent pore radius (r_p) - calculated from mercury porosimeter measurements - then D^f_{eff} could be calculated from Eq. 4.3-1, but when r_p exceeded λ_H, Eq. 4.2-9 held. Their plot of log D_{eff} against log p (Fig. 4.4-1) reveals the resultant discontinuity plainly.

Scott and Cox also measured H_2 permeabilities and calculated D^f_{eff} from Eq. 4.3-5. (The use of Eq. 4.3-5 was not stated, but implied in their discussion.) Their values of D^f_{eff} from their diffusion and permeability experiments are compared in Table 4.4-1. The accompanying analysis of variance shows that the two sets of values are equivalent.

In a later paper, Scott and Dullien (39) assumed that

TABLE 4.4-1
DIFFUSSION COEFFICIENTS OF SCOTT AND COX

	METHOD	
	PERMEABILITY	DIFFUSION
KAOLIN 2	.101	.110
CELITE	.550	.60
SELAS 03 B	.539	.523
SELAS 015	3.68	5.15

ANALYSIS OF VARIANCE

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
METHODS	1	.286146	.286146	1.08 NS
POROUS MEDIA	3	24.403132	8.134377	30.67**
ERROR	3	.795722	.265241	
TOTAL	7	25.48500		

Note: The abbreviations in the analysis of variance table are explained in Section 7.2.2. In this and all succeeding analysis of variance tables, one, two and three asterisks denote significance at the 5, 1 and 0.1 per cent confidence levels respectively.

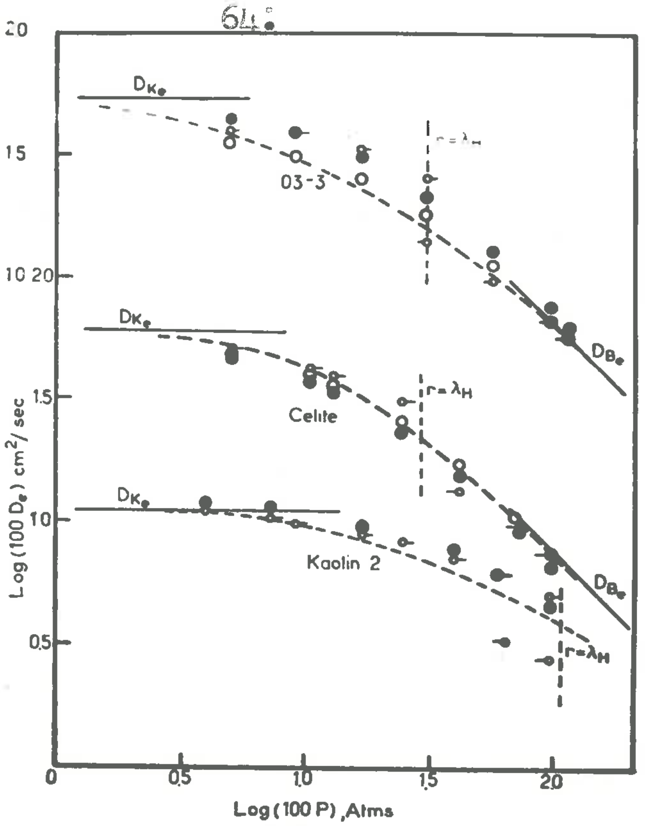

Fig. 4.4-1 Experimental and Calculated values of D_{eff} presented by Scott and Cox

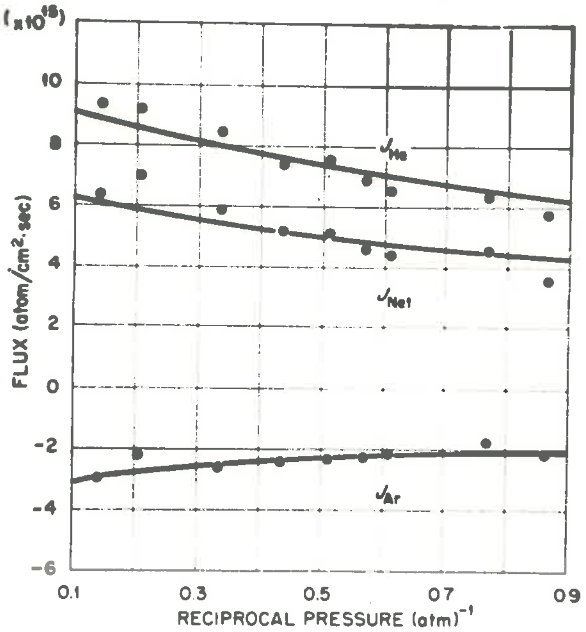

Fig. 4.4-2 Effect of Pressure on Diffusive Fluxes - Results of Evans et al

their model for diffusion in capillaries (Eq. 2.5-7) could be converted into a form applicable to porous media by using the relation

$$(\mathcal{D}_{AB}/D_{kA})_{eff} = (\mathcal{D}_{AB}/D_{kA})_{true} \qquad \ldots\ldots\ (4.4-1)$$

In both papers it was assumed that the high pressure values of D_{eff} were equivalent to $(\mathcal{D}_{AB})_{eff}$ and the low pressure permeability and diffusion values equivalent to $(D_k)_{eff}$. Eq. 4.4-1 was tested by calculating $(D_{kA})_{true}$ from independent measurements of r_p. Eq. 4.4-1 held for both their own and Wheeler's model thus it yielded no information about the diffusion mechanism. In the second paper, D_{eff}, not D^f_{eff} was measured, so low pressure values could not be equivalent to $(D_k)_{eff}$ physically, although they may be equivalent numerically to values of $(D_k)_{eff}$ calculated from r_p.

In the first paper, values of D_{eff} calculated from Wheeler's model were compared graphically (Fig. 4.4-1) with experimental values over the complete pressure range, but in the second, values of D_{eff} were quoted only for each end of the pressure range; the experimental pressure dependence of D_{eff} was not determined although the experiments were performed. The authors merely compared the observed fluxes with the curve calculated by inserting the quoted values of D_{eff} in Eq. 2.5-8. This procedure is consistent with the second empirical approach outlined in Section 2.5, but the use of extreme values only, as distinct from say a least-squares method of fitting theoretical curves, deprived them of the opportunity to compare models and to estimate the precision of their own model.

Evans et al (107) developed a diffusion model in which the porous medium was treated as a dusty gas in which the dust particles behaved like giant molecules uniformly distributed and fixed in space. The "dust" was then treated as another gas component and the model developed from the kinetic theory of multicomponent diffusion assuming

(1) that $\mathcal{D}_{AA}$ could be replaced by $\mathcal{D}_{AB}$ in the Bosanquet formula,
(2) that Eq. 4.4-1 held,
(3) that Eq. 4.3-1 was valid at low pressures and Eq. 4.2-9 at high pressures, and implicitly (in that reference frame differences were not recognised)
(4) that $D_{eff} = D^f_{eff}$.

Their model for binary diffusion is

$$N_A = -(D_A)_{eff}\,\partial C_A/\partial z + x_A(N_A + N_B)\,\delta_A(p) \qquad \text{.....} \quad (4.4\text{-}2)$$

where $1/(D_A)_{eff} = 1/(\mathcal{D}_{AB})_{eff} + 1/(D_{kA})_{eff}$ ..... (4.4-3)

and $\delta_A(p)^{-1} = 1 + \left[(\mathcal{D}_{AB})_{eff}/(D_{kA})_{eff}\right]$ ..... (4.4-4)

(Insofar as Eq. 4.4-2 is an empirical expression relating $\mathcal{D}_{AB}$

to D_{kA}, it is a valid expression, irrespective of whether or not the theoretical development is sound.)

It is to be noted that $(D_A)_{eff}$ is not equal to D_{eff}. If Eq. 4.4-3 and Eq. 4.4-4 are substituted back into Eq. 4.4-2, Eq. 2.5-5 is obtained, i.e. the expressions for N_A derived by Scott and Evans are identical. Evan's model, however, explicitly accounts for the disappearance of the total flux term in Eq. 4.4-2 as the Knudsen region is reached.

The vanishing total flux term is a necessary consequence of assumptions (3) and (4) above.

The results of Evans et al (83,84) do little to establish the validity of the $\delta(p)$ term. All their experiments were carried out in the pressure range 1 to 7 atm. Their factor $\delta(p)$ varied from 0.98 to 1 for the large-pored graphite and from 0.75 to 0.95 for the fine-pored graphite. Like Scott, they compared their calculated fluxes with their experimental ones. It is noticeable that their data for the fine-pored graphite do not fit the theoretical curve for the net flux very well (Fig. 4.4-2). Evans et al (107) considered that $(\mathcal{D}_{AB})_{eff}$ and $(D_{kA})_{eff}$ not only completely defined the diffusion system (in the absence of surface diffusion) but also completely characterised the porous medium. Thus, if Eq. 4.4-1 is written in the form

$$(\mathcal{D}_{AB})_{eff}/(\mathcal{D}_{AB})_{true} = (D_{kA})_{eff}/(D_{kA})_{true} = G \qquad \ldots\ldots (4.4\text{-}5)$$

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their claim is that G is a property only of the porous medium and is independent of the gas mixture used. Such a claim is also implied by Scott, but none of these authors supply any supporting evidence; they used only one gas mixture per specimen.

4.5 Surface Diffusion

In Section 2.4, the limiting expression for Knudsen diffusion is stated to be

$$D_k = d\bar{v}/3 = d(8RT/\pi M)^{\frac{1}{2}}/3 \qquad \ldots\ldots\ldots (2.4-2)$$

from which it is seen that $D_k \propto (1/M)^{\frac{1}{2}}$, i.e. for two gases A and B,

$$D_{kA}/D_{kB} = (M_B/M_A)^{\frac{1}{2}} \qquad \ldots\ldots\ldots (4.5-1)$$

Eq. 4.5-1 has been confirmed experimentally for non-adsorbed gases e.g. Barrer and Grove (109), but it breaks down for adsorbed gases; the calculated values of D_k are invariably lower than the experimental ones. Most workers have defined surface diffusion in terms of the observed flux which is in excess of that predicted by Eq. 4.5-1 using helium as the reference gas (67).

Carman (28), and Rutz and Kammermeyer (110) have provided an extensive summary of the theory and experimental work. In addition, the author, in conjunction with Field and Watts of this laboratory, has examined the basic assumptions underlying the theory of surface diffusion and discussed alternative explanations of the observed effects in a paper presented here in Appendix A. This paper provides a more than adequate review of surface diffusion for the present purposes because Field (58,p.497) has found no evidence for surface diffusion in permeability experiments with Xe and Morgan EY9-166 graphite.

No self or binary diffusion measurements of adsorbable gases have been made. All previous measurements have been made by relating the flow of adsorbable gases, at pressures low enough for Knudsen diffusion to occur, to the flow of He under the same conditions, and then assuming that the flow processes obeyed Fick's first law of diffusion. However, diffusion coefficients defined in this way cannot be related to $\mathcal{D}_{AB}$ or D_K as the flow of a pure component under a total pressure gradient is a hydrodynamic rather than a diffusional process (q.v. Appendix A.3).

Reported flow rates have varied tremendously with surface coverage (28,ch.5) but no concurrent measurement of the pressure gradients within porous materials have been reported, consequently the adsorbate distribution within them has remained unknown. Recently Field (111) has found that the pressure gradient in steady-state flow through graphite is approximately parabolic. Consequently the assumption that adsorption coefficients obtained from isotherm data at the arithmetic mean pressure adequately describe the adsorbate distribution is far from correct.

It may be concluded that the effects of surface diffusion are better evaluated from self diffusion measurements because

(1) self diffusion is a true diffusion process therefore Fick's first law should apply,
(2) there would be no pressure gradients in the system, so the surface concentration could be obtained directly and accurately from adsorption isotherms,
(3) the surface coverage would be uniform, and
(4) the comparison of self-diffusion data with flow data would help clarify the whole concept of surface diffusion.

4.6 <u>Summary and Conclusions</u>

The diffusion of gases in porous media is a special case of the diffusion of gases in a container of known dimensions, so the same driving forces are involved. However, the fluxes produced by these forces are modified by the pore structure of the medium, and the interaction of the gas molecules with the solid surface. To date, the effects of pore structure and gas-solid interactions have been assessed from adsorption, diffusion and permeability data, but no satisfactory differentiation between structure and gas-solid interaction effects by quantitatively combining these measurements has yet been attempted.

4.6.1 Diffusive Processes

Three mechanisms have been defined for diffusion in porous media, viz. bulk, Knudsen and surface diffusion. The controlling mechanism depends on the mean gas pressure and temperature, the pore structure and the nature of the gas-solid interactions. Since most media contain a wide range of pore sizes, all types of diffusion are likely to occur simultaneously in the one specimen.

Because of the difficulty of characterising porous media two overall effective diffusion coefficients D_{eff} and D^{f}_{eff} have been defined, the use of which permits the ready comparison of data obtained on one specimen. To correlate data from more than one specimen, some assumptions about the effects of the pore structure and the gas-solid interactions must be made. The usual assumptions (implicit in the definitions of the three diffusion regions) are

(1) that the porous medium merely reduces the diffusion fluxes by an amount such that $(\mathcal{D}_{AB})_{eff}/\mathcal{D}_{AB}$ and $(D_{KA})_{eff}/D_{KA}$ are constants

independent of A or B, provided the gas-solid interactions can be described solely in terms of diffuse reflections, and

(2) all deviations from the behaviour described in (1) can be ascribed to surface diffusion.

4.6.2 Previous Experimental Work

Previous experimental work has been performed in a somewhat piecemeal fashion. Only the following measurements have been made:

(1) binary diffusion in the absence of surface diffusion, with no more than one pair of gases per specimen,

(2) Knudsen flow, and

(3) surface flow of adsorbable gases in the Knudsen region.

Diffusion in the transition region has been assessed by postulating an empirical relationship between $(\mathcal{D}_{AB})_{eff}$ and $(D_{kA})_{eff}$, then testing it experimentally. The alternative approach (q.v. Section 2.5) of deducing an empirical expression from data obtained from a statistically designed set of experiments has not been attempted.

In the planning and interpretation of their experiments previous authors have assumed

(1) that permeability and binary diffusion measure-

ments extrapolate to the same value at low pressure,

(2) that, in the absence of surface diffusion, Eq. 4.5-1 and Eq. 4.4-5 hold and that diffuse reflection occurs at all gas-solid collisions, and

(3) that all deviations from Eq. 4.5-1 can be interpreted in terms of surface diffusion.

The lack of a clear understanding of the difference between D_{eff} and D^{f}_{eff} is evident in the planning and interpretation of the experimental work published to date. However, such data as are available have

(1) confirmed Eq. 4.5-1 for some non-adsorbed gases,

(2) confirmed Eq. 4.4-1 for one pair of gases (39,85),

(3) offered some supporting evidence for assumption (1) (39,112),

(4) shown that plots of K against p_m behave unpredictably as $p_m \rightarrow 0$, and

(5) shown that flow experiments do not form a sound basis for the study of surface diffusion.

4.6.3 Scope for Future Work

It is suggested that the following experimental investigations would test current assumptions and establish a more unified picture of diffusion in porous media.

(1) Self and binary diffusion measurements with one

specimen, from the Knudsen to bulk diffusion pressure range using more than one gas pair, in order to provide a more stringent test of Eq. 4.4-2 and Eq. 4.4-5.

(2) Self and binary diffusion and flow measurements in the Knudsen diffusion region, under such conditions that $\underset{\sim}{v}^{*} = 0$ for the binary measurements, in order to test the equivalence of flow and diffusion measurements, to test the validity of Eq. 4.5-1, and to find out whether the variable behaviour noted in flow experiments at high N_{Ku} values also occurs in self diffusion experiments.

(3) Self diffusion and adsorption measurements of adsorbable gases on inert media and adsorbents in order to assess the influence of gas-solid interactions on diffusion fluxes.

(4) The experimental determination of the temperature dependence of D_{eff} in order to clarify further the relation between the various diffusion mechanisms.

(5) A theoretical and experimental investigation of the effects of specular reflection on mass and momentum fluxes.

Two untried experimental techniques which had been overlooked by previous workers, and which could prove useful in the execution of the work suggested above were noted.

(1) The measurement of the diffusion of a labelled trace of one component in an equilibrium binary mixture.

(2) The expression of D_{eff} in terms of an explicit function of the measured variates; the nature of the function being deduced from experimental values of D_{eff}.

5. EXPERIMENTAL CONDITIONS AND PRELIMINARY EXPERIMENTS

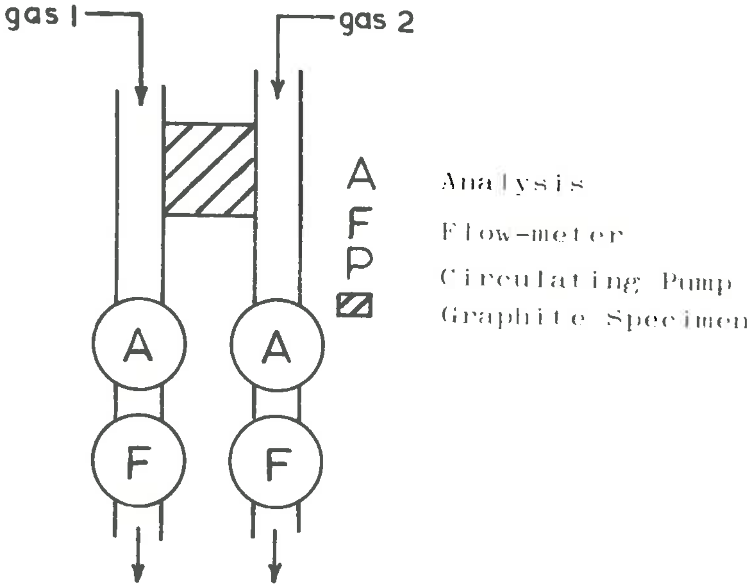
5.1 The Experimental Problem

A preliminary literature survey showed that the early experiments of Wicke and Kallenbach (70) were the only diffusion experiments (as distinct from permeability experiments) that had been carried out in the transition region between Knudsen and bulk diffusion. It was decided, that this transition region should be examined using Morgan EY9-166 and perhaps later impregnated graphites as the porous material.

Permeability experiments performed in this laboratory with Morgan EY9-166 had shown that the transition region would be well below one atmosphere pressure. The aim of the preliminary experiments was to construct an apparatus for measuring diffusion at low pressures using both Morgan EY9-166 and impregnated graphites.

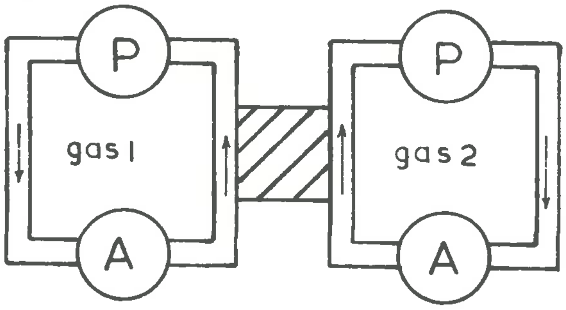
5.1.1 Choice of Experimental Conditions

The paucity of experimental data at pressures below 1 atm. meant that the decision to work with either a steady- or transient-state system had to be made on a rather arbitrary basis. Line diagrams of the three alternative systems considered are shown in Fig. 5.1-1. A fourth alternative involving the combination of system (a) with either (b) or



(a) The Steady-state Flow System

(b) The "Two-bulb" Transient-state System



(c) A Variation of (b) in which the gases are continuously circulated past the specimen

Fig. 5.1-1 Schematic Diagrams of Several Diffusion Systems

(c) was considered too complex for immediate consideration.

System (a) has the normal advantages associated with steady-state methods.

(1) Mathematical simplicity; Fick's first law (Eq. 4.2-9) holds and is readily integrated for most simple specimen geometries,

(2) The exit gas streams can be analysed intermittently and any number of check analyses made,

(3) Analyses may be performed with "on-line" instruments or samples may be collected and analysed with separate equipment,

(4) The duration of a run is governed only by the time taken to reach equilibrium conditions and to perform the analyses.

Experimentally, however, system (a) has several serious disadvantages:

(1) the concentration changes are very small, therefore the flow rates and compositions of the exit streams must be measured very accurately in order to determine the correct pressure dependence of D_{eff}.

(2) the requirement that a zero pressure differential be maintained across the specimen while providing constant flow rates past its faces at pressures

down to 10 torr. is very difficult to achieve experimentally, and

(3) large quantities of gas are required; this is no problem unless rare, expensive, or radio-active gases are used.

System (b), a transient-state system, gives a large concentration change with time, uses far less gas, and does not require the complex control equipment that system (a) would require. However, a continuous or semi-continuous method of measuring concentration changes is essential in order to establish the concentration-time relationship needed to solve the second-order differential equation describing the system. Further the initial and boundary conditions must be clearly defined if an analytical solution is to be used, and if reproducible results are to be obtained.

System (c) is a more complicated version of system (b) which would have to be used if the volume of gas on each side of the specimen had to be large enough for samples to be withdrawn without affecting the course of a run.

A careful analysis of the alternative systems led to the decision to build a preliminary apparatus to test system (b).

5.2 The Preliminary Experiments

5.2.1 Aims and Procedure

The aims of the preliminary experiments were

(1) to test whether or not transient-state experiments would give reliable estimates of D_{eff},

(2) to gain some preliminary information on the pressure dependence of D_{eff},

(3) to determine the most satisfactory specimen size and shape, and

(4) to test whether or not the same approach would be suitable for impregnated graphites.

In these experiments, N_2 and CO_2 were simultaneously introduced to the inner and outer surfaces of a thick hollow cylinder of graphite. The dimensions of the Morgan EY9-166 specimen and the impregnated graphite specimen used in these experiments are given in Appendix B, Table B.4-1. Details of the apparatus, experimental technique and mathematical treatment are discussed in Appendix B.

5.2.2 Results and Conclusions

All the numerical results are listed in Appendix B.4.

The results obtained from runs carried out on the Morgan EY9-166 specimen (Specimen A) indicated that

(1) the length/area ratio was far too small since, for most runs, 40% of the concentration change had taken place in the first five minutes,

(2) the transition region was below 300 torr., and

(3) the initial conditions were not sufficiently well-defined in that values of D_{eff} calculated with the time origin set at the beginning of the experiments were time-dependent whereas values calculated with the time origin fixed at a point five minutes after the experiment had begun were nearly time-independent.

Slow fluctuations of the differential pressure gauge indicated that pressure changes were occurring throughout the course of a run thus confirming the statements of Hartley and Crank (16) and the observations of Kramers and Kistemaker (113) and to some extent foreshadowing the observations of McCarty and Mason (94). The presence of pressure changes in such transient-state measurements means that Fick's second law does not hold for such systems, thus even the accurate solution given by Jaeger (114) (c.f. Appendix B.3) would not adequately describe the preliminary experiments. The validity of Dye and Dallevalle's calculated results (87) could be questioned on the basis of this observation.

Meaningful diffusion coefficients could not be calculated from the data obtained with the impregnated specimen because the initial and boundary conditions were even less well-defined. The differential pressure across the specimen fluctuated markedly throughout a run, and the gas pressure decreased on both sides indicating that adsorption was occurring. Since no absolute pressure measurements could be made, the quantity of gas adsorbed could not be estimated so the composition measurements listed in Appendix B.4 could not be quantitatively interpreted. When these problems were added to those imposed by a room-temperature out-gassing time of about one week, and an experimental run time of about 3 days, it became evident that a different technique would be necessary for impregnated graphites. As a result, all further work was directed at measuring diffusion through Morgan EY9-166.

The results obtained from the preliminary experiments showed that transient-state experiments could be conducted provided

(1) a method for establishing reproducible initial conditions was evolved,

(2) the hollow cylindrical specimens were replaced by discs, in order to obtain a simple solution to Fick's second law,

(3) pressure fluctuations were eliminated by measuring trace or self diffusion coefficients, and

(4) a continuous or semi-continuous method of analysis was available to determine accurately the concentration change with time.

The final apparatus was designed in accordance with these conclusions.

6. FINAL APPARATUS AND PROCEDURE

The transient-state diffusion system adopted for the main experimental programme is shown diagrammatically in Fig. 6.0-1.

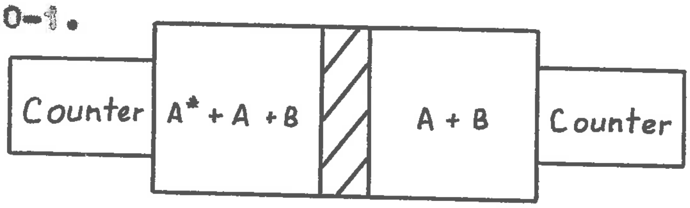


Fig. 6.0-1 Diffusion System for Main Experimental Programme

The graphite septum is soaked in an equilibrium mixture of two gases A and B, then a trace of a radio-active isotope of A (A^*) is admitted to one of the diffusion chambers and its rate of diffusion through the septum to the other chamber is measured.

The effective diffusion coefficient for the case in which the septum is replaced by a capillary of known dimensions is

$$1/\mathcal{D}_{A^*M} = x_A/\mathcal{D}_{AA^*} + x_B/\mathcal{D}_{A^*B} \qquad \ldots\ldots\ldots (2.3\text{-}4)$$

thus D_{eff} for the porous medium system is defined by an expression of the form

$$D_{eff} = g(\mathcal{D}_{AA^*}, \mathcal{D}_{A^*B}, D_{KA^*}, x_A, Q, \phi) \quad \ldots\ldots (6.0\text{-}1)$$

where Q is a function of the pore geometry, and

ϕ represents the gas-solid interaction effects.

The advantages of measuring the diffusion of a trace of A^{*} in an equilibrium mixture of A and B may be restated:

(1) the molar and stationary reference frames coincide, thus $D_{eff} = D^{f}_{eff}$,

(2) Fick's second law holds, and

(3) x_A is constant in a given experiment therefore D_{eff} is constant throughout the experiment, (remembering that D_{eff} is not independent of the experimental method).

The aim of the experimental work was to deduce an explicit function for D_{eff} of the form

$$D_{eff} = g(p, M_A, M_B, x_A, Q) \qquad \ldots\ldots\ldots (6.0\text{-}2)$$

from measurements of D_{eff} in the pressure range 10 to 760 torr, using several gases A and B mixed together in various proportions, thus partially fulfilling item (1) in Section 4.6.3.

The ultimate aim of such experimental work would be to relate Eq. 6.0-2 to Eq. 6.0-1. Because no data for estimating the variability in D_{eff} were available, the ranges of the determining variates needed to establish an explicit form of Eq. 6.0-2 could not be deduced beforehand, hence the extent to which Eq. 6.0-2 could be identified with Eq. 6.0-1 could not be foreseen.

Details of the apparatus and procedure, and the development of the final experimental plan are discussed below.

6.1 The Apparatus

A general view of the apparatus is presented in Fig. 6.1-1. Because the apparatus is rather complex, it is discussed in four parts: the vacuum system, the diffusion cells, the counting and recording equipment and the temperature control system.

6.1.1 The Vacuum System

A line diagram of the vacuum system is shown in Fig. 6.1-2. The vacuum pumps, McLeod gauge and Pirani gauge are omitted from this diagram as these components are standard items on any high vacuum apparatus. The vacuum system can be divided naturally into four sections:

(1) the inactive gas storage line B, to which a maximum of seven flasks of pure gas[†] can be attached by means of greased conical joints,

(2) the active gas storage section, comprising the active gas capsules J, a freezing leg K, a small toepler pump H, and three primary dilution

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[†] All the inactive gases, viz. He, Ne, Ar, Kr and Xe, were supplied in one litre flasks by the British Oxygen Co. who claimed that the He, Ne and Ar were spectrally pure but that the Kr could contain up to 1% Xe and vice versa.

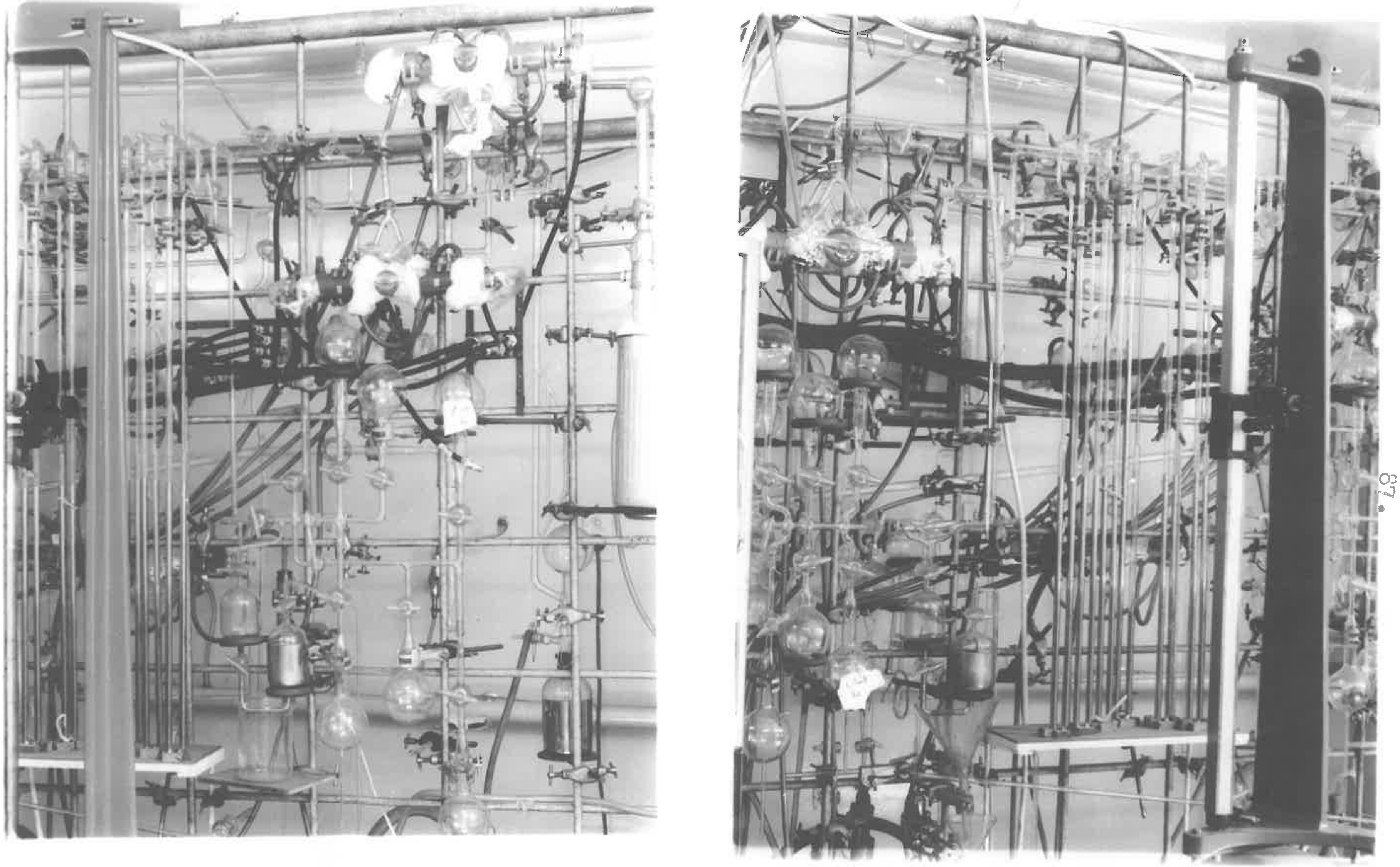

Fig. 6.1-1 Views of the Apparatus

LEGEND

A.	H.V. line to McLeod Gauge, Pirani Gauge, cold trap and Hg diffusion pump.
B.	Primary storage for inactive gases.
C.	Active gas mixture storage bulbs.
D.	Inactive gas mixture storage bulbs.
E.	Toepler pump for making mixtures and filling cells.
F.	A 100 cm manometer.
G.	Primary storage for active gases.
H.	Toepler pump for measuring out small doses of active gases.
J.	Active gas capsules.
K.	Freezing leg.
L.	Cell manometer 100 cm long.
M.	Diffusion cell.
N.	Leads to cell-manometer assemblies similar to L and M.
O.	Modified cell-manometer system.
P.	Additional storage for active gas mixtures.
Q.	Freezing leg.

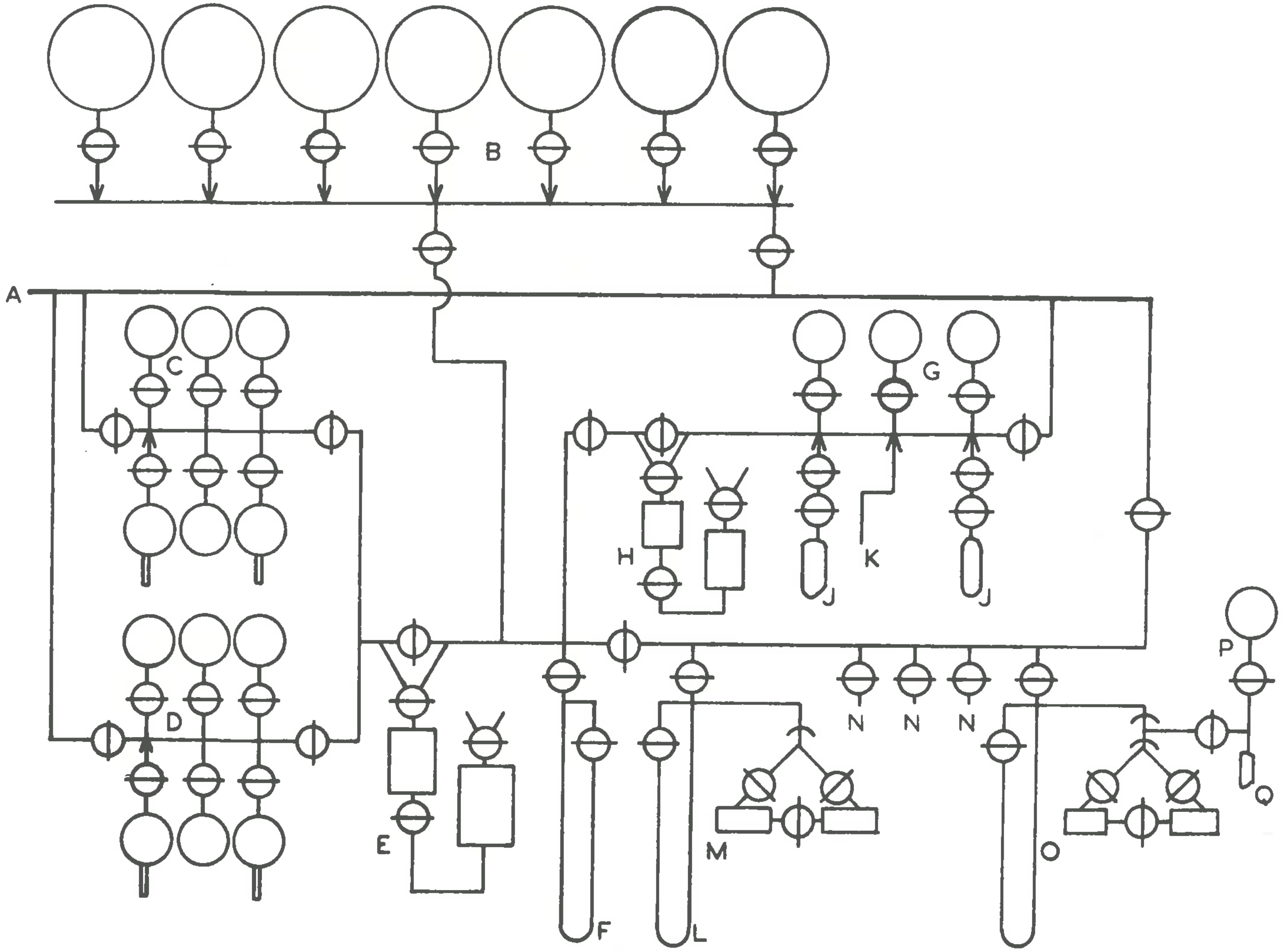

Fig. 6.1-2 Line Diagram of Final Apparatus

bulbs G,

(3) the mixing section, comprising the toepler pump E, the manometer F and the two sets of mixture storage flasks C and D, and

(4) the five diffusion cell-manometer assemblies, L, M, N and O.

An extra storage bulb P and freezing leg Q enabled the apparatus to be used more efficiently by providing some intermediate storage volume.

A detailed description of the more complex components is given in Appendix C.1.

6.1.2 The Diffusion Cells

(1) The Cell

Each diffusion cell consists of two water-jacketed compartments connected by a 15 or 20 mm bore stop-cock as shown in Fig. 6.1-3 and Fig 6.1-4. Each compartment is connected through a 4 mm. bore stopcock and a common ball joint to the cell line. The volume of each compartment was measured by the method described in Appendix C.2. The flanges on the outer ends of the compartments are ground flat so Geiger-Muller counters can be sealed onto them.

(2) The G-M Counter-to-Cell Seal

Since G-M counters have a limited life, a method for sealing them onto the flanges so they could be removed

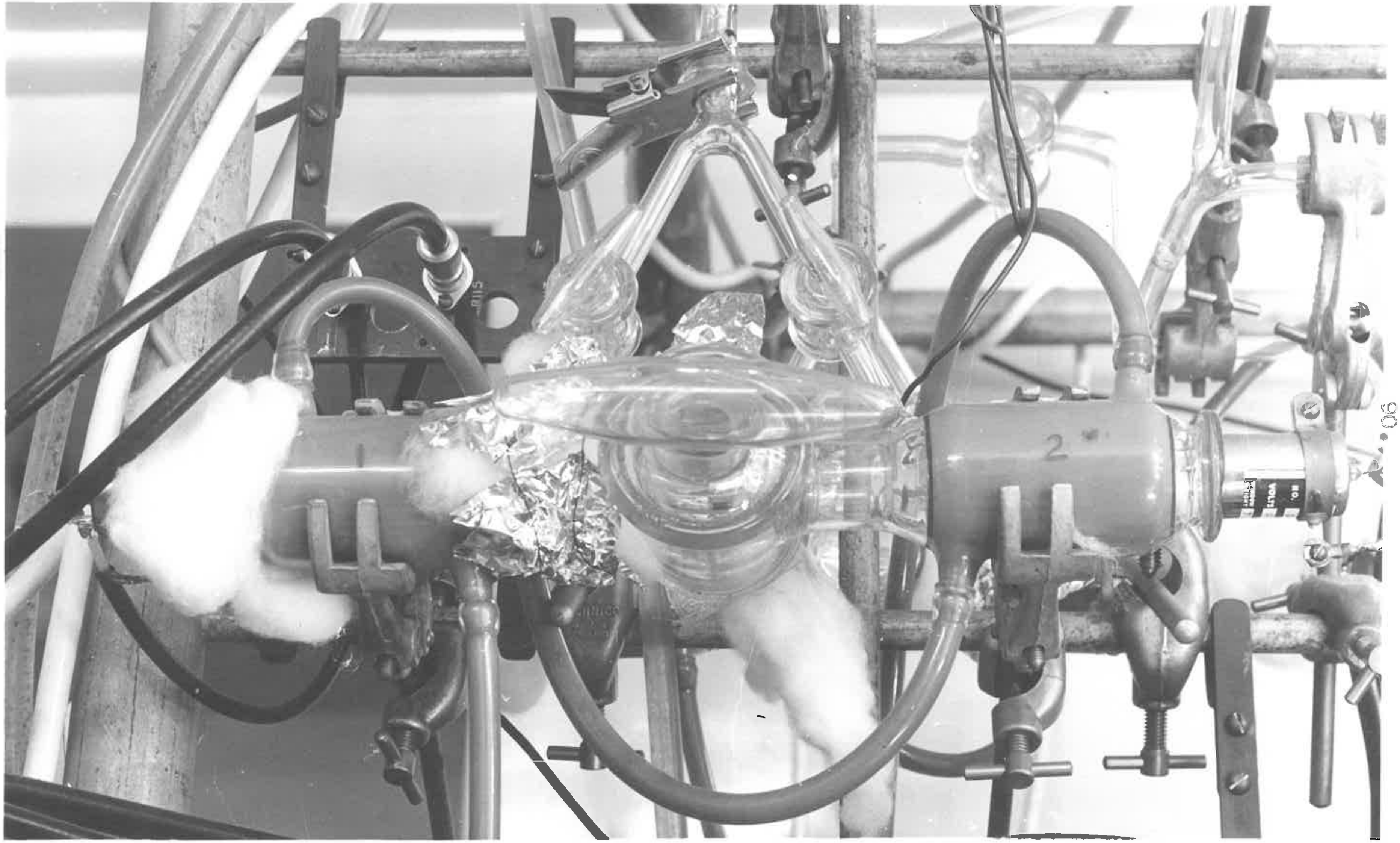

Fig. 6.1-3 Photo of a Diffusion Cell

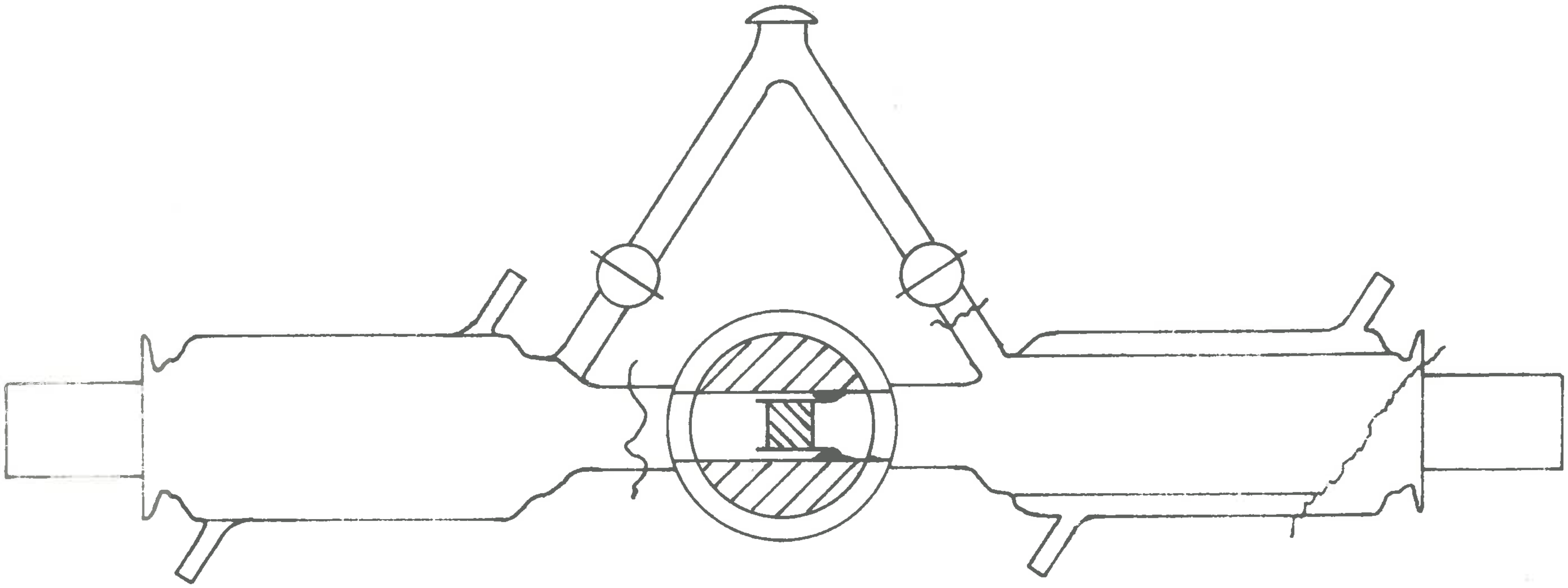

Fig. 6.1-3   A sketch of a Diffusion Cell. The cut-away section reveals the Water-jacket and Mounted Specimen

easily had to be developed. A satisfactory seal was obtained by first sticking a perspex washer onto a counter with epoxy resin then sticking the washer, with counter attached, onto the flanges with stopcock grease. However, the perspex outgassed badly so the counters were sealed directly onto the flanges with epoxy resin.

Dead tubes were unsealed by removing the whole cell from the apparatus, soaking the seal in chloroform for several hours, and scraping away the softened resin until the counter could be pulled off by hand.

(3) The Specimen Seal

All the specimens used in the remaining experimental work to be described in this thesis were prepared from rods of Morgan EY9-166 graphite donated by the Australian Atomic Energy Commission. The physical properties of this graphite are discussed briefly in Appendix C.3.

A thick coat of epoxy resin was cast around the circumference of the graphite rod from which the specimens were to be cut. After the resin had set, the coated rod was turned to the required diameter and specimens in the form of cylindrical plugs were cut off, faced and sealed into a cylinder of aluminium foil with epoxy resin. Each aluminium cylinder was similarly sealed to the bore of the stopcock separating the two halves of the cell. The mounting procedure and the subsequent volume measurements are described fully in Appendix C.2. The dimensions of each specimen, the volume of each cell and the values of the cell constants derived from these data are tabulated in Appendix C.2.

6.1.3 The Counting and Recording System

The counting and recording equipment is shown in Fig. 6.1-6.

The cells are wired in such a way that each G-M counter can be connected to either ratemeter. A time switch is incorporated in each recorder circuit so that the recorder chart-drives can be switched off automatically after a pre-set time has elapsed. A block wiring diagram is presented in Fig. 6.1-5.

6.1.4 The Temperature Control System

A manifold with eight outlets and a $\frac{1}{2}$-in. dia. bypass is fitted to a direct-drive $\frac{1}{2}$-in. centrifugal pump which circulates water from a Townson and Mercer X27A constant temperature bath. The water jackets of each cell are connected in series with one of the outlets on the manifold, thus water flows from the manifold through the two jackets on a cell into the bath. The water in the bath is controlled at $30 \pm 0.1^\circ C$.

LEGEND

A.	The Honeywell-Brown Recorder.
B.	The Leeds and Northrup Recorder.
C.	An electric Venner time switch.
D.	A clock-work Venner time switch.
E.	A 240-110 V transformer.
F.& G.	"EKCO" ratemeters, type N522C.
H.& J.	12-position wafer switches.
K.	An extra lead not connected through H or J.
L.	G-M counters.
M.& N.	Co-axial-cable leads for connecting the ratemeters to the G-M counters.

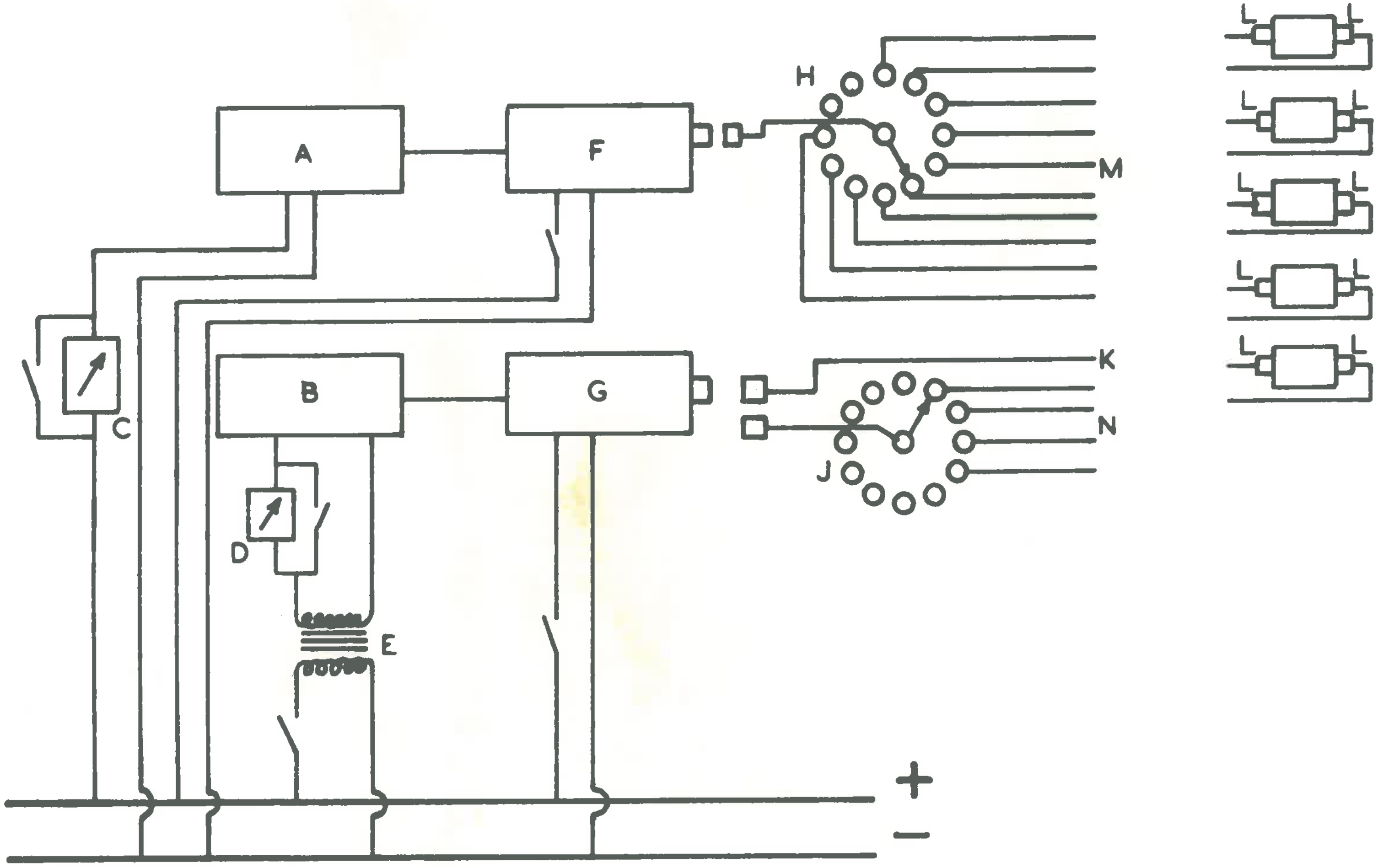

Fig. 6.1-5 Block Wiring Diagram of the Counting and Recording System

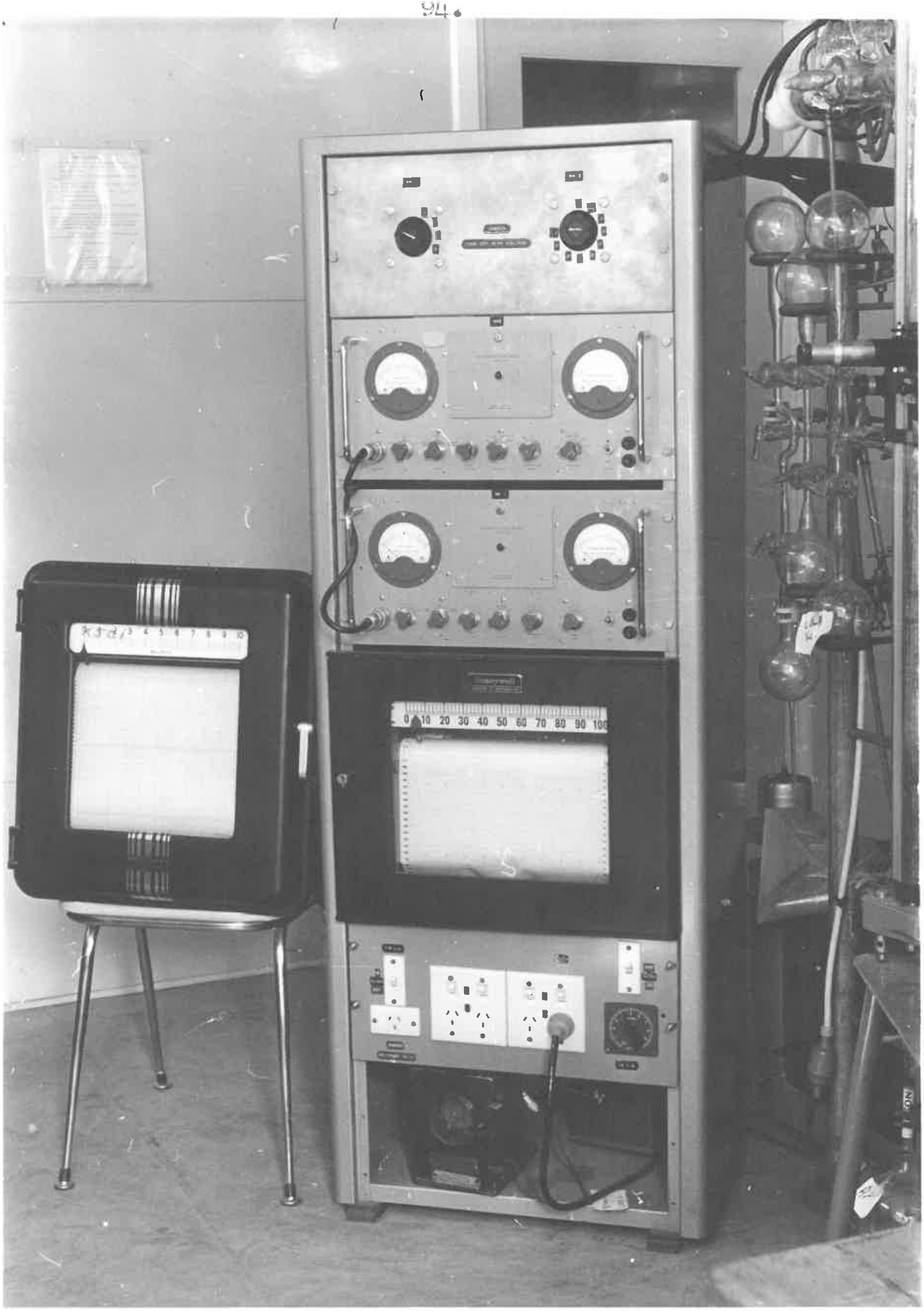

Fig. 6.1-6 Photo of Counting and Recording System

Temperature gradients within the gas chamber of the cell are kept to a minimum by wrapping the unjacketed parts of the cell with cotton wool kept in place by a layer of aluminium foil. A check with a thermocouple in a dummy cell indicated that the temperature in the cell remains very constant at about 29.5°C.

The room temperature is controlled at 22 ± 2°C by a room air conditioner.

6.2 Experimental Plans

The first experimental plan is shown in Table 6.2-1.

Table 6.2-1

First Experimental Plan

Cell	1	2	3	4	5
Active Gas	Inactive Gases				
Kr	Kr	Kr	Kr	Kr	Kr
Kr	Xe	Ar	He	Ne	P
Xe	Xe	Xe	Xe	Xe	Xe
Xe	Kr	Ar	He	Ne	P

A small number of self diffusion measurements with pure Kr and pure Xe were carried out in each cell so that some estimate of the difference between cells could be made, then each cell was used to measure self diffusion in a binary mixture as shown in rows 2 and 4 of the above table. These latter experiments were to be repeated with varying ratios of active to inactive gases, thus there was a planned correspondence of compositions along the rows of Table 6.2-1, but there was no planned correspondence of pressures. (The 'P' in Table 6.2-1 indicates permeability experiments.)

After about seventy runs had been performed in this fashion, several disadvantages of the original plan became very apparent, viz.

(1) the whole pressure range had to be covered with one mixture at a time, thus only one cell could be used, i.e. runs could not be prepared in the other cells because different mixtures were reserved for them,

(2) the pressure dependence of the diffusion coefficient was not linear, so many runs would be required to determine the correct relationship, and

(3) no allowance could be made for any aging effects that the specimens may have exhibited.

The first experimental plan was abandoned, and a plan[†] that would enable a systematic analysis of variance to be

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[†] This plan was prepared with the help of Mr. N.S. Stenhouse of the Department of Mathematical Statistics, C.S.I.R.O., Adelaide.

TABLE 6.2-2

SECOND EXPERIMENTAL PLAN

GAS 1/GAS 2		50/50 (SERIES 20)					75/25 (SERIES 30)					25/75 (SERIES 40)				
PRESSURE (TORR.)		10	25	62.5	156.3	390.6	10	25	62.5	156.3	390.6	10	25	62.5	156.3	390.6
GAS1	GAS2															
KR	KR	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
	XE	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4
	AR	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1
	NE	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3
	HE	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2
XE	KR	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
	XE	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4
	AR	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1
	NE	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3
	HE	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2

carried out on the results prepared. The 150 runs comprising the second plan were arranged in six 5 x 5 Latin squares as shown in Table 6.2-2. The pressures, inactive gases and cells were arranged as the columns, rows and treatments, respectively. The runs underlined were recorded on the Leeds and Northrup recorder, the remainder on the Honeywell-Brown recorder.

This experimental design enables the partitioning of the total variability into portions ascribable to each of the controlling factors, namely, pressures, cells, active gases, inactive gases, gas composition and instrument sets.

6.3 Experimental Procedure

6.3.1 Leak Tests

Once the specimens were fixed in place, the seals were tested for leaks by measuring the permeability of the specimen. Gas on one side of the specimen was permitted to flow through it into a vacuum on the other. The pressure decrease was noted with time, and a rough estimate of the permeability coefficient was made and compared with that obtained for the other specimens. Admittedly this procedure would not detect very small leaks, but, in a system with no total pressure gradient, leaks that were too small to be detected by the permeability measurements were likely to have an insignificant effect on the diffusion results.

These tests could be repeated using say a solid metal block. This idea was discarded because such tests would provide no direct evidence of the soundness of an individual graphite seal.

One seal did fail soon after installation, and the effect on the diffusion rate was so marked that it was felt that the permeability experiments provided sufficient evidence for the soundness of a seal and that any future failure would become immediately apparent.

6.3.2 Conversion of Chart Reading to True Count

The relationship between the output signal from a recorder and the level of radio-activity in one end of a diffusion cell is determined by the ratio of the full-scale deflection of the ratemeter to that of the recorder, the ratio of the scale of the ratemeter to that of the recorder, and the correction factors associated with the dead time of the G-M counters, the half-life of the active isotope and the normal background count.

The methods of determining the values of these factors are discussed below.

(1) The Recorder Adjustments

The full-scale ratemeter output is 100 mV so the recorders were adjusted to give full-scale deflection with an input of 100 mV from a workshop potentiometer. The pen position on each recorder was then adjusted to read exactly 50% of full scale with an input of 50 mV causing errors due to any non-linearity between input and output to be greatest at the extremities of the chart.

(2) Recorder Calibrations

An "Advance" H-1 Pulse Generator was used to feed 20 V square-wave pulses into each ratemeter in turn. The ratemeter outputs were recorded on their respective recorder charts. After a suitable record had been obtained the same generator output was fed to an "EKCO" Automatic Scalar (Type N530F) for two 100-second counting periods. Thus the input to each ratemeter and the corresponding output from each recorder were known, so the relationship between them could be found by plotting chart readings against count rate, drawing in the best straight line, and calculating the constants of the line.

Typical calibration curves are shown in Fig. 6.3-1. The observed count n' is given by

$$n' = CR + G \qquad \ldots\ldots\ldots (6.3\text{-}1)$$

where C and G are constants and R is the chart reading.

It is emphasized that the ratemeters and recorders were high quality instruments which, when properly adjusted and calibrated as described above, should give identical results. Further, since the diffusion coefficients were

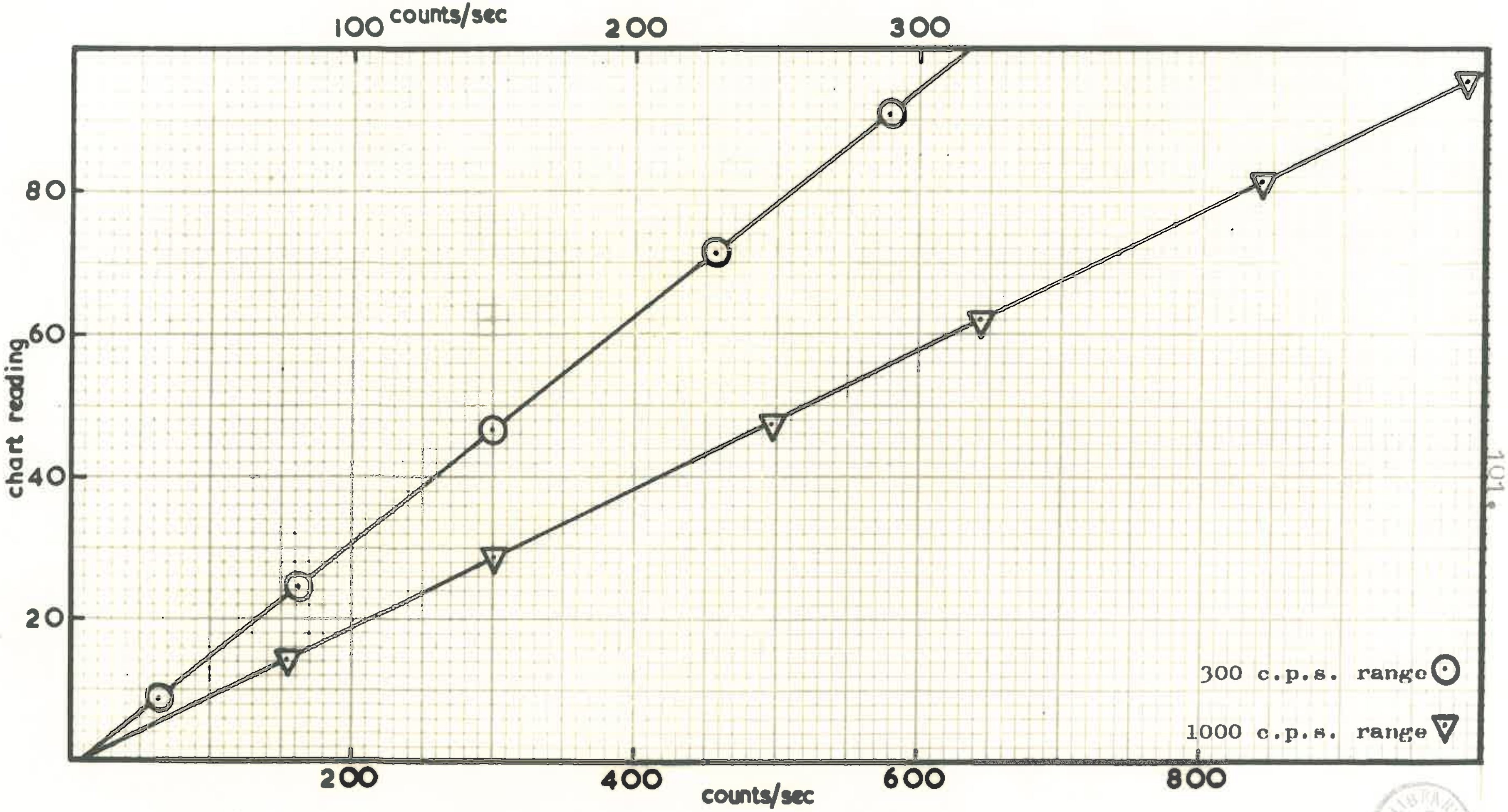

Fig. 6.3-1   A Typical Recorder Calibration Chart

calculated from the difference between two readings on the same record, any absolute differences between the instrument sets would cancel out.

(3) Correction Factors

In most systems for counting events that occur at random time intervals there are some losses due to the finite resolution or dead time of the counter. The true count n can be calculated from the observed count n' by the relation

$$n = n'/(1-n'\tau) \qquad \ldots\ldots\ldots (6.3\text{-}2)$$

where τ is the dead time of the counter. The dead time of a G-M counter is difficult to determine, and may vary, so the dead time was fixed electronically at 200 microseconds which is greater than the natural dead time of the counters.

The half-life correction factor is given by

$$n_t = n_o e^{Ft} \qquad \ldots\ldots\ldots (6.3\text{-}3)$$

where F is the half-life correction factor and t is the time elapsed after the activity measurements have begun. The constant F can be calculated by putting t equal to the known half-life of the isotope, and n_t/n_o equal to $\frac{1}{2}$.

The background count P was measured prior to a run and subtracted from the calculated true count.

The final formula for the true count n is

$$n = (CR + G)\exp(Ft)/\left[1 - \tau(CR + G)\right] - P$$

$$= (CR + G)\exp(Ft)/\left[1 - B(R + G/C)\right] - P \quad \ldots\ldots \; (6.3\text{-}4)$$

where $B = C\tau$.

6.3.3 Primary Dilution of the Active Gases

The radio-active gas capsules J (Fig. 6.1-2) obtained from the Australian Atomic Energy Commission contained a total activity of 100 milli-curies in 2 ml. of gas at 1 atm. A double stopcock assembly was sealed onto each capsule with epoxy resin and elaborate precautions were taken to ensure that the internal seal was not broken before the capsule-stopcock system was thoroughly outgassed (q.v. Appendix C.4). After a capsule had been broken open, a small dose was trapped between the two stopcocks. Some normal isotope of the active gas was transferred from the store B to one of the flasks G, and the dose of active gas released into it.

The activity was measured by expanding the diluted active gas into one chamber of one cell where it was counted. The activity was adjusted to the desired value by freezing the gas back into the tube K and adding more inactive gas, until the desired activity level was attained.

The small toepler pump H was completely superfluous, both for the primary dilution and the mixture-preparation steps.

6.3.4 Mixture Preparation

Inactive gas mixtures were prepared by

(1) filling the bulb of the toepler pump E with one component from storage B, measuring the pressure with the manometer F and pumping the gas contained in the bulb into one of the mixture storage bulbs C,

(2) clearing and evacuating the filling lines and the toepler pump,

(3) filling the toepler pump bulb with the second component (from storage B), and adjusting the pressure so that the two gases would be present in the desired proportions,

(4) pumping this gas into the mixture bulb C containing the first gas,

(5) repeatedly expanding the mixture in C into the toepler pump and pumping it back, and

(6) letting the mixtures stand for at least 30 min. before using it.

For the second set of experiments, a quantity of inactive gas mixture equivalent to the volume of the toepler pump bulb filled to a pressure between 900 and 1000 torr. was sufficient for the five runs planned for each mixture.

Active gas mixtures were prepared in the same way, but much smaller quantities were needed. For the second set of experiments the activity of each mixture was adjusted so that approximately 600 counts/sec. were present in a cell at 10 torr. A quantity of such a mixture equivalent to the volume of the toepler pump bulb filled to 50 torr. was sufficient for the five runs for which it would be required.

6.3.5 Procedure for Diffusion Runs

Before a run could begin, the specimen had to be soaked in the inactive mixture in order to establish a well-defined initial condition, then the inactive mixture in one half of the cell had to be replaced by the active mixture at the same pressure and at an activity such that chart record of the activity in the "inactive" half of the cell should reach an asymptotic value of 90% of full scale. A detailed description of the procedure developed for the final set of experiments is given below.

(1) The inactive gas mixture was pumped into both compartments of the cell in which the run at 390 torr. was to be carried out. The central stopcock was open so that the previously outgassed specimen could be soaked in this mixture.

(2) The pressure was adjusted to the required value by manipulating the toepler pump, then the cell with its manometer was isolated from the cell line, the gas in the line was expanded into the cell to be run at 156 torr. and step (1) was repeated.

(3) Steps (1) and (2) were repeated until all the

cells were filled at successively lower pressures.

(4) The gas mixture was left in the cells for two hours to allow time for complete equilibration with the specimen.

(5) Starting with the cell containing gas at the highest pressure, the pressure of gas in each cell was read, the central stopcock closed and the inactive gas from one side of the cell pumped back into the bulbs C. The cell line was then evacuated.

(6) The active gas was slowly let into the lowest pressure cell until the required activity was present, then the pressure was adjusted by admitting some of the inactive gas mixture. Since the active and inactive gas mixtures were admitted through the same long length of filling line, a high degree of manipulative skill and judgement were required to adjust the activity so that it was within the desired range of 600 ± 50 counts/sec when the pressure was correct.

(7) The gas was left for 30 minutes to come to thermal equilibrium, during which time the background count on the inactive side was recorded, then the pressure was finally adjusted.

(8) The first run (at 10 torr.) was started by isolating the cell from the manometer, opening the central stopcock and switching on the recorder chart.

(9) Steps (6) and (7) were repeated for the remaining cells, but no further runs could be started until the active gas mixture had been admitted to all cells, because one ratemeter was needed to measure the activity put into each cell.

(10) A further run was started as soon as either ratemeter became available - generally two runs were left going overnight under the control of the time switches.

(11) As soon as the last runs were under way, new mixtures were prepared.

(12) At the end of each run the specimens were outgassed for two hours.

(13) Steps (1) to (12) were repeated until all the experiments in Table 6.2-2 were completed.

Data for calculating the diffusion coefficient for each run were taken from the chart recording of the build-up of activity on the inactive side of the specimen. Charts were removed from the recorder and a mean line was drawn by eye on top of each chart record. Chart values at selected time intervals were listed on data sheets so they could be transferred to punched cards.

7. CALCULATION OF EXPERIMENTAL RESULTS

7.1 Solution of Fick's Second Law

The transient-state measurements described in Section 6.3.5 are mathematically analogous to the two-bulb capillary-tube method of measuring diffusion coefficients in bulk gas mixtures. Exact and approximate solutions of Fick's second law for this method have been presented in the literature. These solutions are discussed below using the following nomenclature:

$C(x,t)$ = concentration at a distance x from one end of the capillary at time t,

$C(0,t)$ = concentration at the end of the capillary adjacent to bulb 1 at time t,

$C(L,t)$ = concentration at the end of the capillary adjacent to bulb 2 at time t,

$C_1(t), C_2(t)$ = concentrations in bulbs 1 and 2 respectively, at time t,

L = length of the capillary,

v = volume of the capillary,

V_1, V_2 = volumes of bulbs 1 and 2,

= v/V for the special case of $V_1=V_2=V$, and

D = diffusion coefficient.

When L and v represent the length and volume of a cylindrical disc of porous material, D becomes the effective diffusion coefficient D_{eff}.

Barnes (115) has presented the exact solution of Fick's second law for the conditions.

$$V_1 = V_2 = V \qquad \ldots\ldots (1)$$

$$C_1(0) = C(x,0) = 0, 0 \leq x \leq L \qquad \ldots\ldots (2)$$

$$C_1(t) = C(0,t);\ C_2(t) = C(L,t) \qquad \ldots\ldots (3)$$

$$\partial C_1(0)/\partial t = (D/V)(\partial C(x,t)/\partial x)_{x=0},$$

$$\partial C_2(0)/\partial t = (D/V)(\partial C(x,t)/\partial x)_{x=L} \qquad \ldots\ldots (4)$$

Condition (3) implies that no concentration gradients exist in the two bulbs.

Barnes showed that the concentrations in the bulbs at time t are given by

$$\begin{aligned} C_j(t) = \left[C_2(0)/2\right]\Big[& 1-\gamma/2 + \gamma^2/4 - \ldots \\ & +(-1)^j(1-\gamma/6+\gamma^2/60-\ldots)\exp\left[-2\gamma Dt(1-\gamma/6+\gamma^2/45\ldots)/L^2\right] \\ & +(-1)^j \sum_{i=1}^{\infty} (-1)^i \frac{4\gamma}{i^2\pi^2}(1-6\gamma/i^2\pi^2\ldots)\exp\left[-Dt(i^2\pi^2+4\gamma)/L^2\right]\Big], \end{aligned}$$

$$j=1,2 \qquad \ldots\ldots (7.1\text{-}1)$$

The same solutions were derived by Dye and Dallevalle (87). For the values of γ, L and D encountered in the present experimental work, it is easy to show that the series term vanishes at values of t greater than five minutes. Powers of γ greater than the first can also be neglected, so Eq. 7.1-1 reduces to

$$C_i(t) = \Big[C_2(0)/2\Big]\Big[1- \ /2+(-1)^i(1-\gamma/6)\exp(-2\gamma Dt\Big(1-\gamma/6\Big)/L^2)\Big] ,$$

$$i=1,2 \;.. \qquad \qquad .... \; (7.1\text{-}2)$$

A simplified solution of the two bulb problem was developed by Ney and Armistead (116). They assumed

(1) that a linear concentration gradient was set up in the capillary connecting the two volumes, i.e. a quasi-stationary state existed,

(2) that the concentration gradient was all in the connecting tube, and

(3) that the volume of the connecting tube was negligible compared with the volume of the bulbs.

Their final expression was

$$\frac{C(\infty)-C_2(t)}{C(\infty)-C_2(0)} = e^{-\alpha t} \qquad .... \; (7.1\text{-}3)$$

where $\alpha = (Dv/L^2)\Big[(V_1+V_2)/V_1V_2\Big]$ .... (7.1-4)

and $C(\infty)$ is the concentration at infinite time. It is to be noted that when $V_1=V_2$, $\alpha = 2\gamma/L^2$, so Eq. 7.1-3 becomes

$$C_2(t) = \Big[C_2(0)/2\Big]\Big[1+\exp(-2\gamma Dt/L^2)\Big] \quad .... \; (7.1\text{-}5)$$

and the corresponding equation for the concentration change on the increase side is

$$C_1(t) = \left[C_2(0)/2\right]\left[1-\exp(-2\gamma Dt/L^2)\right] \qquad \ldots\ldots\ldots \ (7.1\text{-}6)$$

These equations are of the same form as Eq. 7.1-2.

Ney and Armistead also suggested a more complicated expression for α that took into account the volume of the capillary and included an end correction factor to allow for the concentration gradient extending a small way into each bulb. The γ terms in Barnes' solution allow for the volume of the capillary in a manner that is mathematically exact, however they do not allow for an end correction. End corrections are meaningless in porous media work and are not considered further.

Summarising, both the exact and approximate solutions are of the form

$$C_i(t) = A+(-1)^i Be^{-\alpha t}, \ i=1,2 \qquad \ldots\ldots \ (7.1\text{-}7)$$

provided γ is sufficiently small to make the series term of the exact solution vanish after the first few minutes, but the constants A, B and α are not the same. In particular, Barnes' solution shows that A/B is constant but not equal to unity, and that the cell constant $E=D/\alpha$ differs slightly from the Ney and Armistead expression. (Values of E are given in Table C.2-3).

In order to solve Eq. 7.1-7 for α and hence D, the constants A and B must be eliminated or separately determined. Most previous workers, with the notable exception of Dye and Dallevalle (87), calculated $A = C(\infty)$ from the initial concentrations and cell dimensions, plotted ln $(|C(\infty)-C_1(t)|)$ against time and fitted the least squares straight line to the data points. The slope of this line gave α. Where the least squares line was not fitted (e.g. Srivastava, 121) they assumed $A/B = 1$. Dye and Dallevalle used a trial and error procedure, which they did not explain, to evaluate D from Eq. 7.1-1.

7.1.1 Development of Numerical Procedures

Direct substitution methods for calculating the diffusion coefficients were used at first. By taking pairs of $C_1(t)$ values, A was eliminated from Eq. 7.1-7, then assuming A/B was defined by Eq. 7.1-2, values of α were calculated from as many pairs of points as desired. When it was found that this procedure did not give consistent values of α, a three-point method which eliminated the assumption that A/B was constant was tried. This method gave improved results, but the derived values of A, B and α did not always define a curve that would fit the data well. A discussion of these methods and their limitations is given in Appendix D.

Because the substitution methods gave rather poor results it was concluded that either the method of averaging the values of α was poor, or the differences between the physical and mathematical boundary conditions was sufficiently great to change the form of the expression for $C_1(t)$. In order to test both these alternatives, the curves

$$C = A - B\exp(-\alpha t)$$

and $$C = A/\left[1 + \exp(-B - \alpha t)\right]$$

were fitted to the data from several runs by the least-squares technique described in Appendix D.3. This analysis showed that the data did not conform to Eq. 7.1-7 and that a least-squares method would give a sufficiently accurate estimate of α.

7.1.2 Calculation of α

The iterative multiple regression procedure developed by Williams (117) was used to calculate the best value of the defined by Eq. 7.1-7, and to estimate the errors in the regression constants.

If Eq. 7.1-7 is written in the form

$$C = A + Bf(t, \alpha) \qquad \ldots\ldots\ (7.1\text{-}8)$$

and if the adjustment to a preliminary estimate of α is $\delta\alpha$, then, by Newton's Rule, an improved value of f is given by

$$f_2 = f_1 + \delta\alpha f'_1 \qquad \ldots\ldots\ (7.1\text{-}9)$$

where $$f' = df/d\alpha \qquad \ldots\ldots\ (7.1\text{-}10)$$

Williams points out that the regression equation becomes, to a first approximation,

$$C = A + B_1(f + \delta\alpha f')$$

$$= A + B_1 f + B_2 f' \qquad \ldots\ldots\ldots \; (7.1\text{-}11)$$

where $B_2 = B_1 \; \delta\alpha$,

$f = \exp(-\alpha t)$

and $f' = -t \exp(-\alpha t)$

To find the best value of α, an initial estimate of α was first obtained using the three-point substitution method, then a multiple linear regression of C on f and f' was carried out to evaluate B_1 and B_2 and hence $\delta\alpha$. The regression coefficients were recalculated using the corrected value of α. In most cases four iterations gave the required accuracy. A final calculation of the regression of C on f was carried out. In most cases the final value of B_2 was so small that it had an insignificant effect on the values of A and B.

7.2 <u>The Computer Input and Output</u>

Because the data were originally punched on cards in a form suitable for calculating α from pairs of $C_1(t)$ values, they had to be rearranged and additional values had to be interpolated before α could be calculated by the more accurate three-point method. Once this was accomplished, the succeeding steps in the calculation were

TABLE 7.2-1
DATA, CONVERTED DATA AND RESULTS FOR RUN 389-40

DATA

```
389 40  30       P=156.36
     5700E1       3000E0         9982E0        628E-2        3140E1        2300E1
     2234-1                      6000E1
  297    310    323    335    348    360    372    384    396    407    417    428
  438    449    459    468    477    486    496    505    514    523    532    541
  550    559    567    575    583    591    505    523    541    559    575    591
  605    618    631    643    654    666    678    689    700    712    721    730
  740    749    757    764    772    780    788    795    801    807    814    819
```

CONVERTED DATA

```
389 40  26          156.36
57.0000E-01 30.0000E-02 22.3400E-03 78.0000E-01 62.7514E-03
98.9683E-00 10.3220E+01 10.7480E+01 11.1418E+01 11.5692E+01 11.9643E+01
12.3600E+01 12.7563E+01 13.1532E+01 13.5176E+01 13.8494E+01 14.2147E+01
14.5474E+01 14.9137E+01 15.2473E+01 15.5478E+01 15.8487E+01 16.1499E+01
16.4851E+01 16.7871E+01 17.0894E+01 17.3921E+01 17.6951E+01 17.9985E+01
18.3023E+01 18.6064E+01 18.8770E+01 19.1479E+01 19.4191E+01 19.6906E+01
19.9284E+01 20.1664E+01 20.3876E+01 20.6089E+01 20.8305E+01 21.0522E+01
21.2571E+01 21.4621E+01 21.6502E+01 21.8384E+01 22.0439E+01 22.2495E+01
22.4553E+01 22.6613E+01 22.8502E+01 23.0393E+01 23.2285E+01 23.4179E+01
23.6246E+01 23.8315E+01 23.9868E+01 24.1421E+01 24.2976E+01 24.4531E+01
24.6261E+01 24.7991E+01 24.9550E+01 25.1109E+01 25.2496E+01 25.3884E+01
25.5099E+01 25.6314E+01 25.7704E+01 25.9094E+01 26.0485E+01 26.1877E+01
26.3270E+01 26.4663E+01 26.5883E+01 26.7103E+01 26.8149E+01 26.9196E+01
27.0244E+01 27.1291E+01 27.2514E+01 27.3738E+01 27.4612E+01 27.5486E+01
```

TABLE 7.2-1 (CONT.)

```
                                          RESULTS

                         RUN  389 40 PRESS= 156.36    26
62.7514E-03
  3
     DF      SS            MS            VR
REGN  2  2.0199E+05  1.0099E+05  7.8252E+05
DEVN 75  9.6800E-00  1.2906E-01
TOTL 77  2.0200E+05

 A= 32.994E+01 B1=-3.3020E+02   B2= 6.1500E-04   C= 6.2671E-02
             SEB1= 2.7743E-01 SEB2= 9.1835E-02 SEC= 2.7812E-04

 A= 32.995E+01 B1=-3.3020E+02   B2=
REGSS=2.0199E+05 D= 1.4000E-03
```

(1) the conversion of chart readings to true counts by Eq. 6.3-4,

(2) the estimation of an initial value of α ,

(3) the calculation of the final regression value of α by the iterative procedure outlined in Section 7.1.2, and

(4) the estimation of the standard error of α .

These calculations were carried out by means of two programmes written for the University's I.B.M. 1620 computer. Using the first programme, the computer rearranged the data, converted the chart readings to true counts, estimated α and punched out the data in a form suitable for the second programme. The final value and the standard error of α were calculated under the control of the second programme. A detailed description of these programmes is given in Appendix E.

The input data, converted data and the final results for one run are given in Table 7.2-1. The input data and final results are discussed below; the converted data are self-explanatory.

7.2.1 The Input Data Cards

The first three data cards for each run contain the constants used in the calculations; the remaining cards contain the data points.

The first number on the first card is a run number which identifies the two gases present in the mixture and the cell in which the run was carried out. The first digit of this number represents the cell, therefore it can have any value in the range 1 to 5, the second the active gas (Kr is represented by 8 and Xe by 9) and the third the inactive gas. Where no third digit occurs, the inactive is the same as the active gas. The numerical symbols for the inactive gas are listed in Table 7.2-2.

Table 7.2-2

Numerical Symbols for Gases

Gas	Symbol
He	5
Ne	6
Ar	7
Kr	8
Xe	9

The second number on the first card represents the volume ratio of gas 1 to gas 2 where gas 1 is the active or differing gas. Its value may be 20, 30 or 40 as gas 1 is present as 50, 75 or 25 per cent of the mixture. To illustrate the coding system, the run numbers 389 and 40 from the data listed in Table 7.2-1 may be cited. They indicate that the rate of diffusion of Kr^{85} in a 25/75 Kr/Xe mixture was measured in cell 3.

The remaining constants used in the calculations are identified and discussed in Appendix E.

The data from the complete set of 150 runs in the second experimental plan is listed in Appendix I. A set of data cards for all the runs carried out, including those not reported in this thesis, is available in the Department of Chemical Engineering.

7.2.2 The Computed Output

Each run produces 14 punched cards (including 3 blank spacer cards) and four lines of printed output. The printed output informs the operator of the progress of the calculations. It is discussed in Appendix E. A line-by-line description of the card listing (see Table 7.2-1) is given below. Blank lines are not counted.

Line 1. The run numbers, pressure and a number equal to one-third of the total number of data points.

Line 2. The initial estimate of α.

Line 3. The number of iterations.

Line 4. Headings for the analysis of variance table.

DF = degrees of freedom.
SS = sum of squares of deviations.
MS = mean squared deviation or variance.
VR = variance ratio.

Line 5. The degrees of freedom for regression, the regression sum of squares of deviations (R.S.S.), the regression variance and the variance ratio.

Line 6. The degrees of freedom (d.f.) for error, the deviation sum of squares (D.S.S.) and the deviation variance.

Line 7. The total d.f. and the total sum of squares of deviations (T.S.S.).

Line 8. The multiple regression coefficients A, B_1 and B_2, and α (denoted by C in the listing).

Line 9. The standard errors in B_1, B_2 and α.

Line 10. The linear regression coefficients A and B_1 (calculated with B_2 set equal to zero.)

Line 11. R.S.S. with $B_2=0$, and the value (D) of α multiplied by the measured cell constant E. The symbol D represents the effective diffusion coefficient D_{eff}.

In the analysis described in Chapter 8, values of α rather than D_{eff} were used in order to avoid compounding the experimental errors in E with those already associated with α.

A listing of the card output for the complete set of 150 runs is given in Appendix H. There were two minor errors in the programme when these results were obtained. They are discussed in Appendix H. Table 7.2-1 contains the correct values for Run 389-40.

7.2.3 Accuracy of the Computed Values of α

The variance ratio and the standard errors in the regression coefficients for all the runs were of the same order of magnitude as the values listed in Table 7.2-1 for Run 389-40. The high variance ratio, the small standard errors in the regression coefficients, and the fact that B_2 accounted for a negligible amount of the variability indicated that, for all the runs, the fitted curves represented the experimental data to a high degree of accuracy. In Fig. 7.2-1, where the fitted curve for Run 389-40 is plotted through the data points, the close agreement predicted by the statistical analysis is well illustrated.

A test was carried out on one run to see whether changing the number of data points significantly altered α. It was found that α was virtually independent of the number of points provided the same proportion of the total experimental curve was used. If however, successively smaller lengths of the curve were used, the value of α became slowly smaller.

An estimate of the proportion of the experimental curve used for each run was made by dividing the last data point by the regression coefficient A (the asymptote to the fitted curve). For 116 of the 150 runs, this ratio lay between 0.80 and 0.87, and for 139 runs the ratio lay

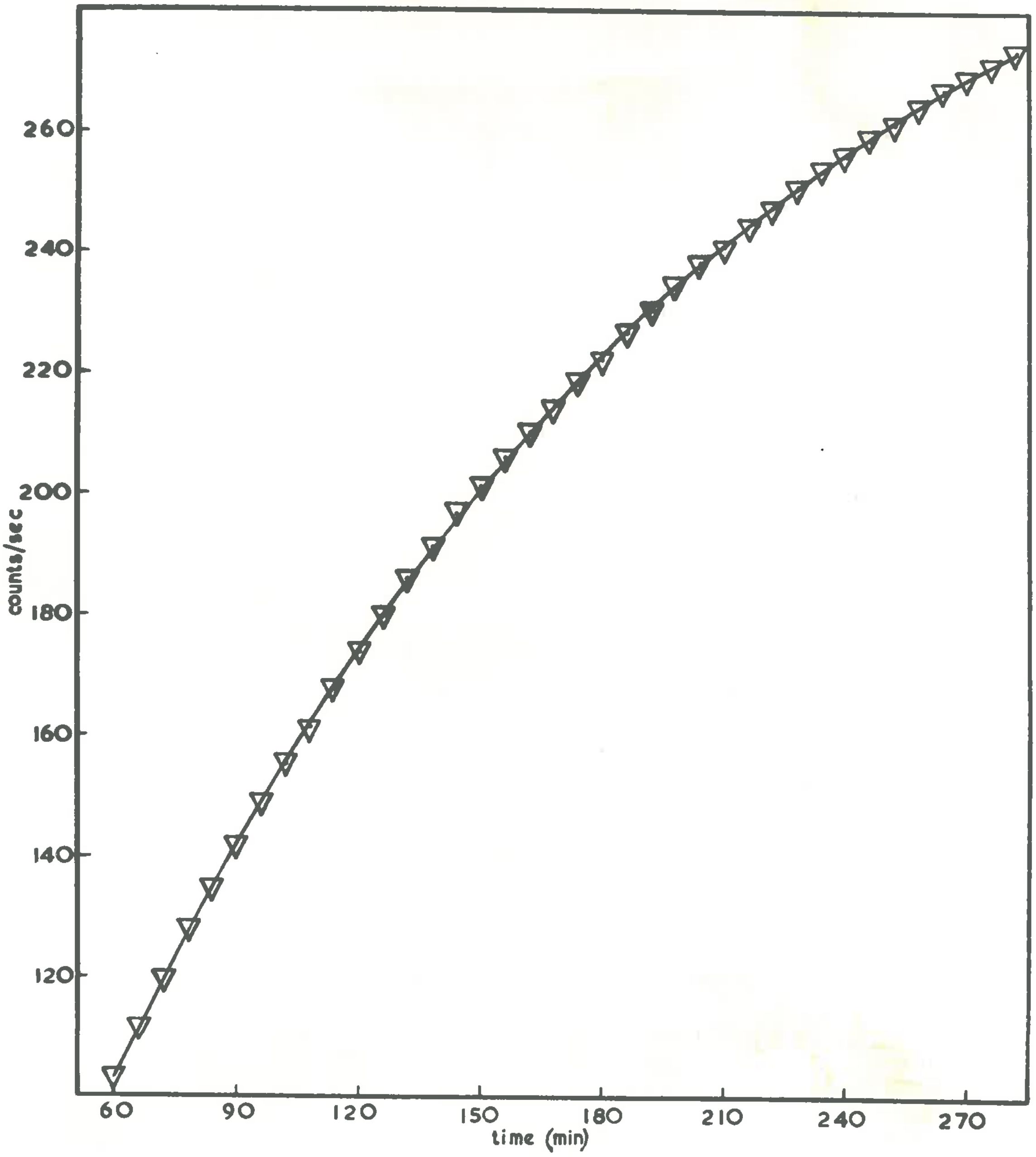

Fig. 7.2-1 Data and the Fitted Curve for Run 389-40

between 0.75 and 0.90. Out of the eleven runs remaining, this ratio was above 0.70 for nine of them, and only just below 0.70 for the tenth. The ratio for the eleventh run was 0.21. The data for this run (number 598-40) indicated that the ratemeter had been set on the wrong scale, with the result that the recorder pen had run off the scale long before the run was complete. At the time of carrying out the experiment it was thought that a sufficient record had been obtained for a satisfactory estimate of α, however, even a casual glance at the α valuesgiven in Table 7.3-1 is sufficient to show that this value is suspect. A similar comparison of the values of α obtained for the ten other dubious runs did not reveal any obvious discrepancies.

It was concluded that, apart from Run 598-40 (marked with an asterisk in Table 7.3-1), errors from this source were likely to be small and that any attempt to compensate for these variations would not significantly reduce the uncertainty of α.

7.3 <u>The Results</u>

The value of α computed from the 150 runs in the second experimental plan are presented below in Table 7.3-1. The valuesunderlined were calculated from the runs recorded on the Leeds and Northrup recorder; the remaining runs were recorded on the Honeywell-Brown recorder.

TABLE 7.3-1

LIST OF ALPHA VALUES
COMPUTED FROM EXPONENTIAL REGRESSION PROGRAMME

SERIES 20
GAS 1/GAS 2 = 50/50

MEAN PRESSURE (TORR.)		10.0	25.0	62.5	156.3	390.6
GAS 1	GAS 2					
	KR	.1392	.1262	.1081	.0628	.0517
	XE	.0905	.1275	.1134	.0692	.0312
KR	AR	.1386	.1214	.0947	.0577	.0546
	NE	.1202	.0843	.1027	.0950	.0746
	HE	.1262	.1011	.0904	.0848	.0622
	KR	.1002	.0951	.0763	.0531	.0365
	XE	.0818	.0963	.0826	.0496	.0352
XE	AR	.1147	.0997	.0753	.0523	.0386
	NE	.0961	.1060	.0942	.0716	.0485
	HE	.1097	.0897	.0660	.0787	.0504

SERIES 30
GAS 1/GAS 2 = 75/25

	KR	.1262	.1143	.0955	.0634	.0333
	XE	.0917	.1178	.0999	.0787	.0432
KR	AR	.1306	.1237	.0892	.0608	.0513
	NE	.1227	.1232	.1124	.0699	.0569
	HE	.1374	.1013	.0598	.0847	.0736

TABLE 7.3-1 (CONT.)

MEAN PRESSURE (TORR.)		10.0	25.0	62.5	156.3	390.6
GAS 1	GAS 2					
XE	KR	.1136	.0856	.0809	.0490	.0370
	XE	.0706	.1052	.0805	.0552	.0327
	AR	.1233	.0889	.0854	.0426	.0463
	NE	.0962	.0693	.0870	.0664	.0388
	HE	.1121	.0988	.0608	.0675	.0408

SERIES 40
GAS 1/GAS 2 = 25/75

KR	KR	.1536	.1139	.1057	.0602	.0378
	XE	.0795	.1175	.1044	.0627	.0340
	AR	.1349	.1241	.0953	.0496	.0636
	NE	.1125	.0832	.1347	.0898	.0633
	HE	.1347	.1091	.0721	.0966	.0836
XE	KR	.1276	.1076	.0898	.0549	.0119*
	XE	.0713	.1124	.0784	.0585	.0340
	AR	.1207	.1062	.0758	.0453	.0569
	NE	.1030	.0742	.1008	.0841	.0606
	HE	.1225	.0948	.0587	.0863	.0680

8. ANALYSIS OF RESULTS

In this and subsequent sections the controlled variates are denoted by the symbols in Table 8.0-1. Numerical subscripts identify particular numerical or descriptive levels of the variates, thus g_{11} represents active Kr and g_{12} represents active Xe.

Table 8.0-1

Symbols for the Controlled Variates

Controlled Variate	Symbol	Levels of Variate
Pressure	p_i i=1,2..5	10, 25, 62.5, 156.3, 390.6 torr.
Cell	c_j j=1,2..5	See Tables C.2-1, C.2-2, C.2-3 for geometry of cells.
Active Gas	g_{1h} h=1,2	Kr, Xe
Inactive Gas	g_{2k} k=1,2..5	Kr, Xe, Ar, Ne, He.
Ratio Active/ Inactive Gas (Series)	s_t t=1,2,3	50/50, 75/25, 25/75.
Instruments	I_r r=1,2	L & N recorder, H-B recorder

For convenience, the six Latin squares are referred to as L_{ht} where h and t have the meaning ascribed to them in Table 8.0-1.

8.1 Preliminary Analysis

The experimental programme was performed with two sets of measuring and recording equipment so that two runs could be carried out simultaneously. Because high-quality instruments were used, and because they were adjusted and calibrated against an accurate scalar counter, there was no reason to suppose that any difference existed between their outputs. Since, apart from instruments, each of the six Latin squares can be regarded as an experiment in itself, the first approach was to analyse each separately, ignoring instrument effects.

The analyses of variance of the squares are presented in Appendix F.1.

It was found that

(1) cells differed significantly in all the squares,
(2) pressures differed significantly in all the squares, and
(3) inactive gases differed significantly only in L_{13} and L_{23}.

In order to examine the relation between α and pressure, the individual cell effects were calculated for each square and every α value was adjusted by the method described in Appendix F.2 (where a complete Table of adjusted values is presented). Then, for each of the thirty combinations of g_1, g_2 and s, the adjusted values of α (denoted by α_c) were plotted against log p. The

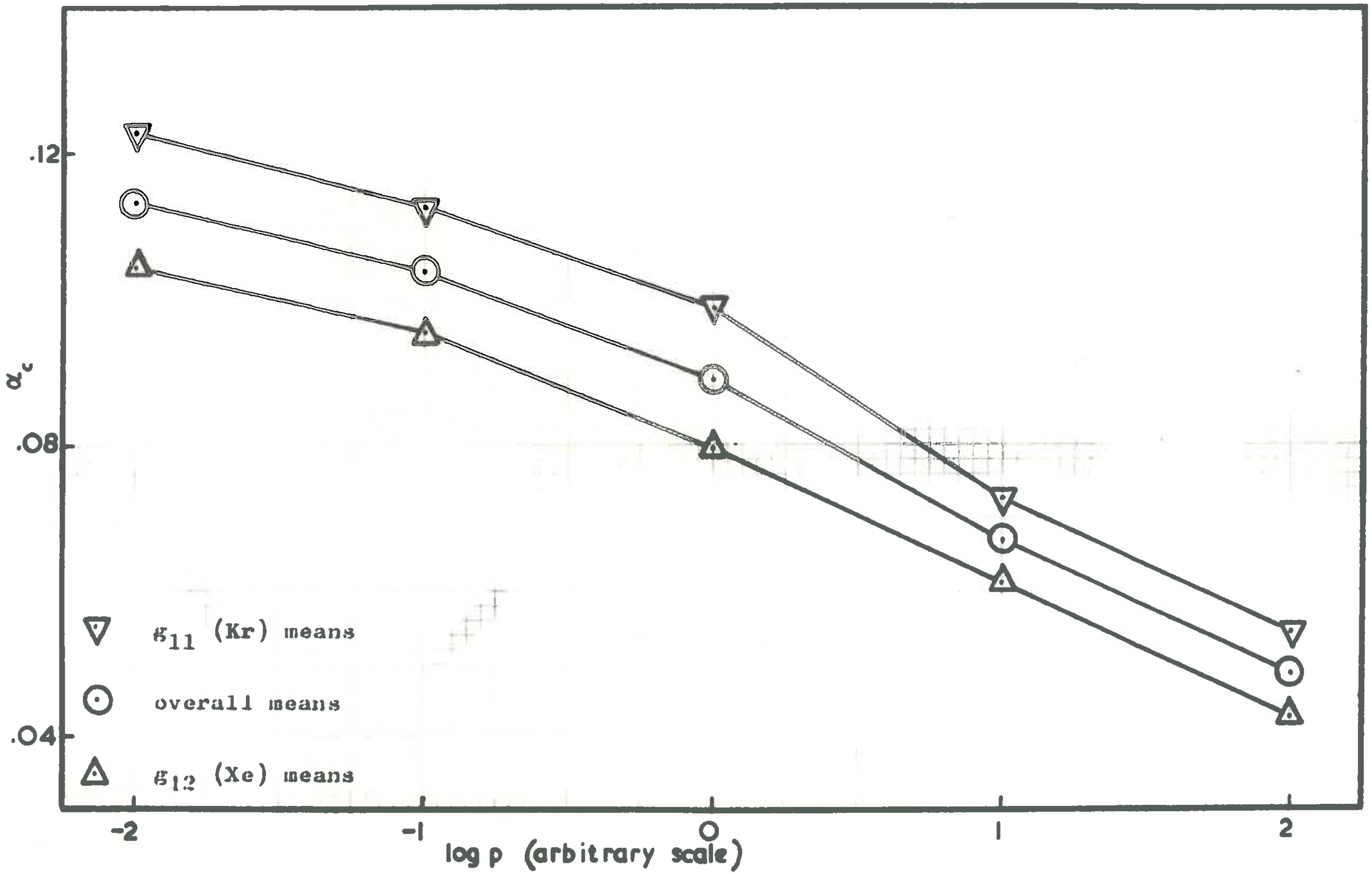

Fig. 8.1-1 The Variation of α_c with Log p

means of the 15 g_{11} and the 15 g_{12} curves together with the overall mean relationship are presented in Fig. 8.1-1. Various functions of α_c and p were examined in an attempt to linearise the relationships and at the same time produce more nearly equal error variances in each square. The most promising pair of functions was log α and log p, so the above analyses of variance were repeated using log α.

8.2 The Analysis of Log α

The values of $\alpha' = \log_{10}(100\alpha)$ together with the appropriate Latin square analyses are presented in Appendix F.3. As before, pressure and cell effects were significant in all squares, however the g_2 effect was significant in L_{13} and L_{21} whereas in the previous analysis it was significant in L_{13} and L_{23}. This result drew attention to the E.S.S. (error sum of squares of deviations) in the L_{23} analysis which increased from 1.5% to 9.5% of the T.S.S. after transformation. Since this square contained the dubious run referred to in Section 7.2.3, the decision was made to discard this value and to replace it for purposes of analysis by a dummy figure calculated by the usual missing value technique (118, p.246).

The analysis of L_{23} using the dummy value is presented in Appendix F.3. The error variance, which was previously 0.009116 on 12 d.f. was reduced to 0.000941 on

11 d.f. The dummy value was used in all subsequent analyses.

8.3 Regression of α'_c on Pressure

The cell effects were removed from the α' values by the method referred to previously and regressions of α'_c on $\log_{10} p$ were calculated. In effect, the regression calculations repartition the sum of the pressure and error terms in each Latin square analysis into two parts, one representing R.S.S. on 5 d.f., the other D.S.S. (deviations from regression sum of squares) on 11 d.f. The Latin square analyses with the T.S.S. partitioned in this way and the Table of α'_c values are listed in Appendix F.4.

For each square, the deviation variance on 11 d.f. was much higher than the error variance on 12 d.f. in the corresponding Latin square analyses. A plot of α'_c against log p revealed a pronounced curvature in the relationship between the two, which possibly accounted for the inflation of the deviation variance. The three curves corresponding to those in Fig. 8.1-1 are presented in Fig. 8.3-1. Thus, although the log transformation produced the desired effects on the E.S.S., the relation between α'_c and log p was unsatisfactory. Nevertheless, the similarity between the curves of Fig. 8.3-1 and those presented by Scott and Cox (85) (Fig. 4.4-1) was noted.

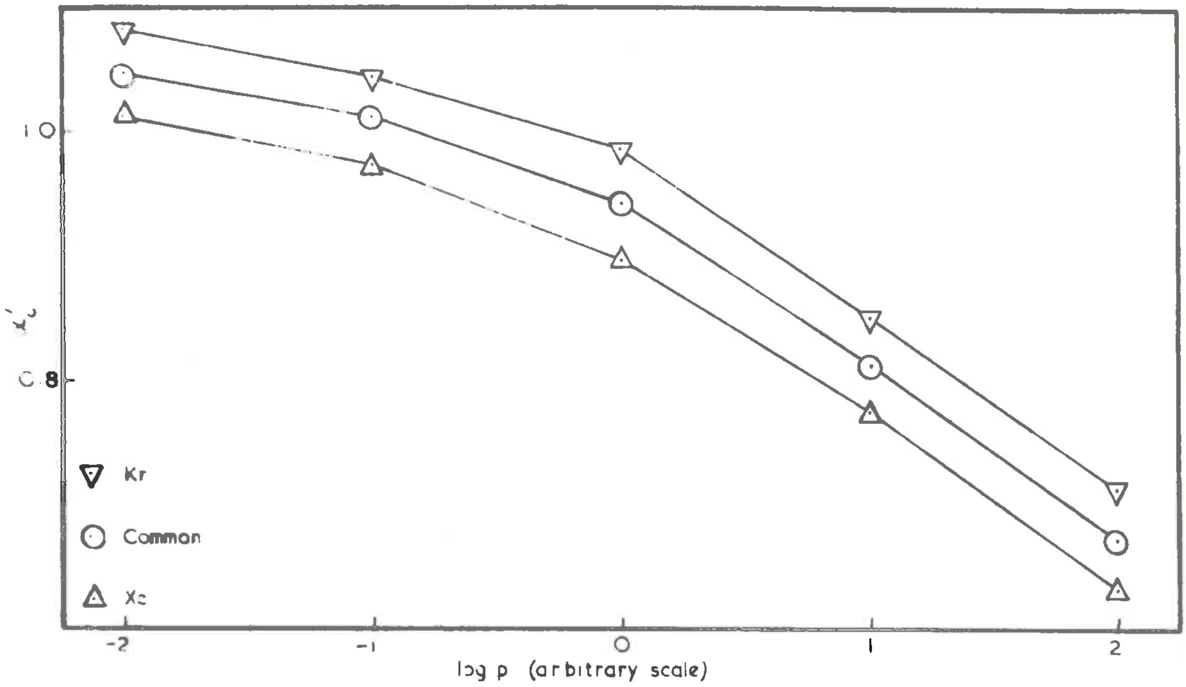

Fig. 8.3-1 The Relation between α'_c & log p

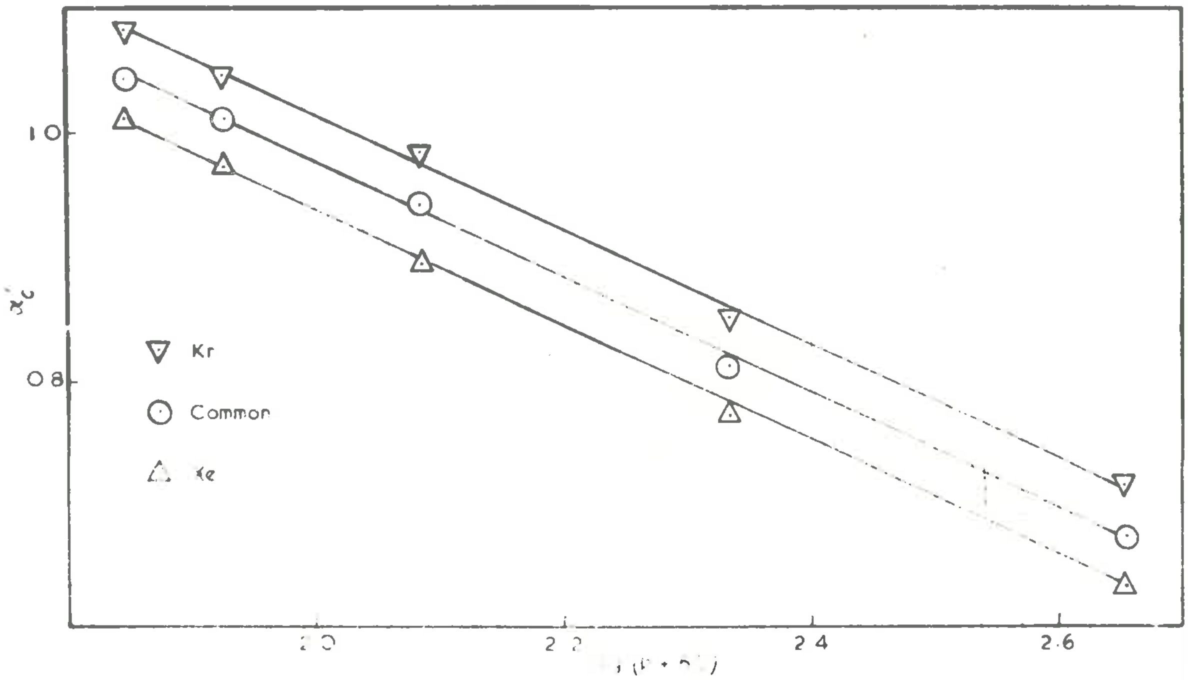

Fig 8.3-2 The q_i & Common Regressions

The shape of the curves in Fig. 8.3-1 suggested that the pressure dependence of α'_c could be linearised by relating α'_c to log (p + H) where H is a constant to be determined.

The use of log (p + H) is in accord with current diffusion theory. Thus in Section 9.3 it is shown that Mason's model (107,119) for gas diffusion in porous materials can be written in the form

$$1/D_{eff} = Kp + H \qquad \ldots\ldots (8.3\text{-}1)$$

and, given the same assumptions, this relation will still hold for the present case of self diffusion through a mixture of gases in graphite. The more general relation

$$\log D_{eff} = A + B \log (p + H) \qquad \ldots\ldots (8.3\text{-}2)$$

reduces the form of Eq. 8.3-1 when B = -1. Thus the use of Eq. 5.3-2 in the form

$$\alpha'_c = A + B \log_{10} (p + H) \qquad \ldots\ldots (8.3\text{-}3)$$

would retain maximum flexibility in the regression model, and at the same time adequately test the validity of Mason's diffusion model.

The iterative technique described in Section 4.4 for fitting non-linear regressions was used to obtain the best

TABLE 8.3-1
RESULTS OF ITERATIVE LOGARITHMIC REGRESSION CALCULATIONS

THE G1 REGRESSION

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
REGRESSION	2	.091703	.045851	365.27***
DEVIATIONS	2	.000251	.000126	
TOTAL	4	.091954		

	COEFFS.	STD. ERROR
A	1.9899	
B1	-0.4802	.07566
H	66.626	25.626

THE G2 REGRESSION

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
REGRESSION	2	.097114	.048557	317.45***
DEVIATIONS	2	.000030	.000015	
TOTAL	4	.097145		

	COEFFS.	STD. ERROR
A	1.8379	
B1	-0.4563	.02263
H	54.048	7.1015

THE COMMON REGRESSION

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
REGRESSION	2	.094374	.047187	977.92***
DEVIATIONS	2	.000097	.000048	
TOTAL	4	.094471		

	COEFFS.	STD. ERROR
A	1.9131	
B1	-0.4681	.04340
H	60.118	14.159

TABLE 8.3-2

COMPARISION OF DEVIATION AND ERROR VARIANCES

	DEVIATION (11 D.F.)		ERROR (12 D.F.)
	LOG P	LOG(P+60)	
L(1,1)	.006103	.002443	.003682
L(2,1)	.004703	.001876	.001524
L(1,2)	.005404	.002443	.003839
L(2,2)	.004511	.001633	.002031
L(1,3)	.004058	.001528	.001644
L(2,3)	.041468	.000825	.000941
L(2,3)	.001468	.000825	.000941

value of H in Eq. 8.3-4. For a logarithmic regression

$$f = \log (p + H) \text{ and } f' = 1/(p + H) \qquad \ldots\ldots (8.3\text{-}5)$$

The thirty single regressions and the mean regressions for each Latin square, each g_1 and the complete experiment were calculated. The analysis of variance and regression analysis for the means of each g_1 and the overall mean are presented in Table 8.3-1. The iterative technique gave many values of H for the thirty single regressions, all with high standard errors. It was obvious that the value of H was not critical, so, because it was necessary for H to be constant for all the regressions if comparisons between them were to be made, linear regressions of α'_c on $\log_{10}(p + 60)$ were calculated, since 60 ± 14 was the H value for the mean of all the regressions. In no case did the use of 60 instead of the best estimate of H from the iterative procedure make any appreciable difference to the R.S.S. Further, Fig. 8.3-2 shows that these relationships were now linear. Of more importance is the fact that the analysis of variance of the regressions on $\log (p + 60)$ in each square (q.v. Appendix F.4) showed that the deviation variances on 11 d.f. were lower than the error variances of the Latin square analyses on 12 d.f. The deviation variances in the analysis of the regressions on $\log p$ and $\log (p + 60)$ are compared with the error variances in the Latin square analyses in Table 8.3-2.

8.4 The Comprehensive Analysis

In the comprehensive analysis, the Latin squares were combined so that all the main effects (g_1, g_2, p, s, c, and I) and their interactions, if any, could be evaluated over the whole experiment.

The 148 d.f. made available[†] by this procedure were partitioned as follows:

(1) 30 d.f. for the regressions on log $(p + 60)$,
(2) 29 d.f. for the main effects g_1, g_2 and s, and their interactions,
(3) 24 d.f. for the cell effects within squares, and
(4) 65 d.f. for error.

The analysis of variance corresponding to this partitioning is presented in Table 8.4-1 where it is shown that the regressions, means and cell effects were all highly significant.

8.4.1 Instrument Effects

Because the instrument effects were confounded with the g_1 effects and because there was no reason to expect

---

[†] The use of the dummy value decreased the d.f. of the error variance from 66 to 65 and the d.f. of the T.S.S. from 149 to 148.

TABLE 8.4-1
COMPREHENSIVE ANALYSIS - MAIN EFFECTS

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
MEANS	29	.416692	.014369	8.169***
REGRESSIONS	30	2.913024	.097100	55.202***
CELLS IN SQUARES	24	.711693	.029654	16.858***
ERROR	65	.114364	.001759	
TOTAL	148	4.155774		

TABLE 8.4-2
ANALYSIS OF MEANS

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
G1	1	.234004	.234004	133.033***
G2	4	.119697	.029924	17.012***
S	2	.018913	.009456	5.376**
G1 X G2	4	.000351	.000088	- NS
G1 X S	2	.010754	.005337	3.057 NS
(G2.S) + (G1.G2.S)	16	.032973	.002061	1.172 NS
MEANS	29	.416692		

them to be different, they were disregarded in the above analysis. Before further analyses were performed, the instrument S.S. were calculated and found to be not significant compared with the error variance given in Table 8.4-1, so they were not included in the final analysis.

The method of separating the I and g_1 effects is described in Appendix F.5 where the values of I and g_1 (free from instrument effects) together with the variance analysis are presented.

8.4.2 Analysis of the Means of the Regressions

The S.S. due to the means of the regressions on 29 d.f. represent deviations due to the g_1, g_2 and s effects and the first and second order interactions between them. The analysis of variance of the components of the S.S. due to means (q.v. Table 8.4-2) showed that only the primary effects were significant, i.e. the interactions between the g_1, g_2 and s means were of no consequence.

8.4.3 Analysis of the Regressions on log (p + 60)

The S.S. due to regressions on log (p + 60) on 30 d.f. were partitioned thus:

(1) S.S. due to the common regression on 1 d.f.,

(2) S.S. due to variations between the g_1 mean regressions on 1 d.f.,

(3) S.S. due to variations between the g_2 mean regressions on 4 d.f.,

(4) S.S. due to variations between the s mean regressions on 2 d.f., and

(5) S.S. due to all other interactions on 22 d.f.

Items (2) to (5) represent variations in the slope of the appropriate regression lines. The analysis given in Table 8.4-3 showed that the common regression accounted for over 97% of the R.S.S. and that the only significant variations in the slope occurred in the g_2 regression lines.

The variations between the means and slopes of the g_1, g_2 and s regressions are shown in Figs. 8.3-2 and 8.4-1 and 2. The series regressions (Fig. 8.4-2) tended to fan out at the high pressure end. To test the significance of this trend the S.S. on 2 d.f. due to the difference in slope of these regressions (not quite significant in Table 8.4-3) were partitioned into linear and quadratic components. The quadratic component was negligible but the linear component was quite significant (q.v. Table 8.4-4).

8.4.4 The Cell Effects

The S.S. due to cells on 24 d.f. were partitioned into two components:

(1) S.S. due to differences between cells on 4 d.f., and

TABLE 8.4-3
ANALYSIS OF REGRESSIONS

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
COMMON REGN	1	2.831366	2.831366	1609.645***
G1	1	.000581	.000581	- NS
G2	4	.027120	.006780	3.854**
S	2	.008643	.004322	2.457 NS
HETEROGENEITY	22	.045314	.002060	1.171 NS
REGRESSIONS	30	2.913024		

TABLE 8.4-4
TRENDS IN SERIES REGRESSIONS

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
LINEAR TRENDS	1	.008598	.008598	4.888*
QUADR. TRENDS	1	.000045	.000045	- NS
S	2	.008643		

TABLE 8.4-5
ANALYSIS OF CELL EFFECTS

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
BETWEEN CELLS	4	.630894	.157724	89.667***
INTERACTIONS	20	.080799	.004040	2.297**
CELLS IN SQUARES	24	.711693		

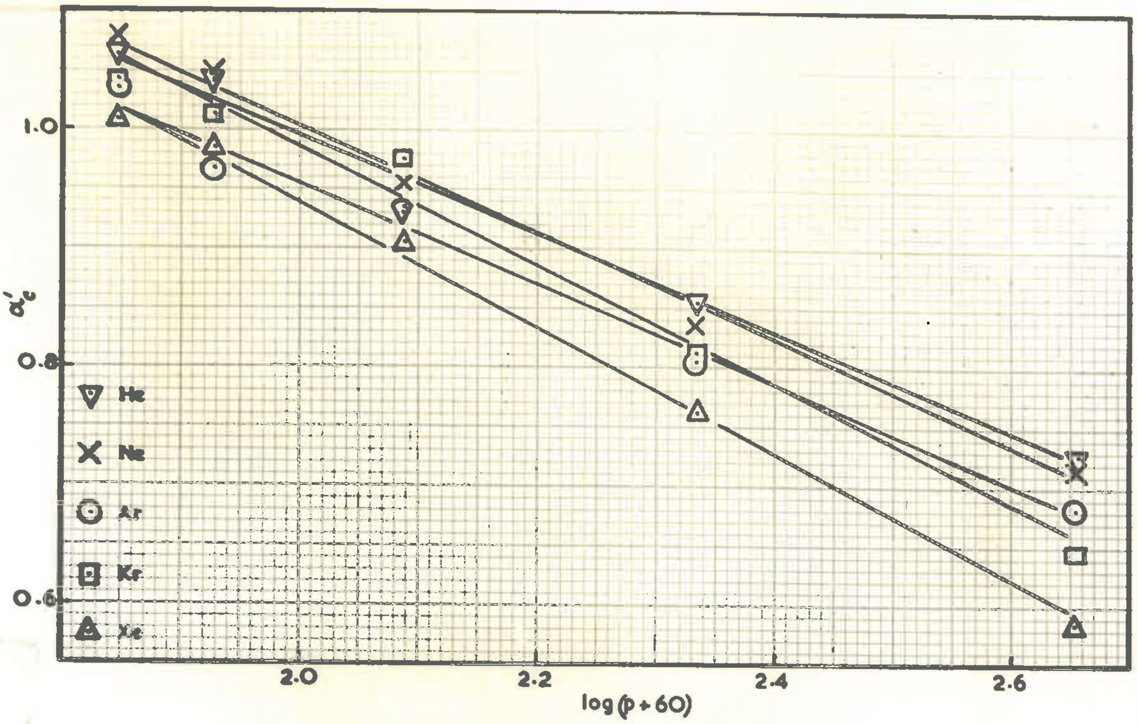

Fig. 8.4-1 The g_2 Regressions

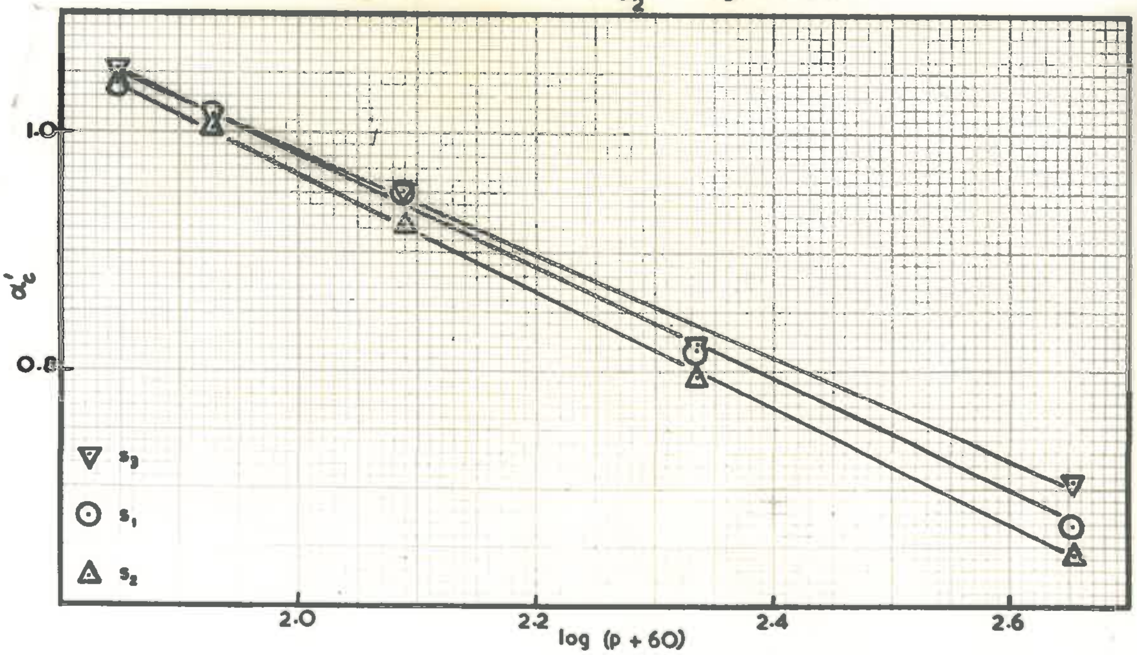

Fig. 8.4-2 The s Regressions

(2) S.S. due to interactions of cells and squares on 20 d.f.

The analysis given in Table 8.4-5 showed that although the variations between cells on 4 d.f. accounted for most of the variability, the interaction term was still significant.

A plot of the cell effects in the order that squares were run (Fig. 8.4-3) confirmed the results of the analysis in that is showed up variations between cells, but it gave no information on absolute cell performance.

All changes, relative or absolute, in cell performance are confounded with the series effects. Absolute changes in cell performance cannot be deduced at all from the results as no method for detecting them was built into the experiment. The magnitude of relative changes can be determined from Fig. 8.4-3 but, since these changes are confounded with the g_1 and series effects it is not possible to decide how much of the change between cells is due to g_1 and series interactions or how much is due to aging effects. The most that can be said is that differences between cells became more marked as the experiment progressed, and that these relative changes were significant.

8.5 Summary of Analysis and the Regression Model

The regression model which provided the basis for the analysis described above may be written in the form

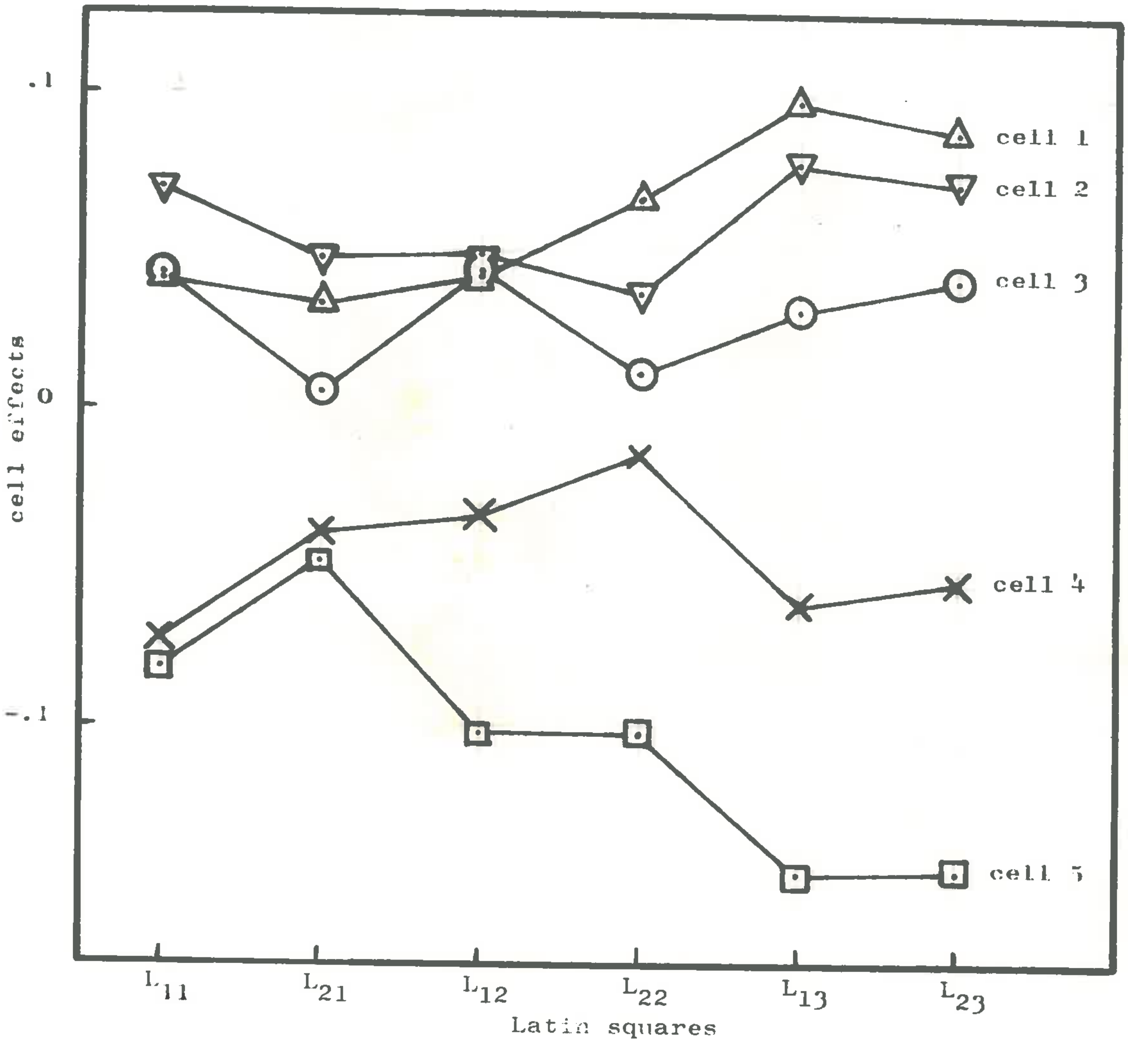

Fig. 8.4-3 Cell Effects

TABLE 8.5-1
SUMMARY OF COMPLETE ANALYSIS

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
G1	1	.234004	.234004	133.033***
G2	4	.119697	.029924	17.012***
S	2	.018913	.009456	5.376**
HETEROGENEITY	22	.044078	.002004	1.139 NS
MEANS	29	.416692	.014369	8.169***
COMMON REGN	1	2.831366	2.831366	1609.645***
G2	4	.027120	.006780	3.854**
LINEAR TRENDS	1	.008598	.008598	4.888*
QUADR. TRENDS	1	.000045	.000045	- NS
S	2	.008643	.004322	2.457 NS
HETEROGENEITY	23	.045895	.001995	1.134 NS
REGRESSIONS	30	2.913024	.097100	55.202***
BETWEEN CELLS	4	.630894	.157724	89.667***
INTERACTIONS	20	.080799	.004040	2.297**
CELLS IN SQUARES	24	.711693	.029654	16.858***
ERROR	65	.114364	.001759	
TOTAL	148	4.155774		

CORRELATION COEFFICIENT R .986

$$\alpha' = m + p_i + o_j + g_{1h} + g_{2k} + s_t + I_r + e_{hijktr} \quad \ldots\ldots \ (8.5\text{-}1)$$

where

$$\sum_i p_i = \sum_j o_j = \sum_h g_{1h} = \sum_k g_{2k} = \sum_t s_t = \sum_r I_r = 0$$

$$\ldots\ldots \ (8.5\text{-}2)$$

and where e_{hijktr} is the error associated with each α'. The e values are assumed to be normally and independently distributed about zero with constant variance.

The analysis of variance tested and established the significance of the main effects, the interactions between them and, where appropriate, the posited relations between the determining variates and their effects. The complete analysis excluding instrument effects, which were shown to be not significant, is given below in Table 8.5-1.

The results of the analysis were used to produce a modified but equivalent form of Eq. 8.5-1 in which only the effects of the significant variates were retained, and in which such relations between determining variates and their effects as had been developed were incorporated. The modified model is

$$\alpha' = m + (o_j)_{ht} + g_{1h} + g_{2k} + s_t + (b_m + d_{gk} + d_{st})$$

$$(\log_{10}[p + 60] - P) + e_{bijktr} \quad \ldots\ldots (8.5\text{-}3)$$

where b_m is the slope of the common regression line,

d_{gk} is the difference in slope of the regression line due to g_{2k},

d_{st} is the difference in slope due to s_t,

and $$P = \left[\sum_{i=1}^{5} \log_{10} (p_i + 60) \right] /5$$

This form of the model without the error term may be used as a prediction equation with a mean square deviation from regression of 0.001759. The data needed to calculate the fiducial limits of all the regression lines represented by Eq. 8.5-3 are contained in the thesis, but such calculations are beyond the scope of the present work.

The values of m, the main effects $(c_j)_{ht}$, g_{1h}, g_{2k} and s_t, the regression coefficient b_m, the interaction effects d_{gk} and d_{st}, and P are collected together for reference in Appendix F.6.

9. DISCUSSION

9.1 Apparatus and Technique

Most transient-state gaseous diffusion experiments, whether in the bulk phase or in porous media, have been performed in cells similar in principle to the two-bulb capillary-tube cell described by Ney and Armistead (116). The cell described in Section 6.1 is no exception. However, the use of radio-active tracer techniques in such cells has been largely confined to high-pressure bulk-phase measurements in which the two bulbs have been ionisation chambers. The use of end-window G-M counters for measuring diffusion in porous slip-cast silica has been reported by Fleming et al (82). Their rather crude exploratory apparatus appears to be the first and only attempt, prior to the experiment reported here, to use a radio-active tracer in porous media work.

The present apparatus is the first in which G-M end-window counters have been incorporated into a diffusion cell to be operated below 1 atm. It is also the first in which radio-active tracers have been used in a large experimental programme with porous media. Therefore a discussion of those features of the apparatus likely to influence the results is presented below.

9.1.1 The Diffusion Cells

In any two-compartment diffusion cell the mechanism for isolating one compartment from the other must be so constructed that the action of connecting the compartments sets up readily defined boundary conditions. The simplest isolating mechanism is a stopcock. By cementing a specimen directly into the bore of a large stopcock this simplicity was retained. However, the use of a stopcock

(1) introduced an uncertain boundary condition on the high-activity side because in every cell there was a space filled with inactive gas between the specimen and the active gas mixture,

(2) prevented outgassing of the specimens above room temperature because the stopcock grease would not hold a vacuum above $30^{\circ}C$, and

(3) prevented interchange of specimens without altering the cell constant.

The necessary assumption that the initial gas phase concentration gradient died out almost immediately appeared to be justified because a step change in the activity of the "hot" compartment was always recorded as soon as a run was started. The non-interchangeability of specimens did not matter because the same specimens were used for all runs, but the inability to bake out the specimens between runs may have introduced some random variability. The change in the relative magnitudes of the cell effects with time could be due in part to variable surface conditions in the specimens (c.f. Section 9.3.3).

The cells used in this work were made much smaller than those described in the literature in order to reduce the total quantity of gas needed, and to decrease the possibility of appreciable concentration gradients within the gas compartments. These advantages were gained at the expense of a larger percentage error in the measured cell constant. This error did not affect the results because α, not D, was used to establish the regression model. Even so, the method described in Appendix C.2 for measuring the cell constants should have yielded values of E correct to within 1%.

The specimens were deliberately cut to different dimensions in order to magnify variations in α due to the pore structure. However, at the beginning of the final experimental programme it was not realised that suitable criteria for separating pore structure effects from the total cell effect were lacking in the experimental design. Thus large differences between cell constants introduced unnecessary variability into the whole experiment with a consequent lowering of the overall accuracy (120,Ch.8).

The G-M counters functioned well under a vacuum. However, since they were filled with an inert gas to a pressure of only 100 torr., their aluminium windows were subjected to fairly severe stresses. As the pressure gradient across them changed direction, the windows "popped" in or out. As a result, they had a variable life. In the rare case of a failure in the course of a run, all five runs on the mixture under test were repeated. The change in cell volume and hence cell constant due to the flexing of the windows was very small ($< 0.5\%$).

The cell temperature was controlled by water-jacketing each gas chamber rather than submerging the whole cell in a constant-temperature bath. Thus stopcocks were readily accessible and the layout of the apparatus could be simplified as the position of the cells was not determined by the location of the constant-temperature bath or box. Because the cells were not completely immersed in a constant temperature medium, a small but constant temperature gradient to mix the gases could be set up by maintaining the water temperature a few degrees above room temperature. The fact that the absolute temperature of the graphite specimen was unknown did not matter because the temperature dependence of α was not being measured. A check with a thermocouple in a dummy cell showed that only very minor variations of the order of $0.2^{\circ}C$ occurred at any one point over a long period of time (q.v. Section 6.1.4). This implied that the main requirement, i.e. reproducible temperature conditions, was achieved.

Looking back, the cells were successfully used to measure the variability in α due to pressure and gas mixtures, but in order to determine the effects of differing pore structures, the cells would have to be modified so that specimens could be interchanged without changing the cell constant. The cells are not suitable for measuring the temperature dependence of α. Such measurements require

(1) no temperature gradients,

(2) some form of stirring[†] with suitable protection for the counter windows,

(3) a central isolating mechanism that is leak-proof over the proposed temperature range,

(4) a high temperature sealing compound (epoxy resin fails above 150°C) for attaching the G-M counters and sealing in the specimen, and

(5) a temperature sensing device within the cell.

9.1.2 Gas Mixture Preparation

The method of preparing the gas mixtures is described

[†] Since gas phase concentration gradients, if present, are small, stirring would be unnecessary if a G-M counter which could "see" along the length of the chamber, and hence "average" the concentration, was used. Such a counter would have to be specially developed.

in Section 6.3.4. Small differences between the compositions of the active and inactive mixtures or some inhomogeneity within them would cause some random variability in α. Such differences would have been least in the runs performed at the three highest pressures because a large proportion of the inactive mixture was added to the active mixture to dilute the activity and largest in the low pressure runs. The results showed that gas composition (g_2 and series) effects were negligible at low pressures. Thus it seems that small variations in composition do not introduce noticeable errors in α.

9.1.3 Procedure for setting up Runs

The method for simultaneously adjusting the activity and the pressure of the active mixture to their respective desired levels (q.v. Section 6.3.5) was the least flexible and most exacting step in the procedure for setting up runs, and the one most likely to increase the overall error variance.

In all runs the pressure was adjusted to be equal to the pressure in the inactive gas chamber at the expense of occasionally allowing the activity to fall outside the limits necessary to obtain the most accurate chart record. If the activity was too high when the pressure was correct, extra inactive gas had to be mixed slowly with the active gas and vice versa - a tedious and somewhat intuitive procedure. Occasionally activities that were a little too low or too high had to be accepted, with the result that either the maximum (i.e. final equilibrium) activity gave a recorder deflection of about 50%, or the recorded trace ran off the chart before the equilibrium value was reached. In the former case, errors in α were introduced because the mean activity curve could not be plotted as accurately as when the full width of the chart was used, and in the latter, because insufficient points at the equilibrium end of the curve could be obtained (q.v. Section 7.2.3).

The best method of overcoming the difficulty described above would be to inject highly active gas into an inactive mixture already in the cell in such a way that the pressure would be unaltered. This would not only overcome the difficulty of adjusting the pressure and activity simultaneously, but would also eliminate the need to make separate active mixtures.

9.1.4 Some Limitations of Radio-isotope Tracer Techniques

In general, the various types of radiation emitted by radio-isotopes may be detected either by ion-collection devices or scintillation counters. The former tend to be more specific in that a given device is best suited to monitoring a particular type of radiation emitted within a limited energy range. Thus G-M counters are suitable for counting beta and some high-energy alpha radiations, but no one counter is entirely suited to all alpha and beta energy levels.

The counters used in this work were suitable for medium to high-energy beta radiations such as those emitted by Kr^{85} or Xe^{133}. Low-energy beta emitters, such as C^{14}, could be counted with G-M tubes fitted with thinner or more "transparent" windows, but such counters may not withstand the stresses caused by repeated evacuations of the diffusion cell.

In any diffusion programme in which radio-isotopes are to be used, due consideration must be given to the following points.

(1) The type and energy level of the radiation emitted by the chosen isotope.

(2) The decay-scheme of the isotope - the stable isotope must be a gas and should preferably be an isotope of the same element as the original isotope. No long-lived intermediate isotopes can be tolerated unless some method for correcting for their presence can easily be established.

(3) The possible methods of detecting the radiation produced by all the isotopes being considered and the availability of suitable detectors. If more than one type of counter must be employed the cells should be designed so that counters can be interchanged without altering the cell geometry and without damaging the counters.

(4) The half-life of the chosen isotopes. Where possible, isotopes with half-lives less than several days should be avoided.

The decision to use Kr^{85} and Xe^{133} was made after evaluating these points. Although the one counter could be used for both isotopes, the cells were designed so that any end-window counter could be cemented onto them without altering the cell constant.

9.2 Comparison of Methods for Calculating α

In Chapter 7 it is shown that transient-state experiments can be arranged so that the instantaneous concentrations in both bulbs of a two-bulb diffusion cell can be expressed by the simple negative exponential function

$$C_i(t) = A + (-1)^i Be^{-\alpha t}, \; i=1,2 \qquad \ldots\ldots \; (7.1-7)$$

Graphical or numerical methods of fitting Eq. 7.1-7 to experimental data are available. All methods require an initial estimate of either A or α where $A = C(\infty)$.

The graphical method, first presented by Ney and Armistead (116), and described in Section 7.1, has been the one most widely used. The numerical method established in Section 7.1.2 is the most accurate method yet developed in that an initial estimate of α is systematically adjusted to give the best least-squares fit of Eq. 7.1-7 to the data. In particular, it gives a more precise regression than a least-squares method using a value of A calculated from the initial concentrations.

The current work showed that the most accurate values of α were obtained when Eq. 7.1-7 was fitted to data from over 80% of the theoretical concentration-time curve. Since many workers using the Ney and Armistead technique followed the course of a run to less than 60% completion [e.g. Srivastava (121)], values of α quoted by them could be in error, particularly where the line, from which α was calculated, was established with only five or six data points.

The error incurred by stopping a run prematurely may not be as high in previous work as the present results indicate because intermittent analyses with a mass spectrometer or thermal conductivity analyser may be more accurate than a continuous trace from a G-M counter. Radio-active decay is a statistical process so the instantaneous count-rate can differ from the mean count-rate by as much as 5%. The mean count-rate is determined either by counting a sample for a long time, or by determining the mean count along a continuous record. The former method of counting should be at least as accurate as the other analytical techniques, but the latter may not. Nevertheless the periodic removal of samples from the system could nullify any additional accuracy achieved by "off-line" analyses. Even if "off-line" analysis is more accurate (and no comparative data exist), previous workers have discarded many valuable data by not following runs to completion.

The difference between the two equations 7.1-7 is

$$C_2(t) - C_1(t) = 2\,Be^{-\alpha t} \qquad \text{.....}\ (9.2\text{-}1)$$

Several authors (82, 122-124) have measured concentration changes in both compartments and calculated α from Eq. 9.2-1 by a graphical method entirely analogous to the Ney and Armistead technique. This method eliminates A but it is not necessarily any more accurate because

(1) plots of concentration against time must be prepared for both bulbs, and the best lines

drawn in so that corresponding values of C_1 and C_2 can be found,

(2) the errors involved in fitting curves to two separate concentration-time plots are compounded, and

(3) if separate built-in detecting devices (e.g. G-M counters) are used to measure the concentration in each bulb, they must be calibrated in situ against each other, hence calibration errors will increase the total error.

In the current work only activity changes in the low activity bulb were measured because the full width of the recorder chart could be used. A maximum of only half the chart width could be used for the high activity bulb because the recorder input range began at zero. Although data from both bulbs should give identical values of α, it may be considered desirable in some future work to apply a more stringent test to the calculation method developed in Chapter 7 by comparing values of α from both sets of data. For such measurements it would be necessary to modify the input range of the high activity recorder (without magnifying the statistical fluctuations in count-rate) so that the full chart width could be used.

If concentration changes in both bulbs were measured it would be possible to integrate Fick's second law numerically. However, the errors introduced by replacing differential quantities by finite differences may be greater than those introduced by adopting a simple analytical solution to Fick's second law. A comparison of the two approaches would be of academic interest only.

9.3 The Regression Model

The analysis necessary to establish an explicit form of Eq. 6.0-2 from the experimental results is presented and discussed in Chapter 8. In this section, the derived regression model, Eq. 8.5-3, is discussed and compared with models suggested by other authors.

The models presented by Scott (39) and Evans (107) are both based on Bosanquet's interpolation formula (Eq. 2.5-2). The essential equivalence of these models is pointed out in Section 4.4. Because the net flux is zero in the present experiments the source of apparent difference between the two models is removed (in particular Evan's $(D_A)_{eff} = D_{eff}$), so their models are considered to be identical in the discussion below.

The form of the Evans-Scott model applicable to the current experiments can be derived by specialising the multi-component form of Eq. 2.5-10; thus

$$\underset{\sim}{\nabla} x_i = \sum_{j=1}^{n} (1/C\mathcal{D}_{ij})(x_i \underset{\sim}{N}_j - x_j \underset{\sim}{N}_i) - N_i/CD_{ki} \qquad \ldots\ldots (9.3\text{-}1)$$

For mixtures of A, A^* and B in which $\underset{\sim}{N}_A = -\underset{\sim}{N}_{A^*}$ and $\underset{\sim}{N}_B = 0$, Eq. 9.3-2 reduces to

$$\underset{\sim}{N}_{A^*} = -\left[(x_A + x_{A^*})/c\mathcal{D}_{AA^*} + x_B/c\mathcal{D}_{A^*B} + 1/cD_{kA^*}\right]^{-1} \underset{\sim}{\nabla} x_A$$

...... (9.3-2)

If x_{A^*} is small, $x_A + x_{A^*}$ may be replaced by x_A. If, following Scott, the equation

$$(\mathcal{D}_{AB})_{eff}/(\mathcal{D}_{AB})_{true} = (D_{kA})_{eff}/(D_{kA})_{true} = G$$

...... (4.4-5)

is assumed to hold for porous media, then

$$1/D_{eff} = G(x_A/\mathcal{D}_{AA^*} + x_B/\mathcal{D}_{A^*B} + 1/D_{kA^*})$$

...... (9.3-3)

for both transient- and steady-state experiments.

Eq. 9.3-3 is an explicit form of Eq. 6.0-1. In order to compare it with Eq. 8.5-3 and hence attempt to identify Eq. 8.5-3 with Eq. 6.0-1 as suggested in the introduction to Chapter 6, Eq. 9.3-3 is written in a form similar to Eq. 8.5-3, by recalling that D_{kA^*} is independent of pressure and that both $\mathcal{D}_{AA^*}$ and $\mathcal{D}_{A^*B}$ are inversely proportional to p at low pressures (q.v. Eq. 2.3-2), i.e.

$$\mathcal{D}_{AB} = 1/K_{AB}p \qquad \text{...... (9.3-4)}$$

where K_{AB} is a complex function of the molecular properties of A and B, thus

$$1/D_{eff} = G(x_A K_{AA^\ast} p + x_B K_{A^\ast B} p + 1/D_{KA^\ast}) \quad \ldots\ldots (9.3\text{-}5)$$

$$= GZ(p + H) \quad \ldots\ldots (9.3\text{-}6)$$

where

$$Z = K_{AA^\ast} x_A + (1 - x_A) K_{A^\ast B} \quad \ldots\ldots (9.3\text{-}7)$$

and

$$H = 1/ZD_{KA^\ast} \quad \ldots\ldots (9.3\text{-}8)$$

By introducing the cell constant E, Eq. 9.3-6 can be written in terms of α , i.e.

$$1/\alpha = GEZ(p + H) \quad \ldots\ldots (9.3\text{-}9)$$

which can be readily transformed to yield

$$\alpha' = -\log_{10}(100GEZ) - \log_{10}(p + H) \quad \ldots\ldots (9.3\text{-}10)$$

The log term may be expanded remembering the physical significance of G (q.v. Eq. 4.4-5) and Z, and assuming that the properties of A and $A^\ast$ are identical, to give

$$\alpha' = A + f_1(E, Q, \phi) + f_2(M_A, M_B, \sigma_{AB}, \sigma_A, \Omega_{\mathcal{D},AB}, \Omega_{\mathcal{D},A})$$

$$-\log(p + H) \quad \ldots\ldots (9.3\text{-}11)$$

which is the desired result.

Wheeler (38) suggested that Eq. 2.5-3 may hold for porous media. Eq. 2.5-3 can also be expressed in a form similar to Eq. 8.5-3. Thus, if Eqs, 4.4-5 and 9.3-4 hold, Wheeler's model becomes

$$D_{eff} = (1/GZp)\left[1-\exp(-p/H)\right] \quad \ldots\ldots (9.3\text{-}12)$$

(where Z and H are still defined by Eqs. 9.3-7 and 9.3-8), which is similarly transformed to

$$\alpha' = A + f_1(E,Q,\phi) + f_2(M_A, M_B, \sigma_{AB}, \sigma_A, \Omega_{\mathcal{D},AB}, \Omega_{\mathcal{D},A})$$
$$-\log\left[p(1-e^{-p/H})\right] \quad \ldots\ldots (9.3\text{-}13)$$

The difference between the Wheeler and Scott-Evans models lies solely in the predicted variation of α with p. The functions f_1 and f_2 are identical in both models.

9.3.1 The Regressions on Log (p + 60)

(1) A Comparison of the Models

Both the Evans-Scott model and the present regression model predict that the best functional relation between α' and p is

$$\alpha' = A + B \log (p + H) \quad \ldots\ldots (8.3\text{-}2)$$

However, whereas the Evans-Scott model predicts that b is independent of the gases used and is equal to -1, the regression analysis showed that

(1) the mean value of b for the current work is −0.47, and

(2) b varies from −0.38 when g_2 is He present as 75% of the mixture, to −0.57 when g_2 is Xe present as 25% of the mixture.

In Fig. 9.3-1 the models presented by Evans and Scott, Wheeler and the author are presented in the form

$$\alpha' = A + f(p) \qquad \ldots\ldots (9.3\text{-}14)$$

where the function appropriate to each model is used. In all cases A was adjusted to give a value of α' approximately equal to the experimental value of m (Eq. 8.5-3) at the mean pressure, and the value 60 torr, was used for H. For ease of calculation, b for the regression model was taken to be 0.5. The plot is limited to the pressure range of the regression model. The Evans-Scott coefficient of −1 does not fit the present results at all well, but if the value of A for Wheeler's model were altered to make his model coincide with the regression model at zero pressure, his model would fit the results quite well at pressures below 100 torr.

As an additional test of the regression model, the values of D_{eff} were read from the graph presented by Scott and Cox (85) (Fig. 4.4-1) for the counter-diffusion of H_2 and N_2 through Celite. These data (presented in Appendix

G.1) were adjusted to fall within the same range as α' for the present work, and plotted on top of the models in Fig. 9.3-1. They fit the regression model very closely. Their results over their full pressure range are plotted in Fig. 9.3-2 and the line

$$\alpha' = A - 0.5 \log (p + 60) \qquad \ldots\ldots (9.3\text{-}15)$$

is drawn through them.

Values of D_{eff} (as distinct from $(D_A)_{eff}$) from the data of Evans et al (84) for the counter-diffusion of He and Ar through a fine-pored graphite, similar in structure to Morgan EY9-166, were calculated using the integrated form of Eq. 4.2-9. Regressions of log D_{eff} on log p and log(p + H) (where 0.08 atm ≃ 60 torr. was used for H) were fitted to these results. For the regression on log p, b = -0.77 and on log(p + H), b = -0.79. Evans data, values of D_{eff}, and a summary of the regression analysis are presented in Appendix G.2, where it is seen that the analysis on log(p + H) gives a slightly better correlation than that on log p. The regression on log(p + H) together with the experimental points is presented in Fig. 9.3-3.

When it is realised that '60' is not the optimum value of H for either Evans' or Scott's results, and that the present results show that b depends on the gases used, it can be concluded that both sets of results confirm the form of

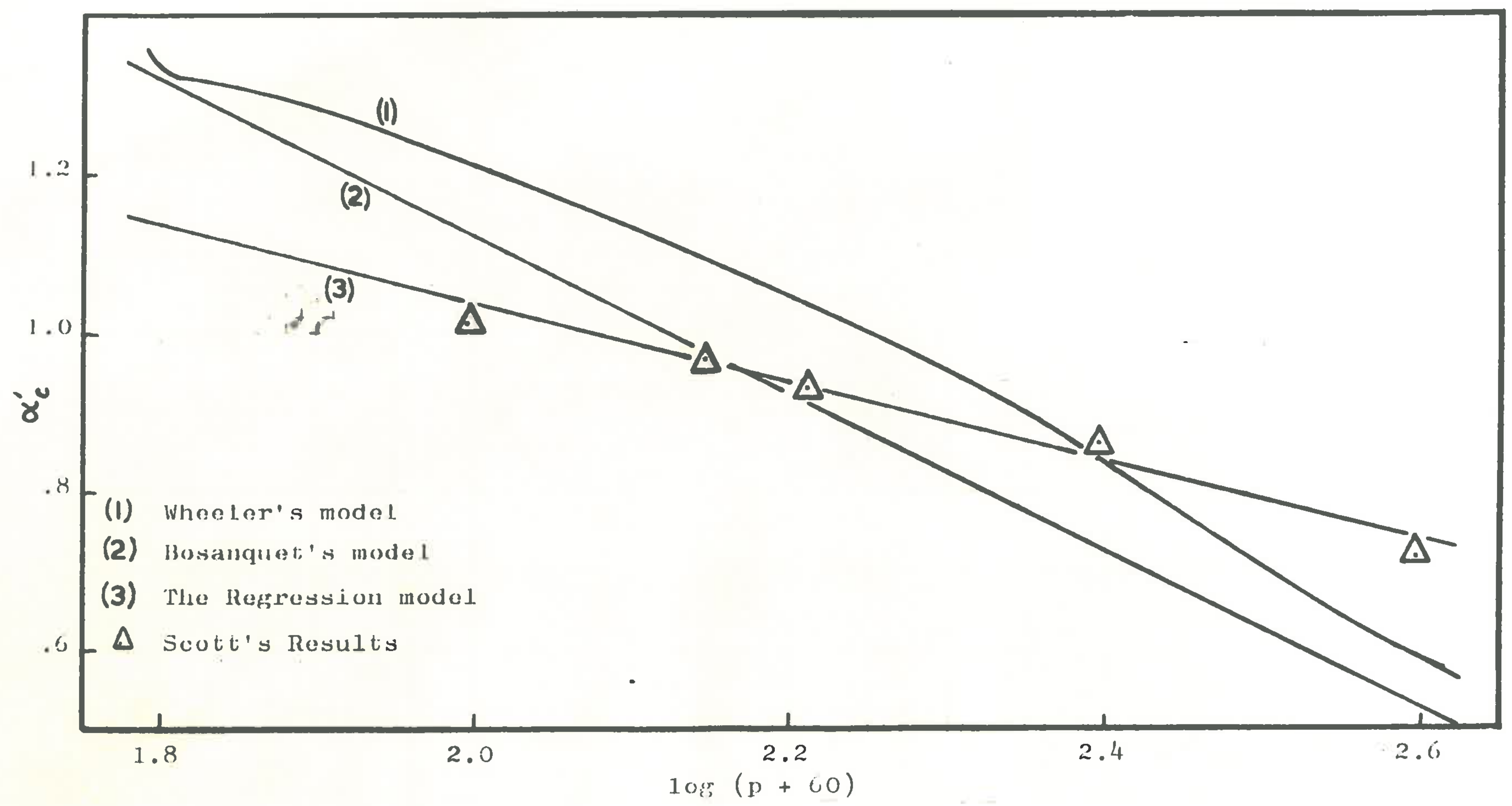

Fig. 9.3-1 Proposed Diffusion Models

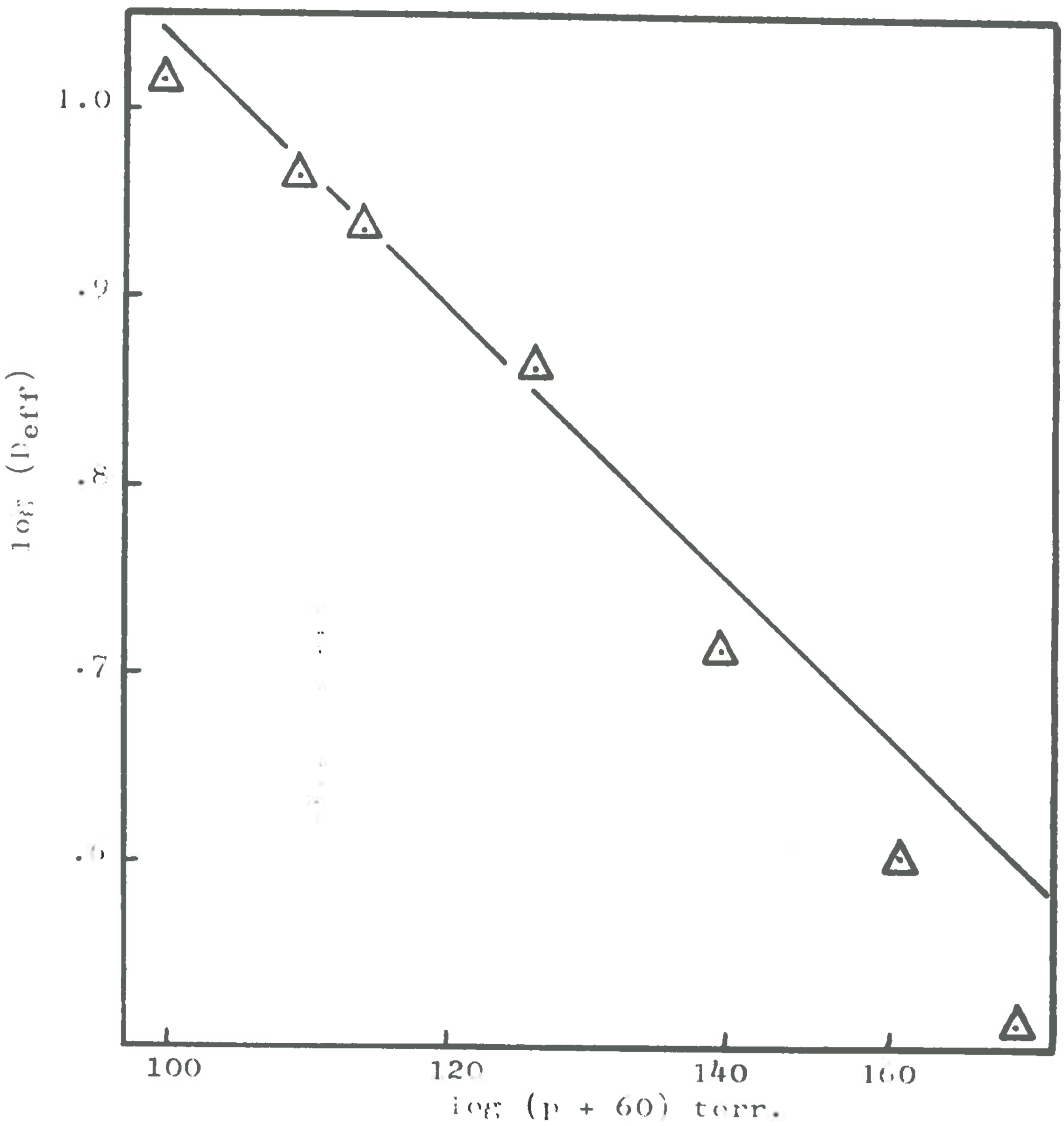

Fig. 9.3-2 Some Results of Scott plotted against Log (p + 60).

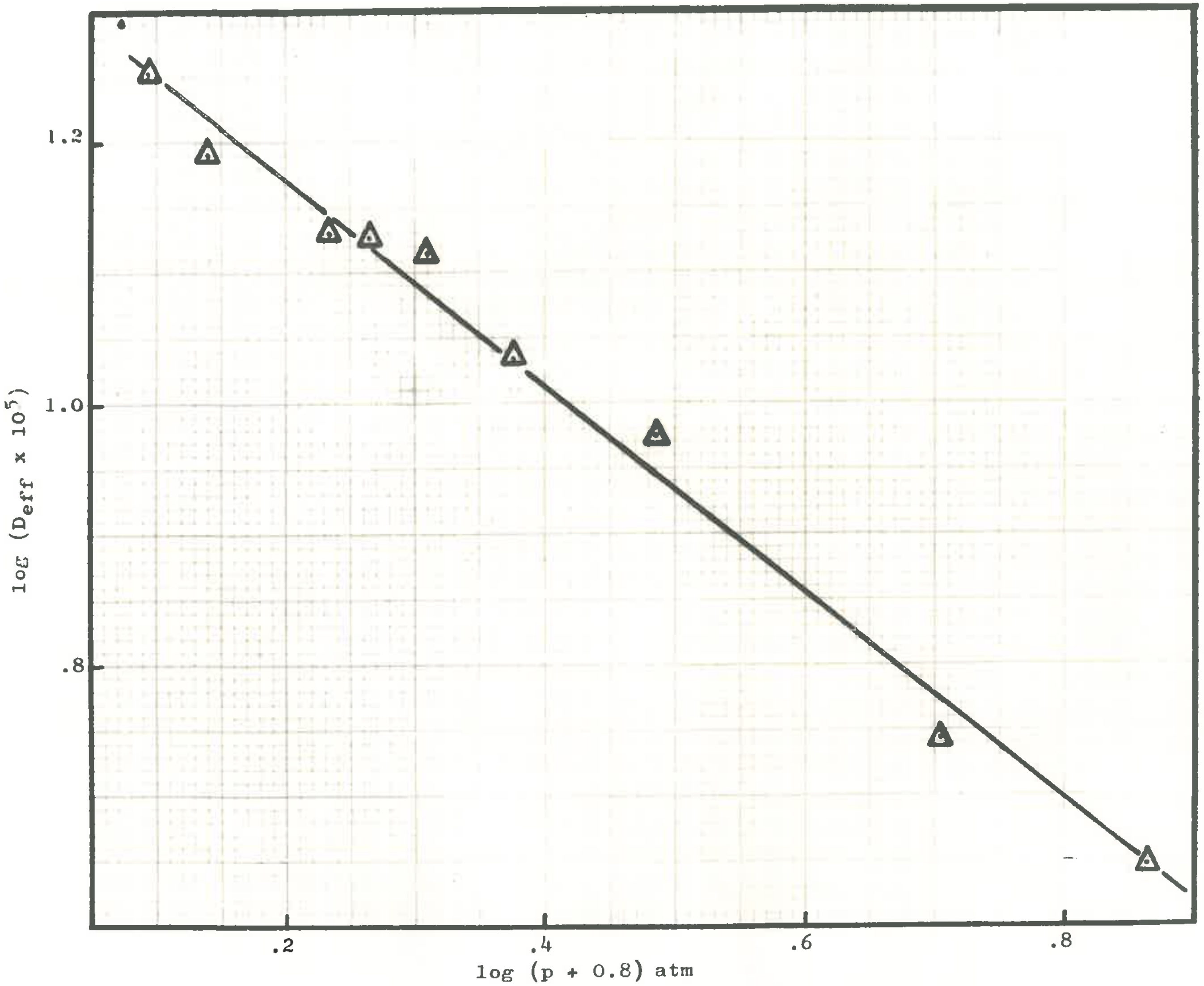

Fig. 9.3-3 Some Results of Evans, plotted against Log (p + H)

the regression model and illustrate its usefulness.

(2) The Constant H

The constant H appears in the Evans-Scott model as a consequence of the assumption that Knudsen and bulk diffusion resistances are additive. Eq. 9.3-8 shows that H is a complex function of the properties of the gas molecules and of the porous medium (insofar as D_{KA}^{z} is a function of the porous medium). It was introduced into the regression model in the first instance as a linearising device, and, as such, it reduced the total error variance. Nevertheless, its appearance in Eq. 9.3-11 was noted.

The significance of H is discussed in Section 8.3 where it is stated that the values of H for the single regressions were not critical. In Table 9.3-1 the best values of H for the g_1 and common regressions together with their standard errors are listed.

Table 9.3-1

Values of H for the g_1 and Common Regressions

Regression	H (torr.)	Standard Error
g_{11} (Kr)	66.6	25.6
g_{12} (Xe)	54.0	7.1
Common	60.1	14.2

$H_{Kr}/H_{Xe} = 1.23$; $(M_{Xe}/M_{Kr})^{\frac{1}{2}} = 1.25$

The ratio of the best values of H for the g_1 regressions is almost equal to the inverse ratio of the square roots of the molecular weights of g_{11} and g_{12}. This result may be fortuitous, particularly as the standard errors in H are quite high, and cannot be used to predict the value of H for any g_1 without further experimental investigation of the behaviour of H.

In the present work, H is regarded simply as a linearising device and its physical implications are not discussed. There may not be a separate, distinct value of H for a given porous medium and set of gases that is independent of the pressure range chosen, thus if the experimental range were extended to several atmospheres, the value of H and hence the value of b may change, simply because $\log(p+H)$ may not be the best explicit function of $f(p)$. In particular, Fig. 9.3-1 implies that it may be possible to fit Wheeler's model to the present results by choosing a different, but arbitrary, value of H, although the same value of H applies to all the models as they are currently understood. Nevertheless, it is stressed that the function $\log(p+H)$ adequately fitted the current results over the selected range of p and that, insofar as the assumption of additive diffusional resistances is correct, it is in accord with present theory. Because of this and because Wheeler's $f(p)$ would be difficult in practice, if not in principle, to handle by the normal least-squares procedures, no attempt was made to fit his model to the results.

(3) The Interaction Effects

The significance of the interaction effects d_{gk} and d_{st} is discussed in Section 8.4-3. In particular, the following points are noted.

(1) Both the Wheeler and Evans-Scott models predict that there should be no interaction effects, but no data to test this prediction have been presented before. The current results show that some interaction effects are significant.

(2) A plot of the g_2 regression coefficients $(b_M + d_{gk})$ against log M_B is linear if the Kr regression coefficient is neglected (q.v. Fig. 9.3-4). While Fig. 9.3-4 does suggest that a linear relation between b_{gk} and log M_B may exist, the Kr coefficient lies so far off the line through the other points that no definite conclusions can be drawn. This trend in b_{gk} needs further investigation.

(3) Theoretically, the g_2 regression lines should all converge to the same value at

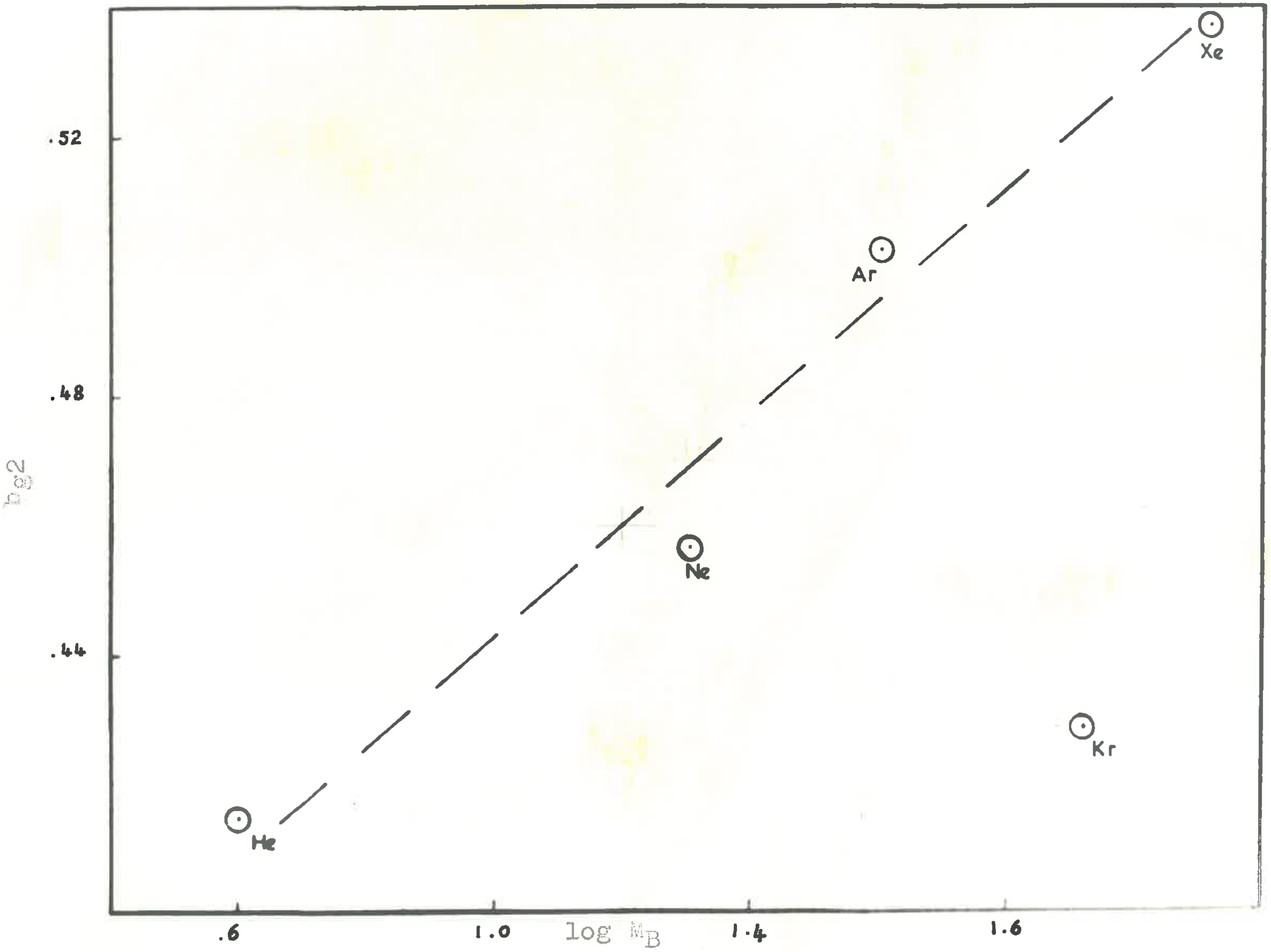

Fig. 9.3-4 The g_2 Regression Coefficients plotted against Log (Molecular Weight)

zero pressure because a g_1 molecule does not then collide with any g_2 molecules in the porous medium. The experimental lines do converge at low pressures (q.v. Fig. 8.4-1), but all their intercepts are different. This result can probably be attributed to experimental scatter, particularly as the g_2 regressions were established from fewer experiments than the other regressions.

(4) The increasing value of $|b_{gk}|$ with increasing M_B is expected because, at a given pressure, λ_B decreases as M_B increases, so A^* molecules undergo proportionately more collisions with B as M_B increases. If no wall collision occurred at all, b would equal -1, thus if the proportion of collisions with B at a given pressure is increased, remembering that at zero pressure there are no collisions between A^* and B, then $|b_{gk}|$ must increase.

(5) The convergence of series regressions at low pressures and the variation in d_{st} with x_A is expected for the same reasons as it is expected in the g_2 regressions. However, an insufficient number of x_A values were incorporated in the experimental plan to establish a regression of

b_{st} on x_A.

(6) There is no interaction between g_1 and pressure. In particular, the expectation that the g_1 regressions would give different intercepts is fulfilled. This point is discussed further in Section 9.3.2.

9.3.2 The Means of the Regressions

Previous models predict that no simple relation exists between the g_1, g_2 and s effects, and the properties of the gases (q.v. Eq. 9.3-11). The present results, which are the first to be reported, tend to confirm this prediction, nevertheless some interesting trends were noticed. These are discussed below.

(1) The g_1 Means

There are no significant interactions between the g_1 effects and the effects of all the other determining variates. If this result could be shown to be generally true, the prediction of the diffusion rates of other gases would be possible, provided a relation between the g_1 means and a suitable gas property such as molecular weight could be established. This result is important because the method described in Chapter 6 for measuring α can only be used with suitable radio-isotopes of which there are only a limited number. Although other techniques for detecting trace concentration are available, e.g. mass spectroscopy, radio-active tracers provide the cheapest and most convenient method of determining g_1 effects.

Because the g_1 effects are caused by the active or diffusing gas, they are likely to be closely related to $(\mathcal{D}_{kA^*})_{eff}$ and $(\mathcal{D}_{AA^*})_{eff}$. Although a regression of the g_1 effects on a characteristic molecular property such as molecular weight cannot be performed on only two gases, information about the physical significance of the g_1 effects can be gained by comparing their ratio with the ratio of the square-roots of M_{Kr^*} and M_{Xe^*} as suggested by Eq. 4.5-1.

In Table 9.3-2 the ratios of the self diffusion coefficients of Xe and Kr as predicted by the regression model (expressed in terms of α rather than α') are also presented.

Table 9.3-2

Predictions of the Regression Model Compared with the Prediction of Eq. 4.5-1

Pressure (torr).	$(\ \mathrm{XeXe}^*/\ \mathrm{KrKr}^*)_{eff}$
0	1.258
10	1.265
88 #	1.297
Ratio of g_1 effects	1.200
$(M_{Xe^*}/M_{Kr^*})^{\frac{1}{2}}$	1.251

\# The pressure corresponding to the mean pressure on the log(p + H) scale.

Two points are to be noted.

(1) The regression model predicts that Eq. 4.5-1 does hold at zero pressure for self diffusion experiments (indicating that $(D_{kA}\varkappa)_{eff}$ can be predicted from the model directly), but that the ratio of the self diffusion coefficients rapidly increases with increasing pressure.

(2) The g_1 effects are not equivalent to $(D_{kA}\varkappa)_{eff}$ although they do account for a large part of its variability.

(2) The g_2 Means

The plot of the g_2 means against log M_B presented in Fig. 9.3-5 is of considerable interest. In particular, a straight line fits all the points, except the one representing He, quite well, but the position of the He mean indicates that the true regression on log M_B is curved at the low molecular weight end.

In the previous section, it was shown that Eq. 4.5-1 held for the present results. Thus, recalling assumptions (2) and (3) listed in Section 4.6.2, surface diffusion was absent, so the curve in the plot of the g_2 means against log M_B cannot be attributed to surface diffusion. However, more results are needed before an

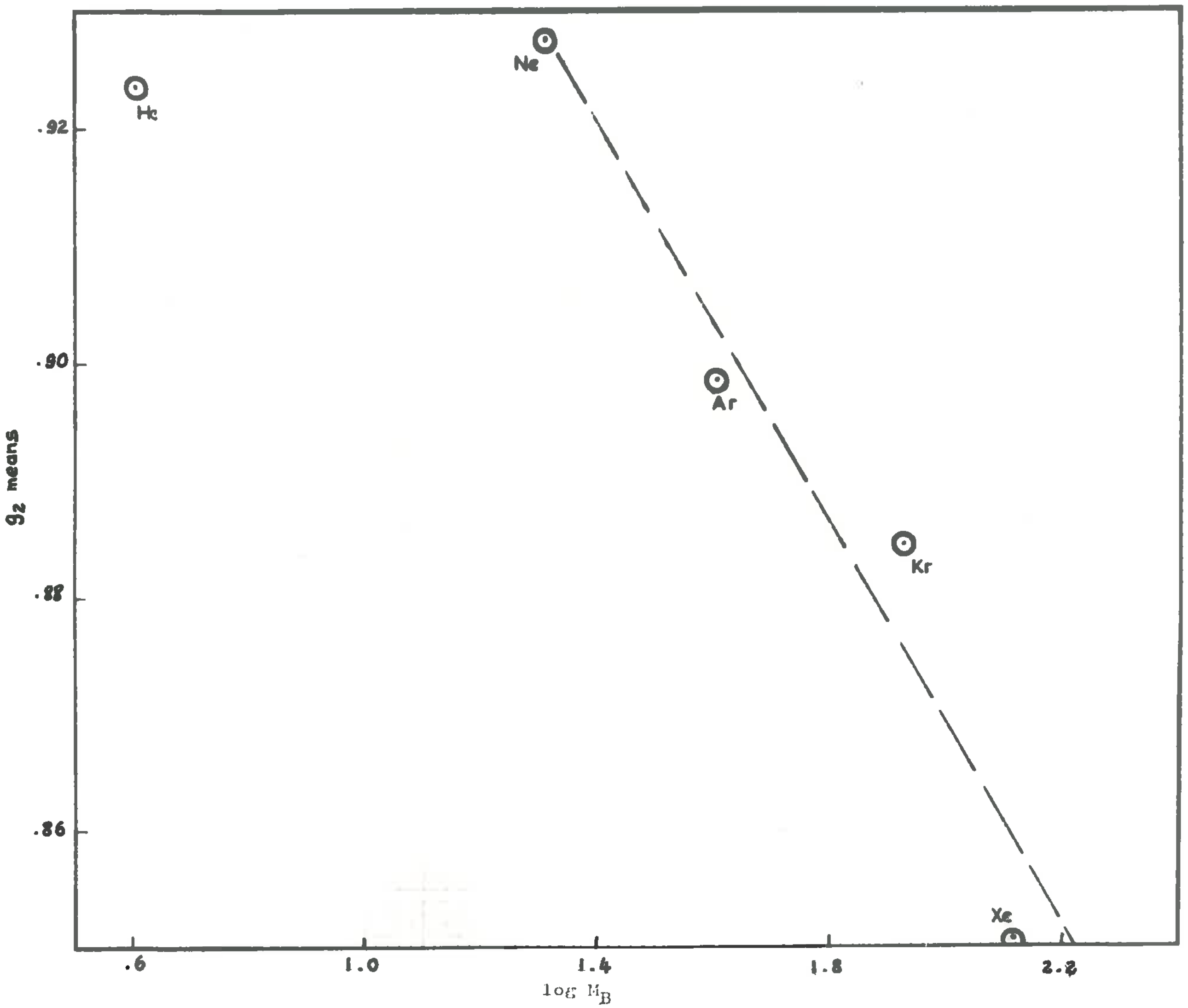

Fig. 9.3-5 A Plot of the g_2 Means against Log (molecular weight)

empirical relation between the g_2 means and the g_2 molecular weights can be proposed with confirdence, and before any conclusions about the use of He in the study of surface diffusion can be drawn.

(3) <u>The Series Means</u>

The series effects are independent of all the other determining variates except pressure. At low pressures they are insignificant but at high pressures they are quite significant. The analysis presented in Table 8.5-1 shows that, over the pressure range investigated, series means are significant, but the series regressions are not, although the tendency to become so at high pressure is significant. The experimental ranges of x_A and p were too small to establish a reliable functional relation between s, and x_A and p, but the results do show that α is concentration dependent.

In Section 2.5 and the introduction in Chapter 6 it is stated that D_{eff} is not independent of the diffusion system. The current results confirm this statement in that they show that values of D_{eff} obtained from systems with high concentration gradients will differ from those obtained from systems with low concentration gradients. Nevertheless, the presence of the series terms in the regression model does mean that the model can be used to estimate an "average" D_{eff} for systems in which high concentration gradients are expected, e.g. fast gas reactions in porous catalysts. Such predictions cannot be made with previous models.

9.3.3 Cell Effects

The factors likely to contribute to the cell effects may be grouped together as follows:

(1) the geometry of the diffusion cell; usually described in terms of a measured cell constant,

(2) the pore structure and surface properties of the specimen some of which may change with time, and

(3) factors associated with the cells such as seals and G-M counters, some of which may also change with time.

Thus the S.S. due to cell effects may be considered to be made up of parts ascribable to variations in each of these factors. Ideally, it would be desirable to arrange the experimental conditions so that, either the indicated partitioning could be carried out, or all the variability could be attributed to item (2). Unfortunately it was not possible under the present circumstances to so order the experiments, consequently variations in factors (1) and (3) should have been minimised.

Because it was originally thought that the effects of the cell constants could be removed by measuring these constants independently, then adjusting the data before they were analysed, differences between the cell constants were intentionally made large (c.f. Section 9.1.1). However, there is always an error associated with a measured cell constant and such errors are different for each cell. If the data are adjusted in accordance with measured cell constants, the total S.S. due to cell effects may be reduced but additional variability due to errors in the measured cell constants will be introduced. In the subsequent analysis, part of this error will be attributed to cell effects and part to the overall error S.S. Because the overall error S.S. is increased irrespective of whether or not the T.S.S. is reduced, greater accuracy is maintained in the analysis if no attempt is made to introduce the cell constant. In Fig. 9.3-6 the cell totals for the whole experiment are plotted against cells and compared with the cell totals predicted by the measured cell constants. While this plot does give some indication of the part played by the cell constant in the overall cell effects, it cannot be interpreted quantitatively because the effects of the errors in the cell constants cannot be separated from the effects of the other cell variates.

The current results are the first in which data from more than one cell have been used to establish a

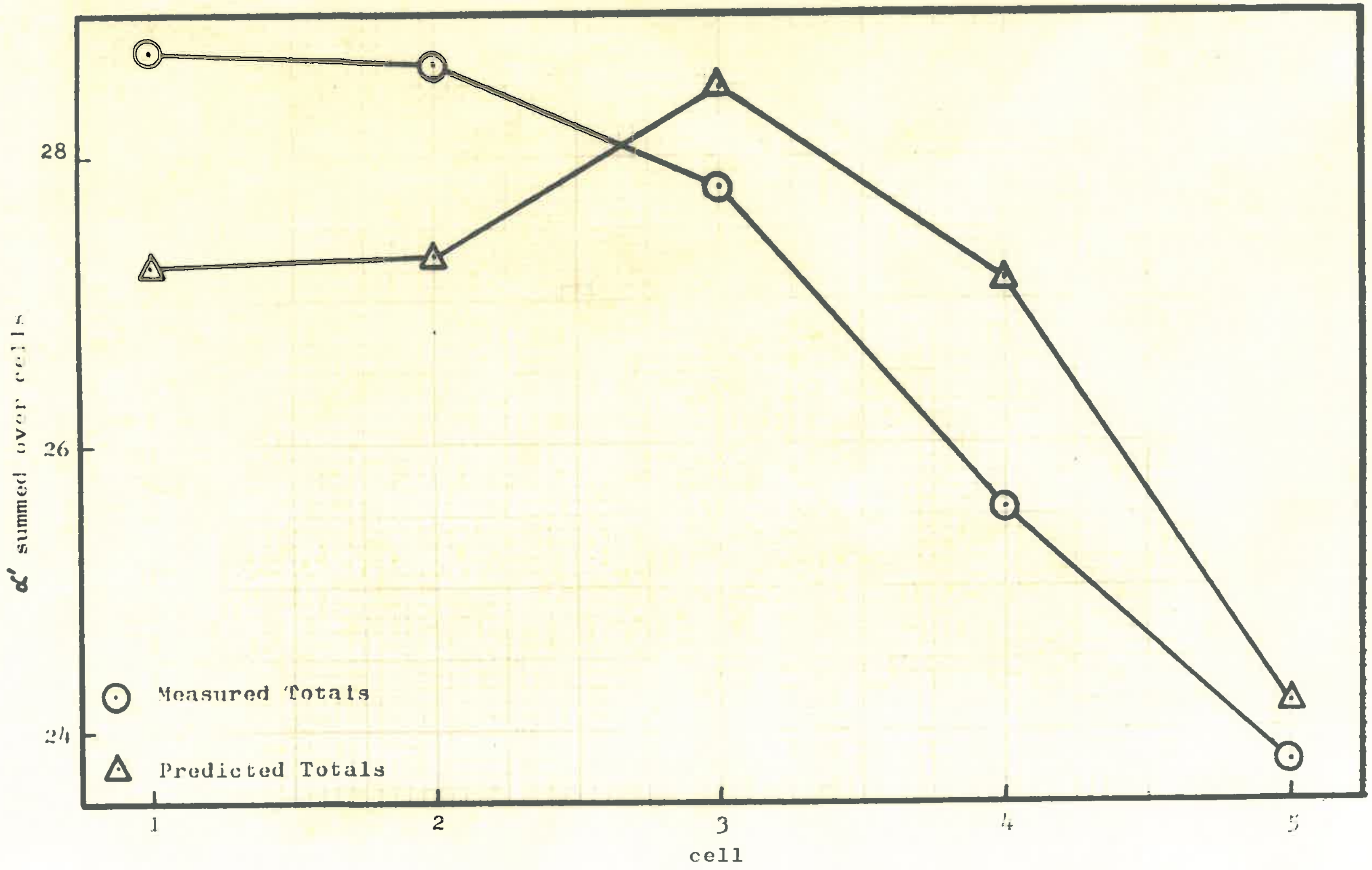

Fig. 9.3-6 A Comparison of the Measured Cell Totals with Those Predicted from the Cell Constants

correlation. Apart from the obvious gain in experimental efficiency, the use of several cells enabled differential aging effects to be detected. As absolute aging effects are difficult to detect without resorting to elaborate experimental designs, differential effects may be the only indication of their presence. Absolute effects could not be detected with the experimental design used here, nor could the magnitude of the differential effects because they were confounded with the g_1 and series effects (q.v. Section 8.4.4). Bearing in mind the findings of Dawe and Stevens (65) (q.v. Section 3.2.2), it is likely that the aging effects are due in part to changes of the internal surface of the specimens wrought by the absorption and desorption of small quantities of different gases, and by varying degrees of outgassing between runs. However, there was no way of verifying this.

The use of more than one cell also highlighted the problem of estimating the effects of different porous media on diffusion rates. Differential effects are easy to establish. For example, the experiment reported here could be repeated, using specimens with different pore properties, to establish a new model. If the new model were adjusted so that its mean coincided with m reported here, differences in the effects of each variate could be attributed to effects of the porous media. Absolute effects involve cell constants. They cannot be evaluated with the same accuracy as the differential effects because of unknown errors in the measured cell constants.

Absolute values of log D_{eff} may be calculated from the present results by adding $(\Sigma \log E)/5$ to α_o'. These values of D_{eff} would be sufficiently accurate for prediction purposes in most engineering calculations. It is seen that the use of several cells of approximately equal cell constant could reduce the error in $(\overset{n}{\Sigma} \log E)/n$, nevertheless the error cannot be readily evaluated.

No attempt was made to fit a pore model to the present results because no equivalent model for diffusion in capillaries exists. Work on such a model is currently in progress in our laboratories (19).

10. CONCLUSIONS

1. The experimental work showed that effective diffusion coefficients for gaseous diffusion in porous media can be calculated from the concentration changes in a simple two-bulb diffusion cell provided

(i) reproducible initial and boundary conditions can be established,

(ii) pressure fluctuations are eliminated by measuring the diffusion velocity of a labelled trace of a gas in a mixture otherwise at equilibrium,

(iii) a continuous or semi-continuous method of determining instantaneous concentrations is available, and

(iv) the cell geometry is such that a simple analytical solution to Fick's second law can be found.

The diffusion cells used with the final apparatus are only suitable for measurements at room temperature and pressures up to one atmosphere. However, their performance under these conditions indicated that similar transient-state measurements could be adopted for other conditions provided the cells were appropriately modified.

2. The standard iterative technique for fitting non-linear regressions (117), as described in Chapter 7, is the most accurate method of estimating α yet to be presented. This method showed that the best value of α is sensitive to

the fraction of the curve used. Therefore, in any transient-state measurements of α, points from the complete concentration (or activity) range should be used.

3. This is the first statistically designed experiment to be reported for either bulk-phase or porous media gaseous diffusion experiments. As such, it enabled highly efficient statistical techniques for establishing a regression model to be applied to the data. It is also the first experiment in which more than one cell was used to obtain a correlation. The advantages of high experimental efficiency, effective isolation of cell effects by statistical methods and a higher accuracy in the average cell constant are clearly demonstrated.

4. The factors likely to be responsible for the major part of the overall error variance are

   (i) errors in establishing the mean concentration-time curves,

   (ii) variations in the fraction of the concentration-time curve used,

   (iii) large differences in cell constants, in that the total variability in α was unnecessarily increased, and

   (iv) the fact that a highly inaccurate α_{15} value in the sixth Latin square (L_{23}) was included in the original set of data, necessitating its replacement by a missing value.

Apart from (ii) these sources of error could be easily reduced in any subsequent programme. Item (ii) could be reduced and the experimental procedure simplified if some method of injecting a small amount of highly concentrated activity directly into the cells could be devised.

5. The regression model represents the first attempt to express D_{eff} as an explicit function of the determining variates in the manner described in Section 2.5. It is only possible to find an explicit functional relation between the pressure and its effects from the present results, so the model cannot be used to infer an explicit relation between D_{eff} and the corresponding bulk-phase coefficients as suggested in the introduction to Chapter 6. Nevertheless, the model accounted for 98.6% of the observed variability and enables the following important conclusions to be drawn:

(i) The pressure dependence of α is not a simple reciprocal one as predicted by the Evans-Scott model, but is approximately inversely proportional to $(p + H)^{0.5}$ where the exponent depends on the gases present. In particular, the dusty-gas model, as currently understood does not hold for this particular experiment where $(D_A)_{eff} = D_{eff}$.

(ii) The data of both Evans and Scott can be fitted to the present model with high accuracy, thus further establishing its validity.

(iii) The model confirms Eq. 4.5-1 for Kr and Xe.

(iv) The coefficient D_{eff} is concentration-dependent.

6. Because no more than one gas pair per specimen has been used in previous work, the present results must be regarded as exploratory in this regard. The ranges of gases, mixtures and pressures are all not sufficiently large to form adequate regressions on molecular weight, therefore the trends noted in the current work need further investigation. The following results would be particularly useful:

(i) independent regressions of the g_1 and g_2 means on molecular weight,

(ii) a regression of the b_{g2} pressure regression coefficients on molecular weight, and

(iii) regressions of the series means and series pressure regression coefficients b_{st} on the mole fraction of A.

The nature of the constant H also needs to be clarified.

7. The effects of the pore structure and surface properties cannot be assessed from the current work because

no comparable model exists for diffusion in capillaries and because only one type of porous medium was used.

8. The effects of He, both as the diffusing and non-diffusing gas, need further investigation before He can be considered to be a suitable reference gas in surface diffusion measurements.

9. The regression model can only be used with predictable accuracy to estimate values of α_c' for Morgan EY9-166 within the ranges of the determining variates set by the experiment. Thus, because gas-cooled reactors are designed to run at high pressures with impregnated graphites, the present data have no immediate application in this field. However, the experiment is of considerable practical interest in the field of gas reactions within porous catalysts, as such reactions are frequently carried out at low pressure. Whereas the numerical data may be of little use, the form of the model and the method of obtaining it should find immediate application.

10. The scope for future work is described in general terms in Section 4.6.3, and particular points from the current work which need further investigation are listed in the appropriate places above. In addition, experiments with a given set of gases on a variety of porous media need to be performed to assess the effects of pore structures and surfaces on diffusion rates, and to test

the validity of Eq. 4.4-5. In particular, experimental methods for measuring diffusion rates in impregnated graphites need to be developed.

APPENDIX A

A PUBLISHED PAPER

"Diffusion of Gases Physically Adsorbed on Solids"

Diffusion of Gases Physically Adsorbed on Solids

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APPENDIX B

THE PRELIMINARY EXPERIMENTS

B.1 The Apparatus

A line diagram of the apparatus is presented in Fig. B.1-1. The components of the apparatus are briefly described below,

A. Two mercury manometers, each one meter long. They were used to measure the gas pressure in the expansion vessels before and after expansion into the diffusion cell.

B. A vessel whose volume could be adjusted by raising or lowering the mercury level.

C. The expansion vessel for the gas to be admitted to the outer graphite surface. CO_2 was used exclusively in this vessel.

D. The diffusion cell. Details of the cell and specimen mount are shown in Fig. B.1-2.

E. The differential pressure gauge. The sensitive element was a glass spiral spring, on the end of which a pointer was mounted so that it could rotate freely. A small mirror was attached to the pointer with shellac. The sensitivity of the gauge was about 5 torr/mm at one metre, however, because the apparatus was abandoned after the preliminary experiments, the sensitivity of the gauge was not accurately determined.

F. The expansion vessel for the gas to be admitted to the inner graphite surface. It was made smaller than C so that approximately the same pressure drop would occur in both vessels on expanding their contents into the diffusion cell. N_2 was the only gas used in F.

G. The freezing tube; a small tube approximately 20 cm long and 3 cm in diameter.

B.2 The Experimental Technique

Before any experimental work was done, the volumes of the expansion vessels, the diffusion cell, and the connecting tubing were measured by expanding gas from an accurately calibrated flask which was permanently attached to the apparatus.

Prior to a run, the expansion vessels were filled with the gases to be used (i.e. CO_2 and N_2) and the pressure in each vessel was measured by its respective manometer. The pressure in each vessel was adjusted so that, on expansion into the diffusion cell, the gas pressures on either side of the specimen would be equal. The final adjustment was made by altering the volume of vessel B.

A run was started by simultaneously admitting gas

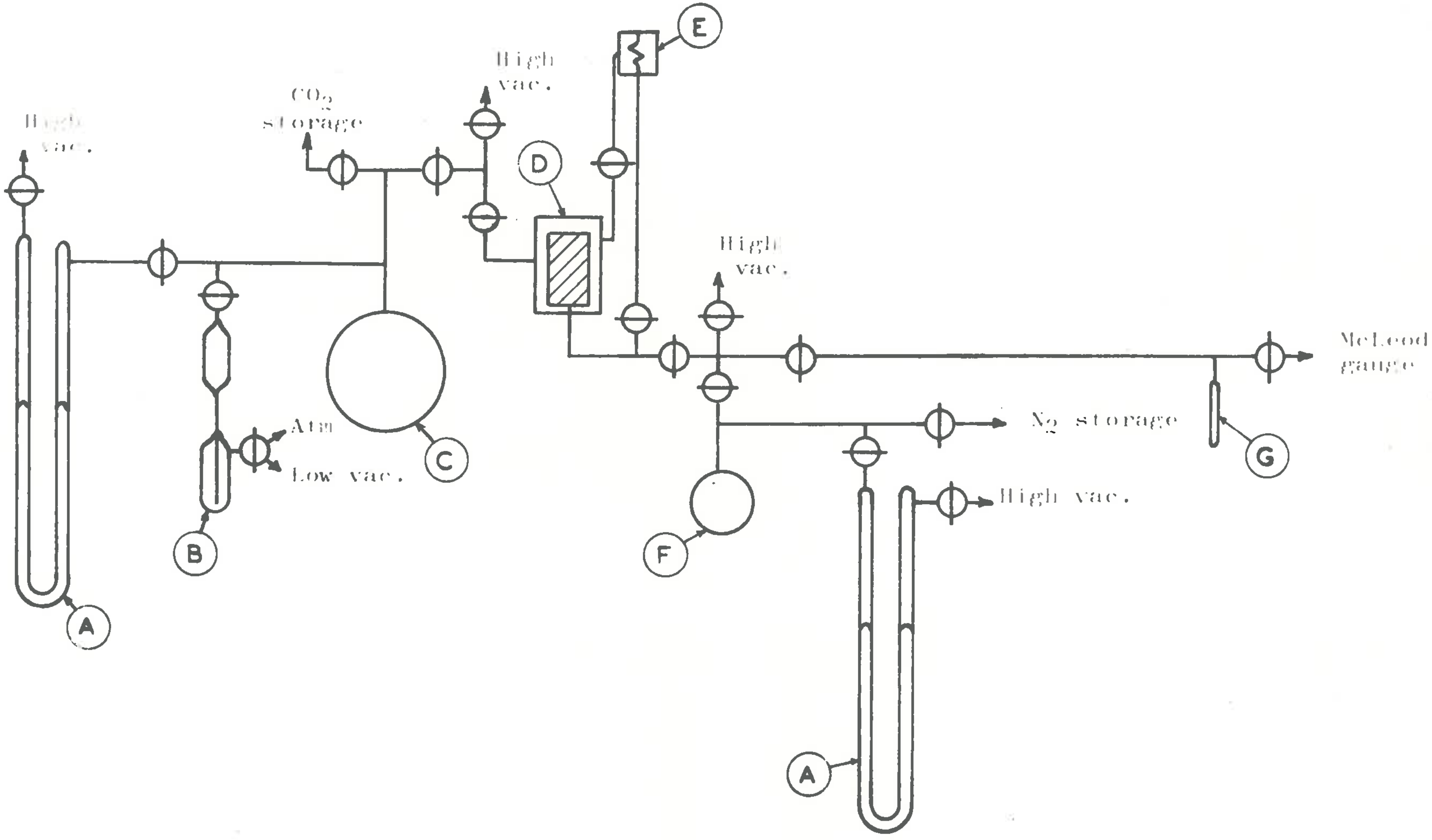

Fig. B.1-1 Line Diagram of the Preliminary Apparatus

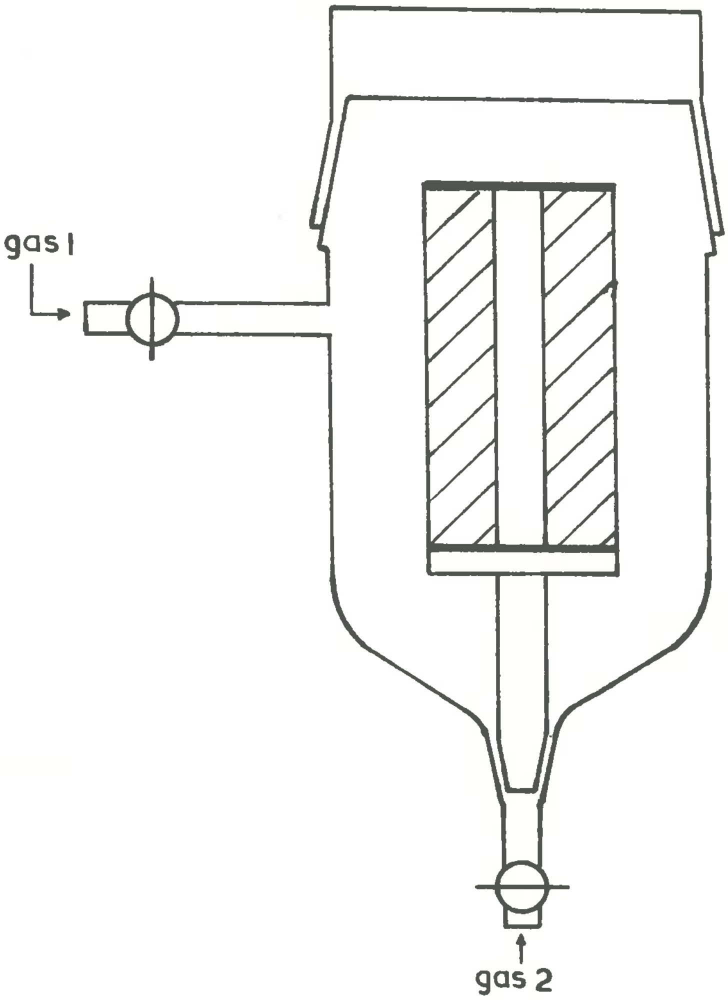

Fig. B.1-2 A Sketch of the Diffusion Cell and Specimen Mount

Note: The thick black lines at the top and bottom of the specimen represent epoxy resin seals. The specimen was sealed to a standard pyrex flat joint.

to both sides of the out-gassed specimen then closing the stopcocks on either side of the cell as soon as the manometer had stopped oscillating. A stop-clock was started immediately the diffusion-cell stopcock was closed. The initial position of a beam of light reflected from the mirror of the differential pressure gauge was marked, and its subsequent position noted at intervals throughout the run.

At the end of a run, a sample from the small volume side of the diffusion cell was admitted to the McLeod gauge. After reading the pressure the CO_2 was frozen out in the freezing tube and the pressure was re-read. The gas composition at the end of the run was calculated from these measurements. Sample from both sides of the specimens were analysed when the impregnated graphite specimen was used. Watts (124) has stated that the freezing method is accurate to about 1% with CO_2/N_2 mixtures.

B.3 Mathematical Procedure

An approximate mathematical expression for the instantaneous concentration in the volume enclosed by a thick hollow cylinder was derived assuming that the conditions approximated to the steady-state, and that the cross-sectional area for diffusion was the logarithmic mean of the inner and outer cylindrical surfaces. Under these conditions Fick's first law of diffusion

$$J_{Az} = -D\, dC_A/dz \qquad \ldots\ldots (B.3\text{-}1)$$

would hold over small time intervals, and thus could be re-written in the form

$$V_1\, \delta C_1 = \frac{2\pi L D (C_2 - C_1)\, \delta t}{\ln \quad b/a} \qquad \ldots\ldots (B.3\text{-}2)$$

where D = diffusion coefficient,

V_1 = volume enclosed by the hollow cylinder,

C_1 = concentration of component A in V_1,

C_2 = concentration of A in the volume outside the cylinder,

L = length of the cylinder,

b = outer radius of the cylinder,

a = inner radius of the cylinder,

and where

$V_1 \delta C_1$ = change of mass within the cylinder over the small time interval St.

The differential equation involving C_1 only is derived by writing Eq. B.3-2 in the form

$$dC_1/dt = \alpha (C_2 - C_1) \qquad \ldots\ldots (B.3\text{-}3)$$

differentiating again with respect to t and substituting an expression similar to Eq. B.3-3 for dC_2/dt.

The resultant differential equation is

$$d^2C/dt^2 + B\, dC_1/dt = 0 \qquad \ldots\ldots \text{(B.3-4)}$$

Using the boundary conditions -

$$t = 0, \qquad C_1 = C_1(0)$$

$$t = \infty, \qquad C_1 = C_1(\infty) = V_1 C_1(0)/(V_1 + V_2)$$

$$\ldots\ldots \text{(B.3-5)}$$

Eq. B.3-4 can be integrated to yield eventually the required expression for $C_1(t)$, viz.

$$C_1(t) = \frac{C_1(0)}{V_1 + V_2} \left[V_2 \exp\left(- \frac{2\pi L D \left(\frac{1}{V_1} + \frac{1}{V_2}\right) t}{\ln \; b/a} \right) + V_1 \right] \qquad \ldots\ldots \text{(B.3-6)}$$

That Eq. B.3-6 is a gross approximation can readily be seen by comparing it with Jaeger's exact analytical solution of Fick's second law (114) which gives $C_1(t)$ in terms of Bessel functions.

B.4 Results

Table B.4-1

Specimen Dimensions

Property	Morgan EY9-166 (Specimen A)	Impregnated Morgan EY9-166 (Specimen B)
Inner diam (cm)	0.95	0.75
Outer diam (cm)	2.52	2.55
Length (cm)	9.79	8.02
Length:Area ratio (cm^{-1})	0.0159	0.0242

Table B.4-2

Results from Specimen A

Total Pressure (torr.)	Time (min)	% N_2	% Equilibrium Value	Diffusion Coefficient D. (cm^2/sec)
53.6	120	31.3	96.5	2.06×10^{-4}
54.2	45	40.2	81.7	3.35×10^{-4}
53.5	20	54.1	67.6	4.38×10^{-4}
51.6	5	71.3	39.2	14.7×10^{-4}
32.2	120	26.8	100	-
31.9	45	36.9	86.2	3.49×10^{-4}
32.3	20	49.9	68.4	6.75×10^{-4}
15.5	20	38.3	84.3	8.20×10^{-4}
6.2	20	27.6	98.9	20.0×10^{-4}

Table B.4-3

Results from Specimen B

Total Pressure (torr.)	Time (hr)	% N_2 (N_2 side)	% N_2 (CO_2 side)	% completion (N_2 side)	% completion (CO_2 side)
57.1	1.7	97.9	-	2.8	-
55.0	12	73.6	6.9	35.0	28.0
53.3	65	29.3	10.3	93.8	41.9
34.3	15	73.3	12.3	35.4	50.0
33.1	20	59.5	20.2	53.6	82.0

APPENDIX C

SOME DETAILS OF THE FINAL APPARATUS AND PROCEDURE

C.1 Description of Components

C.1.1 The Vacuum Apparatus

(1) Vacuum Pumps

The backing pump was an Edwards "Speedivac" 2SC20A rotary oil pump. The second 2SC20A provided the rough vacuum for operating the toepler pump and McLeod Gauge.

The high vacuum pump was a Jena 3Q6 mercury diffusion pump.

(3) Pressure Gauges

The Jena McLeod gauge graduated to read from 10^{-5} to 3 torr. was connected directly to the main high vacuum line. This gauge was used for accurate low pressure measurements. However, since pressure measurement in the range 10^{-5} to 3 torr. were not an essential part of the experimental procedure, it was not calibrated against a standard gauge.

An Edwards B2 Pirani gauge connected to a G-6 gauge-head gave a continuous indication of the pressure in the main high vacuum line.

Mercury manometers one metre long were used for measuring all cell pressures and for preparing all mixtures. The manometers were arranged so that they could all be read with one metre-long cathetometer (supplied by the Precision Tool and Instrument Company).

(3) Toepler Pumps

The toepler pump E consisted of two bulbs connected by a stopcock as shown in Fig. 6.1-2. The lower, slightly larger bulb was filled with mercury until the level rose just above the connecting stopcock. It then contained sufficient mercury to fill the upper bulb without allowing air to bubble through from the lower bulb. The lower bulb could be either vented to the atmosphere or opened to the low vacuum system. The two-way stopcock at the top of the upper bulb enabled gas to be extracted from the mixture storage bulbs and pumped to other parts of the apparatus or vice versa. The volume of the upper bulb was approximately 250 ml.

The toepler pump H was similar to E but the volume of its gas bulb was only about 50 ml.

The rest of the vacuum apparatus needs no further description.

C.1.2 The Counting and Recording Equipment

The components of the counting and recording system shown diagrammatically in Fig. 6.1-5 are described below:

A. A Honeywell-Brown "Electronik" strip-chart recorder Model No. 153x12-VG-II-III-6-A8AA. Its range was originally 0-3 mV, but the range was changed to 0-100 mV.

B. A Leeds and Northrup "Speedomax" strip-chart recorder Type G Model S 69800/P9/Q1. Its range is 0-10 mV. A shunt was connected between the ratemeter and this recorder to increase the range to 0-100 mV.

C. An electric Venner time switch connected in parallel with the chart drive switch on the recorder.

D. An old clock-work Venner time switch with an external switch connected in parallel with it.

E. A 240-110 V transformer.

F. & G. Two "EKCO" ratemeters type N522C. These ratemeters have an 8-position range switch enabling the instrument to be used anywhere in the range 1 to 10000 counts/sec. The 300 to 1000 counts/sec ranges were the most useful in this work.

H. & J. Two 12-position wafer switches.

K. An extra lead not connected through H or J.

L. Ten end-window G.E.C. G-M counters, Type GM4/LB. The aluminium end windows weighed 7 mg/cm^2. Leads from these counters were attached to female line-connectors so that connecting leads from either ratemeter could be used.

M. & N. Co-axial-cable leads for connecting the ratemeters to the G-M counters. These leads were fitted with male line connectors.

C.2 The Diffusion Cells

A general description of the cells is given in the main text. Only details of the techniques used to mount the specimen and to measure the cell and specimen volume are described here.

C.2.1 The Cell Volume Measurements

The volume of each cell compartment was determined by measuring the volume of water needed to fill the cell. Before water was admitted to the cell, all the stopcocks were turned off and a perspex plate with a small hole drilled in it was stuck to the end flange of the cell with stopcock grease. Water from a 100 ml burette was run into the compartment through the hole in the perspex plate until the compartment was full. All air bubbles were removed by carefully tapping the cell when it was nearly full. The volume of water run in was recorded.

The volume of the bore of the central stopcock was calculated from measurements of its diameter and length.

C.2.2 The Specimen-Mounting Technique

Morgan EY9-166 graphite was supplied by the

A.A.E.C. in the form of 1-in diameter rods 12-in in length. A piece 5-in long was cut from one of these rods and turned to the required diameter in a lathe. After measuring the diameter in several places with a micrometer, a thick coat of epoxy resin was cast around the circumference of the rod. After the resin had set, the coated rod was turned down to leave a layer of resin about 1.5 mm thick around the rod.

Specimens were prepared by cutting the rod into short lengths with a parting tool and carefully cutting away the graphite core protruding from the new face of the disc afterwards. The thickness of the plug was measured with a micrometer.

Aluminium foil was wrapped around and sealed to the circumference of each specimen with epoxy resin. The cylinder of foil so formed was about three times the length of the specimen centrally located within it. To ensure that a gas-tight seal existed between the specimen and the aluminium, more resin was placed on one of the internal cylindrical edges formed by the specimen face and the foil. Only one end of the aluminium cylinder was stuck to the bore of the stopcock thus minimising the inclusion of air between the foil and the stopcock wall (q.v. Fig. 6.1-3).

The volume of the stopcock bore on either side of the specimen was calculated from depth-gauge measurements of the distance each face was from the surface. The total gas space open to each specimen face is equal to the compartment volume plus the volume of the stopcock bore between the specimen and the compartment. Volumes on either side were equalised by adding pieces of glass rod to the larger volume. The volumes of the cells and the specimens are tabulated below.

Table C.2-1

Cell Volumes

Cell	Compartment	Vol. (ml)	Vol. bore (ml)	Vol. mounted specimen (ml)	Vol. bore remaining (ml)	Total Vol. (ml)	Corr. Total Vol. (ml)
1	1	81.5	14.74	2.35	8.35	87.85	
	2	83.5			4.1	87.6	87.6
2	3	76.7	14.70	2.43	6.7	83.4	
	4	76.8			4.95	81.75	81.8
3	5	67.45	6.50	0.69	4.55	72.00	
	6	69.9			1.25	71.15	71.2
4	7	68.95	6.62	0.82	2.35	71.30	
	8	68.45			3.45	71.90	71.3
5	9	67.9	6.70	1.22	3.35	71.25	
	10	71.15			2.1	73.25	71.3

Table C.2-2

Specimen Volumes

Cell	Diam. (cm)	Length (cm)	Vol. (ml)	spec. Vol./Vol. ½ cell (γ)
1	1.718	0.832	1.929	0.02202
2	1.668	0.824	1.800	0.02202
3	1.209	0.432	0.496	0.00697
4	1.209	0.515	0.591	0.00829
5	1.209	0.757	0.869	0.01220

Eq. 7.1-2 was used to define the cell constants listed in Table C.2-3. Thus

$A = 1 - \gamma/2$

$B = 1 - \gamma/6$

$W = (A/B + \sqrt{A/B})/2$ — (q.v. Appendix D.4)

and $E = L^2/1200\gamma B$.

Table C.2-3

Cell Constants

Cell	A	B	W	E
1	0.9890	0.9963	0.9945	0.02629
2	0.9890	0.9963	0.9945	0.02579
3	0.9965	0.9988	0.9983	0.02234
4	0.9959	0.9986	0.9980	0.02670
5	0.9939	0.9980	0.9970	0.03922

Note that

(1) the constants A and B must be multiplied by the final equilibrium concentration to make them equal to the constants A and B in Eq. 7.1-7, and

(2) a factor of 600 appears in the denominator of E, because, in the calculations reported here, time was measured in units of 10 minutes, so E has the units cm^2, 10 min/sec, and α the units $(10\ min)^{-1}$, hence the product E α has the units cm^2/sec.

C.3 Pore Structure of Morgan EY9-166 Graphite

The pore structure parameters listed in Table C.3-1 were determined by Field and the A.A.E.C. (58). In the present work these parameters are only of interest insofar as they characterise the porous medium. The numerical values are not used in a strictly quantitative fashion at all. For this reason, further determinations of these parameters with specific reference to this work were considered unnecessary.

Table C.3-1

The Pore Structure Parameters of Morgan EY9-166

Measurement	Sample No.		Laboratory
	S21	S22	Field
Weight (g)	5.464	5.148	
Porosity	0.129	0.168	
Bulk Density (g/ml)	1.720	1.716	
Helium Density (g/ml)	1.974	2.069	
% unopened pores	35.5	21.0	
Kr Surface Area			Field
Monolayer Capacity (ml)	0.568	0.637	
Surface/mass (m^2/g)	0.545	0.649	
Surface/bulk Volume (m^2/ml)	0.937	1.115	
Isotherm temp. (^{o}K)	80.7	79.7	
Pore Size Distribution	P23		A.A.E.C.
Porosity	0.141		
Mean pore radius (microns)	0.440		
Surface/mass (m^2/g)	0.596		
N_2 Permeability	K24		Field
B_o (cm^2)	4.09×10^{-12}		
K_o (cm)	2.57×10^{-7}		

C.4. Active-gas Capsule Installation

Active gases were supplied in 2 ml. capsules as shown in Fig. C.4-1. Such a capsule had to be attached to the

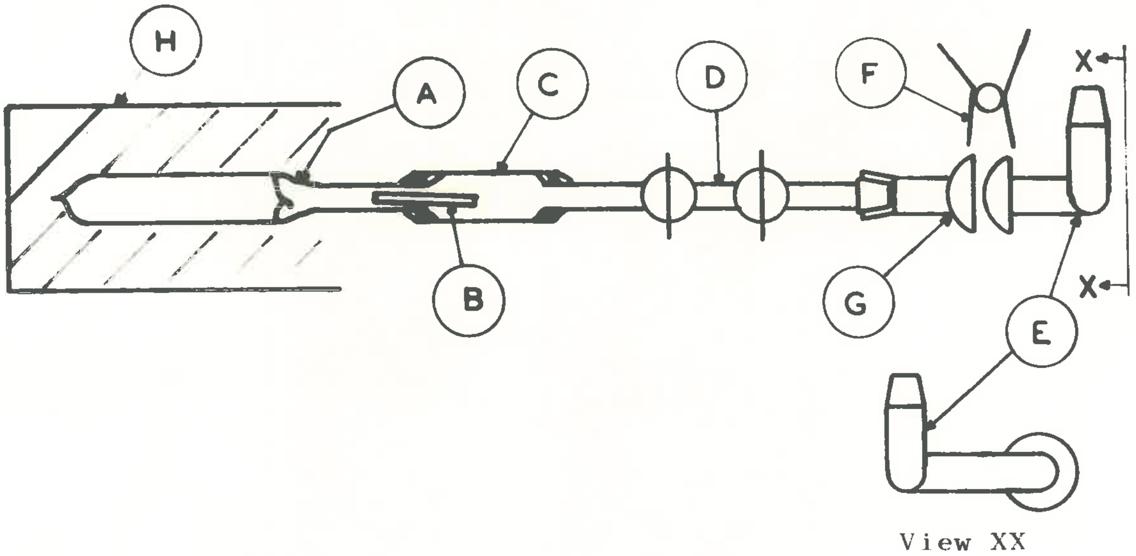

Fig. C.4-1 Active-gas Capsule Outgassing Assembly

A. The Capsule
B. Glass Rod
C. Glass Sleeve
D. Stopcock Assembly
E. Connecting Piece for Initial Outgassing
F. Spring Clip
G. Connecting Piece for Initial Outgassing

stopcock assembly D without prematurely breaking the internal seal. The following procedure was adopted.

(1) The cap was removed from the lead container H to expose the neck of the capsule A.

(2) The container was clamped so that A remained horizontal, and a small piece of glass rod B was placed just inside the neck of A.

(3) A glass sleeve C was sealed to the capsule neck with epoxy resin. Its other end was similarly sealed to the stopcock assembly D.

(4) After the resin had set, the capsule, still in its horizontal position, was attached to the apparatus through the connecting pieces E and G. The ball joint prevented strains being set up through poor alignment of the B7 conical joints.

(5) The assembly was outgassed as far as the internal seal in the capsule, then the assembly was filled with the normal isotope of the gas in the capsule.

(6) The stopcocks D were closed, the assembly was removed from the apparatus, and the internal seal was broken by bouncing the rod B on the internal seal.

(7) The capsule and stopcock assembly were re-attached to the apparatus, this time in a vertical position.

(8) The active gas was ready for use as soon as the apparatus was outgassed to the first stopcock.

APPENDIX D

NUMERICAL PROCEDURES FOR CALCULATING THE DIFFUSION COEFFICIENT

D.1 Introduction

The first step in any numerical procedure for calculating the diffusion coefficient is to convert the chart readings into true counts by using Eq. 6.3-4. Since this step is straightforward, and is independent of any succeeding steps, it is not considered further. The succeeding steps must produce

(1) a mean value of α consistent with the data obtained at all values of t, and

(2) an estimate of the error in α.

In this appendix, the alternative methods for calculating the best mean value of α are discussed.

In the notation that follows, $C_i(t)$ is denoted simply by C. Unless the full notation is used, i is to be taken to be unity, therefore the concentration at time t_n can be denoted by C_n without any confusion.

D.2 Direct Substitution Methods

Measured values of C, α and t are substituted in Eq. 7.1-3 directly. Thus, if n values of C and t are available, n equations can be solved simultaneously for

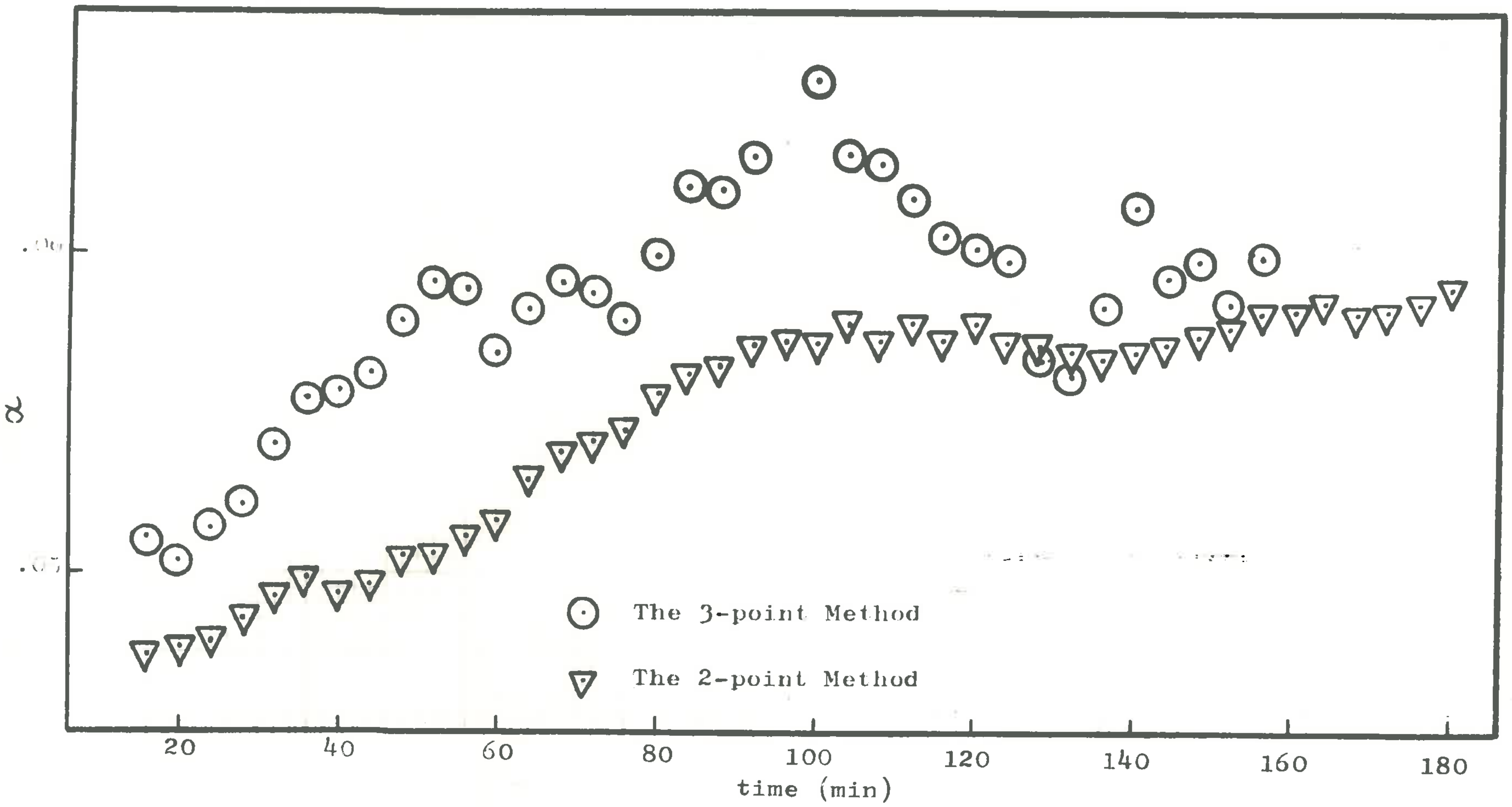

Fig. D.2-1 Variation in α with Time - A comparison of the 2- and 3-point Methods for Run 396-40

$C_2(0)$ and α.

D.2.1 The Two-point Method

In the two point method the n equations are grouped in pairs so that $t_2 = 2t_1$. First, $C_2(0)$ is eliminated from each pair of equations, then n/2 values of α are calculated from the remaining equations. The arithmetic mean of these values is considered to be the best value of α and the root-mean-square error the best estimate of the error. The explicit expression for α in these calculations is

$$\alpha = -\left[\ln(C_2/C_1 - W)\right] /t_1 \qquad ..... \text{(D.2-1)}$$

where $$W = (A/B + \sqrt{A/B})/2 \qquad ..... \text{(D.2-2)}$$

and A and B are the constants in Eq. 7.1-7. Eq. D.2-2 is a good approximation for the constant W only when the ratio A/B is close to unity. The derivation of Eq. D.2-1 given in Section D.4 makes this clear. For many runs calculated by the two-point method, the individual values of α either increased or decreased steadily with time as illustrated in Fig. D.2-1. This phenomenon indicated that the numerical procedure could well be at fault.

D.2.2 The Three-point Method

Since the two-point expression for α contains a cell constant which must be determined by separate

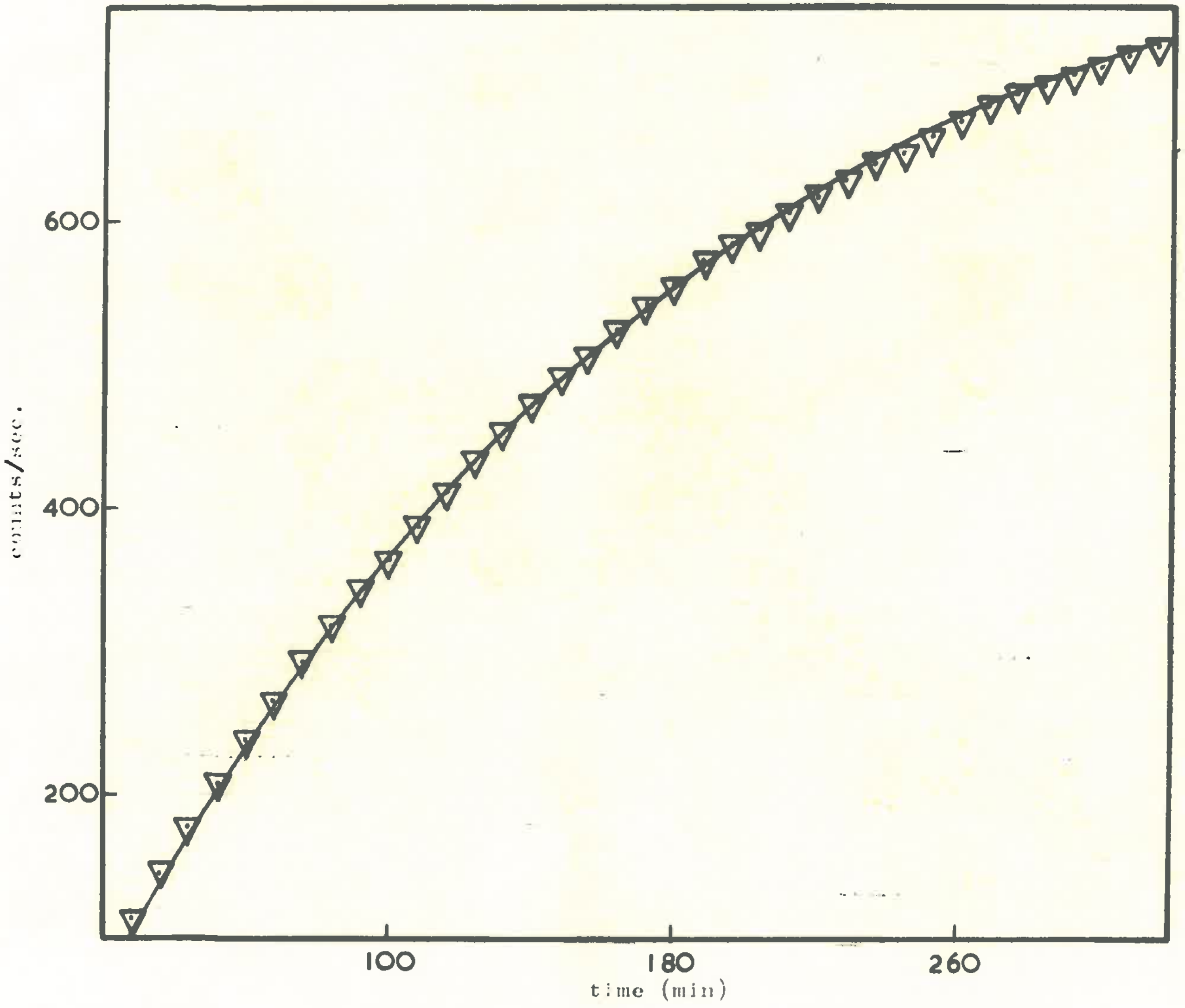

Fig. D.2-2 Curve Calculated by 3-point Method and Data for Run 396-40 measurements, a simple improvement is achieved by eliminating W. If the n equations in α are grouped in threes so that

$$t_2 = t_1 + \theta \text{ and } t_3 = t_1 + 2\theta \qquad \ldots\ldots \text{ (D.2-3)}$$

where θ is a fixed arbitrary time interval, the explicit equation for α becomes

$$\alpha = \ln \left[(C_2 - C_1)/C_3 - C_2) \right] / \theta \qquad \ldots\ldots \text{ (D.2-4)}$$

For the particular run illustrated in Fig. D.2-1, the three-point method yielded values of α that were hardly any more consistent than those obtained with the two-point method. Further, Fig. D.2-2 shows that the curve defined by the constants derived by this method still did not fit the data well.

It was concluded that either the experimental data did not define a negative exponential curve or the method of averaging was inadequate. In order to test these alternatives a formal curve-fitting procedure was adopted.

D.3 Curve-fitting Procedures

The equations

$$C = A - Be^{-\alpha t} \qquad \ldots\ldots \text{ (7.1-7)}$$

$$C = \alpha / \left[1 + \exp(-b - \alpha t) \right] \qquad \ldots\ldots \text{ (D.3-1)}$$

were fitted to the experimental data points by the least-squares technique outlined below.

(1) Expressions for A and a were derived by substituting the values C_1, C_2 and C_3 defined by Eq. D.2-3 into both Eq. 7.1-7 and Eq. D.3-1, and solving the resultant simultaneous equations for A and a respectively. The desired expressions were

$$A = (C_1C_3 - C_2^2)/(C_3 - 2C_2 + C_1) \quad \ldots\ldots \text{(D.3-2)}$$

$$a = C_2(C_1 + C_3C_2 - 2C_2C_3)/(C_2^2 - C_1C_3) \quad \ldots\ldots \text{(D.3-3)}$$

(2) The means of n/3 values of A and a were used to calculate n values of $\ln(A - C_n)$ and $\ln\left[C_n/(a - C_n)\right]$. If the data conformed to either of the curves to be fitted then one of these logarithmic expressions would be linear with time since

$$\ln(A - C) = \ln B - \alpha t \quad \ldots\ldots \text{(D.3-4)}$$

and

$$\ln\left[C/(a - C)\right] = b + \alpha t \quad \ldots\ldots \text{(D.3-5)}$$

(3) The least-squares values of α, ln B and b were computed.

(4) The fitted curves were plotted on top of the experimental curves as illustrated in Fig. D.3-1. They showed conclusively that the data conformed to Eq. 7.1-7.

Negative exponential curves were fitted to all the runs by an iterative procedure discussed in Section 7.1.2.

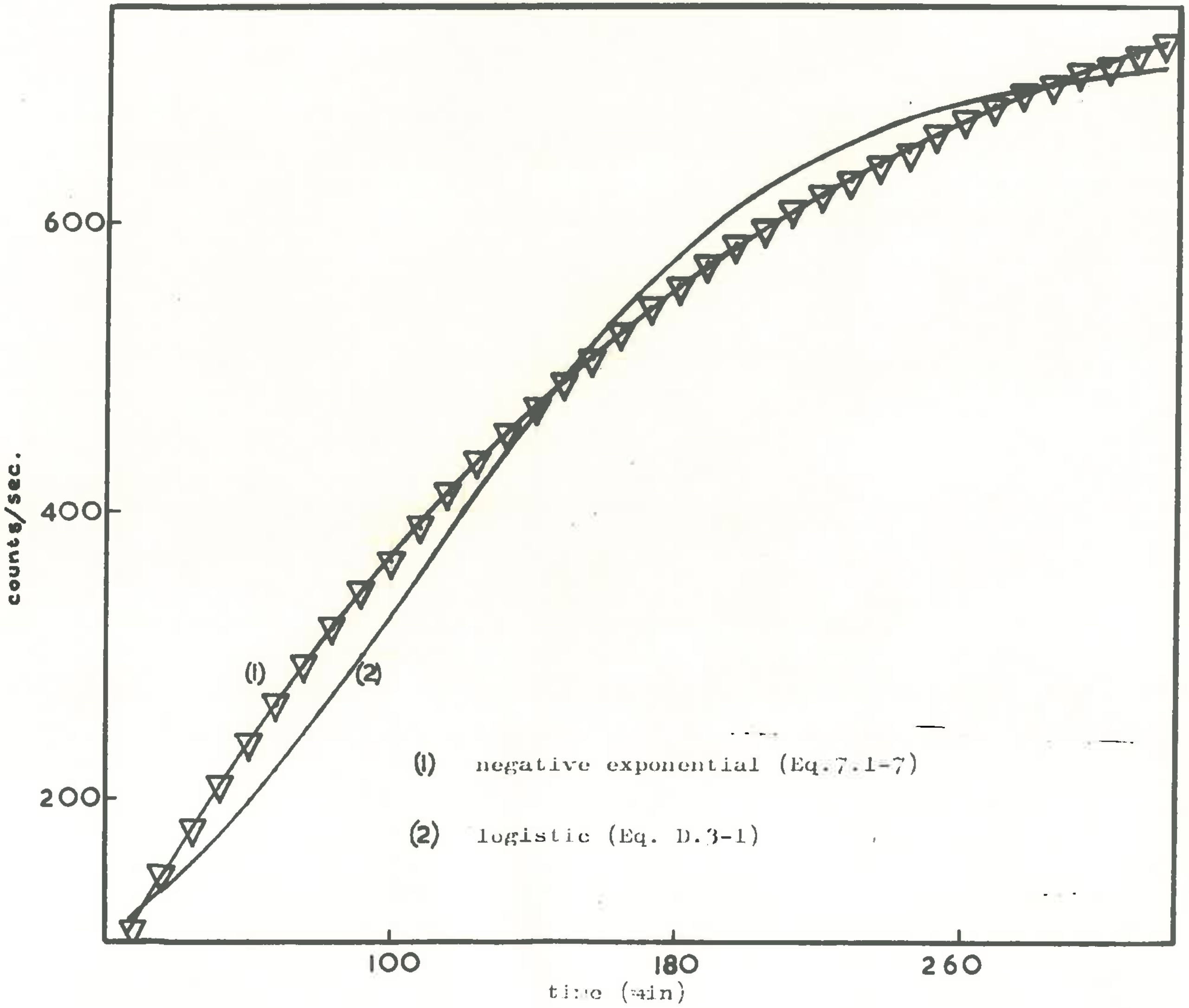

Fig. D.3-1 Fitted Curves and Data for Run **396-40**

D.4 Derivation of Explicit Expressions for α

The starting point in these derivations is

$$C = A - Be^{-\alpha t} \qquad \ldots\ldots (7.1-7)$$

D.4.1 The Two-point Expression

The two starting equations are

$$C_1 = A - Be^{-\alpha t_1} \qquad \ldots\ldots (D.4-1)$$

$$C_2 = A - Be^{-2\alpha t_1} \qquad \ldots\ldots (D.4-2)$$

Dividing and rearranging gives

$$e^{-2\alpha t_1} - C e^{-\alpha t_1}/C_1 + A/B(C_2/C_1 - 1) = 0$$

$$\ldots\ldots (D.4-3)$$

a quadratic equation in $e^{-\alpha t_1}$

Thus

$$e^{-\alpha t_1} = (K_1 \pm \sqrt{K_1^2 - 4W'K_1 + 4W'})/2 \qquad \ldots\ldots (D.4-4)$$

where $K_1 = C_2/C_1$ and $W' = A/B$.

If W' is approximately equal to one, then $e^{-\alpha t_1}$ lies between $(K_1 - W')$ and $(K - \sqrt{W'})$.

Let $W = (W' + \sqrt{W'})/2$,

then to a very good approximation

$$\alpha = -\left[\ln \left(C_2/C_1 - W \right) \right]/t_1 \qquad \ldots\ldots (D.2\text{-}1)$$

which is the required result.

D.4.2 The Three-point Expression

The three starting equations are

$$C_i = A - B \exp \left(-\alpha \left[t_1 + (i-1)\,\theta \right]\right), \; i=1,2,3 \qquad \ldots\ldots (D.4\text{-}5)$$

If these are denoted 1, 2 and 3 then subtracting 2 from 1, and 3 from 2 and dividing the first result by the second yields

$$(C_2 - C_1)/(C_3 - C_2) = e^{\alpha\theta} \qquad \ldots\ldots (D.4\text{-}6)$$

which gives the desired result

$$\alpha = \ln \left[(C_2 - C_1)/(C_3 - C_2) \right]/\theta \; \ldots\ldots (D.2\text{-}4)$$

The three-point expressions for A and a are derived in a similar fashion.

APPENDIX E

COMPUTER PROGRAMMES

E.1 The Programme Language

The programmes listed below are written in the FORTRAN source language, therefore in principle, they can be compiled for use on any computer for which a FORTRAN compiler is available. However FORTRAN compilers are specific for a particular type of machine, and as such the allowable statements vary slightly from one compiler to another. The programmes described here were written specifically for the University of Adelaide I.B.M. 1620 computer (20K store) and the compiler known locally as FORTRAN A. The FORTRAN A compiler accepts multiple format statements and eighty-column programme statements; in all other respects it is similar to the I.B.M. programme "FORTRAN with FORMAT" (code 1620-FO-004). If the following programmes are to be used on any other computer then the specifications of the available compilers should be checked. If a FORTRAN A compiler is not available the programmes would have to be modified to suit local requirements.

E.2 The Data Conversion Programme

The data conversion programme converts chart readings into true counts by means of Eq. 6.3-4 and estimates an initial value of α from Eq. D.2-4. However as most of the data was punched in two sets suitable for use with Eq. D.2-1, the programme also rearranges the "two point" data to form "three point" data.

There are five main steps in the programme.

Step 1. The computer decides whether two or three sets of data are supplied and reads in the data points accordingly.

Step 2. "Two point" data are converted to "three point" data. For this to occur T/DELTA (see programme listing for definition of variables) must be an integral number and the first point in the second set of data must not occur later than two DELTA intervals after the last point in the first set of data. If one of these conditions is unfulfilled, the calculations are terminated and the next run is read in. If these conditions are fulfilled then the points are arranged so that a continuous set of points is produced at time intervals of DELTA. Missing points are calculated by linear interpolation. Since no more than one point is missing between given values, linear interpolation is just as accurate as reading the values from the original chart.

Step 3. The chart readings are converted to true counts.

Step 4. Individual values of $\alpha(00)$ are calculated for each trio of points.

Step 5. The mean value of α is calculated and the constants and converted data are punched in a form suitable for the regression programme.

E.2.1 Input Data Cards

There are no header cards which must precede the whole data deck or any individual run so data for any number of runs can be processed consecutively.

CARD 1. contains the three fixed-point numbers NA, NB and NC, and the floating point number PRESS. The symbols P = were punched on most of the first data cards used in this work, but these are not essential.

CARD 2. contains the floating-point constants T, DELTA, W, B.C. and P.

CARD 3. contains the floating-point constants E, F, G and TINT.

The significance of each constant is indicated in the listing of the programme. The special meaning of the run numbers is discussed in Section 7.2 of the main text. The cell constant W is not used in the programme, but is included as an additional piece of data.

The remaining cards contain the data points punched so that each "set" is read successively into the computer. The programme will accommodate a maximum of 150 data points i.e. $NC < 50$ irrespective of whether two or three-set data are supplied.

E.2.2 Sense-switch settings

The programme uses sense switches 1, 2 and 3.

If switch 1 is *on*, the rearranged data from step 2 in the calculation are punched. This setting is only useful to test the programme, and is in any case inoperative if three-point data are supplied.

If switch 2 is *on* at the same time as switch 1, the converted data will also be punched. A pause statement follows so that switch 2 can be turned off immediately. If more than one run is to be processed switch 2 must be off to return the computer to the beginning of the programme.

If any errors are detected in Step 4, the computer proceeds under control of switch 3. If swith 3 is *off*, the calculations are terminated, the values in error are printed, an error message is printed, and the next run is read in. If switch 3 is *on*, the points in error are printed but the computer then assumes the points are acceptable and proceeds normally.

For testing the programme with "two-point" data the recommended settings are

SW 1	ON
SW 2	ON then OFF
SW 3	ON

For normal running all switches must be off. If some data points are poor, then some runs may be rejected by switch 3.

TABLE E.2-1
DATA CONVERSION PROGRAMME - SAMPLE INPUT AND OUTPUT

INPUT DATA

```
389 40  30     P=156.36
     5700E1      3000E0      9982E0      628E-2      3140E1      2300E1
     2234-1                  6000E1
  297   310   323   335   348   360   372   384   396   407   417   428
  438   449   459   468   477   486   496   505   514   523   532   541
  550   559   567   575   583   591   505   523   541   559   575   591
  605   618   631   643   654   666   678   689   700   712   721   730
  740   749   757   764   772   780   788   795   801   807   814   819
```

REARRANGED DATA (SW1 ON)

```
389 40  26        156.36
57.0000E-01 30.0000E-02 99.8200E-02 62.8000E-05 31.4000E-01 23.0000E-01
22.3400E-03   .0000E-99 60.0000E-01 78.0000E-01
29.7000E-00 31.0000E-00 32.3000E-00 33.5000E-00 34.8000E-00 36.0000E-00
37.2000E-00 38.4000E-00 39.6000E-00 40.7000E-00 41.7000E-00 42.8000E-00
43.8000E-00 44.9000E-00 45.9000E-00 46.8000E-00 47.7000E-00 48.6000E-00
49.6000E-00 50.5000E-00 51.4000E-00 52.3000E-00 53.2000E-00 54.1000E-00
55.0000E-00 55.9000E-00 56.7000E-00 57.5000E-00 58.3000E-00 59.1000E-00
59.8000E-00 60.5000E-00 61.1500E-00 61.8000E-00 62.4500E-00 63.1000E-00
63.7000E-00 64.3000E-00 64.8500E-00 65.4000E-00 66.0000E-00 66.6000E-00
67.2000E-00 67.8000E-00 68.3500E-00 68.9000E-00 69.4500E-00 70.0000E-00
70.6000E-00 71.2000E-00 71.6500E-00 72.1000E-00 72.5500E-00 73.0000E-00
73.5000E-00 74.0000E-00 74.4500E-00 74.9000E-00 75.3000E-00 75.7000E-00
76.0500E-00 76.4000E-00 76.8000E-00 77.2000E-00 77.6000E-00 78.0000E-00
78.4000E-00 78.8000E-00 79.1500E-00 79.5000E-00 79.8000E-00 80.1000E-00
80.4000E-00 80.7000E-00 81.0500E-00 81.4000E-00 81.6500E-00 81.9000E-00
```

TABLE E.2-1 (CONT.)

CONVERTED DATA (SW1 OFF)

```
389 40  26         156.36
57.0000E-01 30.0000E-02 22.3400E-03 78.0000E-01 62.7514E-03
98.9683E-00 10.3220E+01 10.7480E+01 11.1418E+01 11.5692E+01 11.9643E+01
12.3600E+01 12.7563E+01 13.1532E+01 13.5176E+01 13.8494E+01 14.2147E+01
14.5474E+01 14.9137E+01 15.2473E+01 15.5478E+01 15.8487E+01 16.1499E+01
16.4851E+01 16.7871E+01 17.0894E+01 17.3921E+01 17.6951E+01 17.9985E+01
18.3023E+01 18.6064E+01 18.8770E+01 19.1479E+01 19.4191E+01 19.6906E+01
19.9284E+01 20.1664E+01 20.3876E+01 20.6089E+01 20.8305E+01 21.0522E+01
21.2571E+01 21.4621E+01 21.6502E+01 21.8384E+01 22.0439E+01 22.2495E+01
22.4553E+01 22.6613E+01 22.8502E+01 23.0393E+01 23.2285E+01 23.4179E+01
23.6246E+01 23.8315E+01 23.9868E+01 24.1421E+01 24.2976E+01 24.4531E+01
24.6261E+01 24.7991E+01 24.9550E+01 25.1109E+01 25.2496E+01 25.3884E+01
25.5099E+01 25.6314E+01 25.7704E+01 25.9094E+01 26.0485E+01 26.1877E+01
26.3270E+01 26.4663E+01 26.5883E+01 26.7103E+01 26.8149E+01 26.9196E+01
27.0244E+01 27.1291E+01 27.2514E+01 27.3738E+01 27.4612E+01 27.5486E+01
```

If there is no obvious error these runs may be re-run with switch 3 on.

E.2.3 Output

(1) Printed Output

The normal printed output consists of the run numbers NA and NB, and the number NC. If the "two point" data cannot be converted to "three point" data, the error message NEED MORE DATA is printed and no punched output results. If errors are detected in step 4 then the points in error are printed and further output is dictated by the position of switch 3.

(2) Punched Output

The output is controlled by switches 1 and 2 as described above. The data for one run together with both types of output from that run are listed in Table E.2-1.

E.2.4 The Programme

The programme is listed below.

```
C                               DATA CONVERSION PROGRAMME
C   WRITTEN BY K R WELLER, CHEM ENGINEERING DEPT. UNIVERSITY OF ADELAIDE
C
C         PROGRAMME ACCEPTS EITHER 2- OR 3-POINT DATA, REARRANGES 2-POINT
C         DATA TO FORM 3-POINT DATA, CONVERTS CHART READINGS TO TRUE COUNTS,
C         CALCULATES AN INITIAL VALUE OF ALPHA AND PUNCHES OUT THE CONVERTED
C         DATA IN A FORM SUITABLE FOR THE EXPONENTIAL REGRESSION PROGRAMME
C
C   INPUT DATA  SYMBOL                     DESCRIPTION                      FORMAT
C                NA,NB    RUN NUMBERS                                        I4,I3
C                NC       NUMBER OF POINTS PER SET                           I4
C                PRESS    PRESSURE                                          7XF6.2
C                T        START TIME                                         E12.4
C                DELTA    TIME INTERVAL BETWEEN SUCCESSIVE POINTS            E12.4
C                W,E      CELL CONSTANTS                                     E12.4
C                B,C,G    CHART CONVERSION FACTORS (EQ. 4.3-4)               E12.4
C                P        BACKGROUND COUNT                                   E12.4
C                F        ISOTOPE HALF-LIFE FACTOR                           E12.4
C                TINT     TIME INTERVAL BETWEEN SETS (3-PT DATA)             E12.4
C                R(I)     DATA POINTS                                       12F6.1
C
C   IN 2-PT DATA (1) TIME AT GIVEN POINT IN 2ND HALF DATA = 2*TIME AT
C                    CORRESPONDING POINT IN 1ST HALF,
C                (2) TIME GAP BETWEEN 2 HALVES MUST BE LESS THAN 3*DELTA,
C                (3) T/DELTA MUST BE AN INTEGRAL NUMBER,
C                (4) TINT=0.
C
C   IN 3-PT DATA (1) TIME AT GIVEN POINT IN LAST THIRD DATA = TINT + TIME
C                    AT CORRESPONDING POINT IN 2ND THIRD = 2*TINT + TIME
C                    AT CORRESPONDING POINT IN 1ST THIRD
C                (2) TINT MUST BE SOME +VE NUMBER, PREFERABLY A MULTIPLE
C                    OF DELTA
C
```

```
C                                   THE PROGRAMME
C
      DIMENSIONR(150),D(105)
    3 FORMAT(I4,I3,I4,7XF6.2)
    6 FORMAT(I4,I3,I4,7XF7.2)
    4 FORMAT(6E12.4)
    5 FORMAT(12F6.1)
   11 FORMAT(2XE10.3,3F8.2)
   60 FORMAT(13X38HDATA CONVERSION AND 1ST ESTIMATE ALPHA/)
   61 FORMAT(30X4HRUN ,I4,I3/I4)
   63 FORMAT(6HD(J)= ,E10.3,3F8.2)
   65 FORMAT(14HNEED MORE DATA)
      PRINT60
C  STEP 1.
C        CONSTANTS READ IN AND AS TINT IS ZERO OR +VE SO 2- OR 3-PT DATA READ IN
    2 READ3,NA,NB,NC,PRESS
      IF(NA)99,99,20
   20 PRINT61,NA,NB,NC
      DO31I=1,150
   31 R(I)=0.
      DO32I=1,105
   32 D(I)=0
      READ4,T,DELTA,W,B,C,P,E,F,G,TINT
      IF(TINT)1,1,9
    1 NX=2
      GOTO8
    9 NX=3
    8 MM=NX*NC
      DO7I=1,MM,12
      J=I+1
      K=I+2
      L=I+3
      M=I+4
      N=I+5
      JI=I+6
```

```
      JK=I+7
      JL=I+8
      JM=I+9
      JN=I+10
      KI=I+11
7READ5,R(I),R(J),R(K),R(L),R(M),R(N),R(JI),R(JK),R(JL),R(JM),R(JN),R(KI)
C  STEP 2.
C        2-PT DATA CONVERTED TO 3-PT DATA. STEP OMITTED IF 3-PT DATA SUPPLIED
      GOTO(18,18,19),NX
   18 TEA=T/DELTA
      NX=TEA
      ANC=NX
      IF(TEA-ANC)24,38,24
   24 PRINT65
      GOTO2
   38 ANC=NC
      IF((ANC-1.)*DELTA-T)21,22,22
   21 IF((ANC+1.)*DELTA-T)24,25,26
   25 NX=NC
      D(1)=(R(NC)+R(NC+1))/2.
      GOTO27
   26 NX=NC-1
      D(1)=R(NC)
   27 D(2)=R(NC+1)
      M=2
      GOTO28
   22 M=0
      NX=NX+1
   28 J=NC-1
      DO29I=1,J
      KAY=NC+I
      K=2*I+M
      KI=2*I+M-1
      D(KI)=(R(KAY)+R(KAY+1))/2.
   29 D(K)=R(KAY+1)
      DO40I=1,K
```

```
    JN=NX+I
  40 R(JN)=D(I)
    MM=NX+K
    NC=MM/3
    D(1)=NC
    TINT=D(1)*DELTA
    MM=3*NC
    IF(SENSESWITCH1)41,19
  41 PUNCH6,NA,NB,NC,PRESS
    PUNCH4,T,DELTA,W,B,C,P,E,F,G,TINT
  42 DO72I=1,MM,6
  72 PUNCH4,R(I),R(I+1),R(I+2),R(I+3),R(I+4),R(I+5)
    IF(SENSESWITCH2)43,2
  43 PAUSE
C STEP 3.
C       CHART READINGS CONVERTED TO TRUE COUNTS
  19 TEA=T
    SUM=0
    L=0
    DO44I=1,NC
    KAY=I+NC
    KAZ=KAY+NC
    R(I)=((C*R(I)+G)/(1.-B*(R(I)+G/C)))*EXPF(TEA*F)-P
    R(KAY)=((C*R(KAY)+G)/(1.-B*(R(KAY)+G/C)))*EXPF((TEA+TINT)*F)-P
    R(KAZ)=((C*R(KAZ)+G)/(1.-B*(R(KAZ)+G/C)))*EXPF((TEA+TINT*2.)*F)-P
C STEP 4.
C       VALUES OF ALPHA CALCULATED FROM EACH TRIO OF POINTS
    D(4)=(R(KAY)-R(I))/(R(KAZ)-R(KAY))
    IF(D(4))12,12,13
  13 D(5)=LOGF(D(4))/TINT
    IF(D(5))15,14,14
  12 PRINT11,D(4),R(I),R(KAY),R(KAZ)
    GOTO16
  15 PRINT63,D(5),R(I),R(KAY),R(KAZ)
  16 L=L+1
    IF(SENSESWITCH3)44,24
```

```
   14 SUM=SUM+D(5)
   44 TEA=TEA+DELTA
C  STEP 5.
C        ARITH. MEAN OF ALPHA CALCULATED, AND CONSTANTS AND CONVERTED
C        DATA PUNCHED
      JK=NC-L
      D(6)=JK
      D(7)=SUM/D(6)
      PUNCH6,NA,NB,NC,PRESS
      PUNCH4,T,DELTA,E,TINT,D(7)
      GOTO42
   99 STOP
      END
```

E.3 The Exponential Regression Programme

The exponential regression programme is the main programme presented in the thesis. The method of calculation is described in Section 7.1.2. The main steps in the calculation are indicated by comment cards in the programme listing.

E.3.1 Input Data Cards

No header cards are required; the programme accepts the output from the data conversion programme exactly as it is punched.

CARD 1. contains the numbers NA, NB, NC, and PRESS as before.

CARD 2. contains the constants T, DELTA, E, TINT and CO. The remaining cards contain the converted data. Again, a maximum of 150 points can be accommodated.

E.3.2 Sense-switch Settings

Only switch 1 is used in the programme. Under normal conditions it is switched off. If it is turned on before the analysis of variance step is reached, this step will be entered, and output will result. If switch 1 remains on, the computer pauses at the end of the variance analysis and a new iteration is begun as soon as the START button is depressed. If switch 1 is turned off before the pause statement is reached, the rest of the programme is entered. This facility enables the operator to interrupt or terminate the iterative procedure if an undue number of iterations is encountered.

E.3.3 Output

(1) Printed Output

There are normally four lines of printed output per run. The run numbers NA and NB, the pressure, and the number NC appear on the first line, the initial value of CO (i.e. α) on the second, the number of iterations on the third, and the final value of CO and the coefficients B_1 and B_2 on the fourth. The last two lines are repeated if switch 1 is used to produce some intermediate results.

(2) Punched Output

The punched output is described in Section 7.2 of the main text.

E.3.4 The Programme

The programme is listed below.

```
C             NEGATIVE EXPONENTIAL MULTIPLE REGRESSION PROGRAMME
C   WRITTEN BY K R WELLER, CHEM ENGINEERING DEPT. UNIVERSITY OF ADELAIDE
C
C         PROGRAMME IS BASED ON ITERATIVE PROCEDURE IN WILLIAMS,  E.J.,
C         REGRESSION ANALYSIS (WILEY, N.Y. 1959) P.59.
C         PROGRAMME ACCEPTS OUTPUT FROM DATA CONVERSION PROGRAMME, FORMS
C         SUMS OF SQUARES AND PRODUCTS. AND CALCULATES THE MULTIPLE LINEAR
C         REGRESSION ON F AND FDASH (Q AND G'. USING THE INITIAL VALUE OF
C         ALPHA. THE RATIO OF THE REGRESSION CONSTANTS B2/B1 GIVES THE
C         ADJUSTMENT FOR ALPHA. THE PROGRAMME REPEATS THE MULTIPLE REGRESSION
C         WITH NEW ALPHA VALUES UNTIL THE ALPHA ADJUSTMENT IS NEGLIGIBLE.
C         THEN IT SETS UP AN ANALYSIS OF VARIANCE ON THE FITTED CURVE.
C         DETERMINES THE COEFFICIENTS A,B1, B2 AND THEIR STANDARD ERRORS.
C         THE REGRESSION COEFFICIENTS A, AND B1 WHEN B2 = 0, AND CALCULATES
C         A DIFFUSION COEFFICIENT BASED ON A MEASURED CELL CONSTANT E.
C
C   INPUT DATA   SYMBOL                    DESCRIPTION                    FORMAT
C                 NA,NB    RUN NUMBERS                                     I4.I3
C                 NC       NUMBER OF POINTS PER SET                        I4
C                 PRESS    PRESSURE                                       7XF6.2
C                 T        START TIME                                      E12.4
C                 DELTA    TIME INTERVAL BETWEEN SUCCESSIVE POINTS         E12.4
C                 E        CELL CONSTANT                                   E12.4
C                 CO       1ST ESTIMATE OF ALPHA                           E12.4
C                 R(I)     DATA POINTS                                    6E12.4
C         DATA MUST BE RECORDED AT EQUAL TIME INTERVALS. THE TOTAL NUMBER
C         OF POINTS MUST BE A MULTIPLE OF 3 SO THAT DATA CAN BE SPLIT INTO
C         3 PARTS AS IN DATA CONVERSION PROGRAMME.
C
C                                 THE PROGRAMME
C
      DIMENSIONR(150),A(2,2),C(2,2),H(2),B(2)
    3 FORMAT(I4,I3,I4,7XF7.2)
    4 FORMAT(6E12.4)
   60 FORMAT(15X40HEXP REGRESSION FOR DIFFUSION COEFFICIENT/)
   61 FORMAT(20X4HRUN ,I4,I3,7H PRESS=,F7.2,2XI4)
```

```
   62 FORMAT(6X2HDF,5X2HSS,10X2HMS,10X2HVR)
   63 FORMAT(8HREGN   2,1XE11.4,1XE11.4,1XE11.4)
   64 FORMAT(4HDEVN,I4,1XE11.4,1XE11.4)
   65 FORMAT(4HTOTL,I4,1XE11.4/)
   66 FORMAT(4H  A=,E11.3,4H B1=,E11.4,6H   B2=,E11.4,5H   C=,E11.4)
   67 FORMAT(14X5HSEB1=,E11.4,6H SEB2=,E11.4,5H SEC=,E11.4/)
   68 FORMAT(6HREGSS=,E11.4,3H D=,E11.4/)
      PRINT60
      PUNCH60
C  STEP 1.
C        CONSTANTS AND DATA READ IN, DATA AND (DATA)**2 SUMMED.
    2 READ3,NA,NB,NC,PRESS
      IF(NA)99,99,20
   20 PRINT61,NA,NB,PRESS,NC
      PUNCH61,NA,NB,PRESS,NC
      DO31I=1,150
   31 R(I)=0.
      READ4,T,DELTA,E,TINT,C0
      PUNCH4,C0
      PRINT4,C0
      MM=3*NC
      DO21I=1,MM,6
   21 READ4,R(I),R(I+1),R(I+2),R(I+3),R(I+4),R(I+5)
      SUMY=0
      SUMYY=0
      DO22I=1,MM
      SUMY=SUMY+R(I)
   22 SUMYY=SUMYY+R(I)*R(I)
      J=0
      N=0
C  STEP 2.
C        EXPONENTIAL FUNCTION AND ITS DERIVATIVE EVALUATED FOR EACH POINT,
C        AND SUMS OF SQUARES AND PRODUCTS FORMED.
   23 SUMQ=0
      SUMQQ=0
      SUMQG=0
```

```
      SUMQY=0
      SUMG=0
      SUMGG=0
      SUMGY=0
      TEA=T
      DO24I=1,NC
      K=NC+I
      L=NC+K
      TEB=TEA+TINT
      TEC=TEB+TINT
      Q1=EXPF(-C0*TEA)
      Q2=EXPF(-C0*TEB)
      Q3=EXPF(-C0*TEC)
      SUMQ=SUMQ+Q1+Q2+Q3
      SUMQQ=SUMQQ+Q1*Q1+Q2*Q2+Q3*Q3
      SUMQY=SUMQY+Q1*R(I)+Q2*R(K)+Q3*R(L)
      IF(N)24,26,26
   26 G1=-TEA*Q1
      G2=-TEB*Q2
      G3=-TEC*Q3
      SUMG=SUMG+G1+G2+G3
      SUMQG=SUMQG+Q1*G1+Q2*G2+Q3*G3
      SUMGG=SUMGG+G1*G1+G2*G2+G3*G3
      SUMGY=SUMGY+G1*R(I)+G2*R(K)+G3*R(L)
   24 TEA=TEA+DELTA
      AMM=MM
      A(1,1)=SUMQQ-(SUMQ*SUMQ)/AMM
      H(1)=SUMQY-(SUMQ*SUMY)/AMM
      IF(N)44,27,27
   27 A(1,2)=SUMQG-(SUMQ*SUMG)/AMM
      A(2,1)=A(1,2)
      A(2,2)=SUMGG-(SUMG*SUMG)/AMM
      H(2)=SUMGY-(SUMG*SUMY)/AMM
      ADET=A(1,1)*A(2,2)-A(1,2)*A(2,1)
C  STEP 3.
C        MULTIPLE REGRESSION COEFFICIENTS B1 AND B2 CALCULATED AND ALPHA
```

```
C        (C0) RE-ESTIMATED.
      C(1,1)=A(2,2)/ADET
      C(1,2)=-A(1,2)/ADET
      C(2,1)=-A(2,1)/ADET
      C(2,2)=A(1,1)/ADET
      B(1)=C(1,1)*H(1)+C(1,2)*H(2)
      B(2)=C(2,1)*H(1)+C(2,2)*H(2)
      C0=C0+B(2)/B(1)
C  STEP 4.
C        IF ALPHA CHANGED SIGNIFICANTLY, PROGRAMME RETURNS TO STEP 2,
C        OTHERWISE STEP 5 ENTERED.
      N=N+1
      I=J*10+N
      IF(I-14)35,35,36
   36 IF(SENSESWITCH2)35,25
   35 IF(10-N)41,41,42
   41 PRINT3,I
      J=J+1
      N=0
   42 IF(SENSESWITCH1)25,43
   43 IF(ABSF(B(2)/B(1))*1.E6-5.)25,23,23
C  STEP 5.
C        ANALYSIS OF VARIANCE SET UP AND MULTIPLE REGRESSION COEFFICIENTS
C        A, B1, AND B2 CORRESPONDING TO FINAL VALUE OF ALPHA PUNCHED.
   25 PRINT3,I
      PUNCH3,I
      PRINT4,C0,B(1),B(2)
      TOTSS=SUMYY-(SUMY*SUMY)/AMM
      REGSS=B(1)*H(1)+B(2)*H(2)
      DEVSS=TOTSS-REGSS
      REGMS=REGSS/2.
      DEVMS=DEVSS/(AMM-3.)
      Q2=(SUMY-B(1)*SUMQ)/AMM
      SEB1=SQRTF(C(1,1)*DEVMS)
      SEB2=SQRTF(C(2,2)*DEVMS)
      SEC=ABSF(SEB2/B(1))
```

```
      Q1=REGMS/DEVMS
      PUNCH62
      PUNCH63,REGSS,REGMS,Q1
      I=MM-3
      PUNCH64,I,DEVSS,DEVMS
      I=MM-1
      PUNCH65,I,TOTSS
      PUNCH66,Q2,B(1),B(2),C0
      PUNCH67,SEB1,SEB2,SEC
      IF(SENSESWITCH1)40,45
   40 PAUSE
      GOTO23
C  STEP 6.
C          REGRESSION ANALYSIS REPEATED WITH B2 = 0. REGRESSION SUM OF
C          SQUARES AND CONSTANTS A AND B1 PUNCHED. DIFFUSION COEFFICIENT D
C          EVALUATED.
   45 N=-1
      GOTO23
   44 B(1)=H(1)/A(1,1)
      Q2=(SUMY-B(1)*SUMQ)/AMM
      REGSS=B(1)*H(1)
      PUNCH66,Q2,B(1)
      Q3=E*C0
      PUNCH68,REGSS,Q3
      GOTO2
   99 STOP
      END
```

APPENDIX F

ANALYSIS OF RESULTS

F.1 Analysis of Variance of Latin Squares

The 25 values of α in each Latin square together with the corresponding analysis of variance are presented in the six Tables below.

```
                          TABLE F.1-1
                       ANALYSIS OF L(1,1)

                             L(1,1)

MEAN PRESSURE
   (TORR.)      10.0     25.0     62.5    156.3    390.6

       GAS 2
         KR    .1392    .1262    .1081    .0628    .0517

         XE    .0905    .1275    .1134    .0692    .0312

         AR    .1386    .1214    .0947    .0577    .0546

         NE    .1202    .0843    .1027    .0950    .0746

         HE    .1262    .1011    .0904    .0848    .0622

                             TOTALS
                      GAS 2      CELLS     PRESSURES

                      .4880      .5088       .6147

                      .4318      .5354       .5605

                      .4670      .4995       .5093

                      .4768      .4100       .3695

                      .4647      .3746       .2743

GRAND TOTAL 2.3283

                      ANALYSIS OF VARIANCE

VARIATIONS DUE TO   D.F.     S.S.        M.S.        V.R.

 CELLS                4    .0038520   .0009630   10.22***
 GAS 2                4    .0003545   .0000886      -  NS
 PRESSURES            4    .0157955   .0039489   41.92***
 ERROR               12    .0011305   .0000942

 TOTAL               24    .0211325
```

```
                          TABLE F.1-2
                       ANALYSIS OF L(2,1)

                             L(2,1)

MEAN PRESSURE
   (TORR.)      10.0    25.0    62.5   156.3   390.6

      GAS 2
        KR     .1002   .0951   .0763   .0531   .0365

        XE     .0818   .0963   .0826   .0496   .0352

        AR     .1147   .0997   .0753   .0523   .0386

        NE     .0961   .1060   .0942   .0716   .0485

        HE     .1097   .0897   .0660   .0787   .0504

                             TOTALS
                     GAS 2     CELLS    PRESSURES

                     .3612     .4080     .5025

                     .3455     .4144     .4868

                     .3806     .3838     .3944

                     .4164     .3494     .3053

                     .3945     .3426     .2092

GRAND TOTAL 1.8982

                     ANALYSIS OF VARIANCE

VARIATIONS DUE TO    D.F.     S.S.       M.S.        V.R.

 CELLS                 4   .0008633   .0002158     3.99*
 GAS 2                 4   .0006157   .0001539     2.84 NS
 PRESSURES             4   .0122744   .0030686    56.67***
 ERROR                12   .0006498   .0000542

 TOTAL                24   .0144032
```

```
                              TABLE F.1-3
                          ANALYSIS OF L(1,2)

                                L(1,2)

MEAN PRESSURE
   (TORR.)       10.0     25.0     62.5    156.3   390.6

       GAS 2
         KR     .1262    .1143    .0955    .0634   .0333

         XE     .0917    .1178    .0999    .0787   .0432

         AR     .1306    .1237    .0892    .0608   .0513

         NE     .1227    .1232    .1124    .0699   .0569

         HE     .1374    .1013    .0598    .0847   .0736

                                TOTALS
                     GAS 2       CELLS     PRESSURES

                     .4327       .4924       .6086

                     .4313       .4883       .5803

                     .4556       .4922       .4568

                     .4851       .4198       .3575

                     .4568       .3688       .2583

GRAND TOTAL 2.2615

                         ANALYSIS OF VARIANCE

VARIATIONS DUE TO    D.F.      S.S.        M.S.       V.R.

 CELLS                 4    .0025049    .0006262    4.85*
 GAS 2                 4    .0003864    .0000966      -   NS
 PRESSURES             4    .0174914    .0043728   33.88***
 ERROR                12    .0015488    .0001291

 TOTAL                24    .0219315
```

TABLE F.1-4
ANALYSIS OF L(2,2)

L(2,2)

MEAN PRESSURE (TORR.)	10.0	25.0	62.5	156.3	390.6
GAS 2					
KR	.1136	.0856	.0809	.0490	.0370
XE	.0706	.1052	.0805	.0552	.0327
AR	.1233	.0889	.0854	.0426	.0463
NE	.0962	.0693	.0870	.0664	.0388
HE	.1121	.0988	.0608	.0675	.0408

TOTALS

GAS 2	CELLS	PRESSURES
.3661	.4196	.5158
.3442	.3966	.4478
.3865	.3759	.3946
.3577	.3621	.2807
.3800	.2803	.1956

GRAND TOTAL 1.8345

ANALYSIS OF VARIANCE

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0022526	.0005631	6.84**
GAS 2	4	.0002313	.0000578	- NS
PRESSURES	4	.0132515	.0033129	40.25***
ERROR	12	.0009876	.0000823	
TOTAL	24	.0167229		

```
                         TABLE F.1-5
                      ANALYSIS OF L(1.3)

                            L(1,3)

MEAN PRESSURE
   (TORR.)       10.0    25.0    62.5   156.3   390.6

       GAS 2
         KR     .1536   .1139   .1057   .0602   .0378

         XE     .0795   .1175   .1044   .0627   .0340

         AR     .1349   .1241   .0953   .0496   .0636

         NE     .1125   .0832   .1347   .0898   .0633

         HE     .1347   .1091   .0721   .0966   .0836

                            TOTALS
                      GAS 2     CELLS    PRESSURES

                      .4712     .5660      .6152

                      .3981     .5266      .5478

                      .4675     .4905      .5122

                      .4835     .4111      .3589

                      .4961     .3222      .2823

GRAND TOTAL 2.3164

                      ANALYSIS OF VARIANCE

VARIATIONS DUE TO    D.F.     S.S.       M.S.       V.R.

 CELLS                 4   .0075856   .0018964   27.75***
 GAS 2                 4   .0011630   .0002907    4.25*
 PRESSURES             4   .0152531   .0038133   55.80***
 ERROR                12   .0008200   .0000683

 TOTAL                24   .0248217
```

TABLE F.1-6
ANALYSIS OF L(2,3)

L(2,3)

MEAN PRESSURE (TORR.)	10.0	25.0	62.5	156.3	390.6
GAS 2					
KR	.1276	.1076	.0898	.0549	.0119
XE	.0713	.1124	.0784	.0585	.0340
AR	.1207	.1062	.0758	.0453	.0569
NE	.1030	.0742	.1008	.0841	.0606
HE	.1225	.0948	.0587	.0863	.0680

TOTALS

GAS 2	CELLS	PRESSURES
.3918	.4840	.5451
.3546	.4588	.4952
.4049	.4376	.4035
.4227	.3625	.3291
.4303	.2614	.2314

GRAND TOTAL 2.0043

ANALYSIS OF VARIANCE

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0065079	.0016270	63.79***
GAS 2	4	.0007164	.0001791	7.02**
PRESSURES	4	.0127157	.0031789	124.64***
ERROR	12	.0003061	.0000255	
TOTAL	24	.0202461		

F.2 Procedure for Removing the Cell Effect

The procedure for removing the cell effects (c_j) from each α value is outlined for L_{11}.

If each c_j were zero then the cell totals in Table F.1-1 would be identical. If each cell total is denoted by T_j and the mean value of α for L_{ht} by m_{ht} then

$$c_j = (T_j - nm_{ht})/n \qquad \ldots\ldots \text{(F.2-1)}$$

where n equals the number of rows or columns in L_{ht}. The T_j and c_j for L_{11} are listed in Table F.2-1.

Table F.2-1

Cell Effects for L_{11}

Cell	T_j	c_j
1	.5088	.0086
2	.5354	.0139
3	.4995	.0068
4	.4100	-.0111
5	.3746	-.0182
Total (n^2m_{11})	2.3283	.0000
nm_{11}	.4657	

The cell effect is removed by subtracting c_j from each α value. For example, the first entry in L_{11} is $\alpha = 0.1392$ using cell 1, so the corrected value $\alpha_c = 0.1392 - 0.0086 = 0.1306$.

The c_j were calculated for each square and each α value was similarly adjusted. The 150 α_c values are presented below in Table F.2-2.

TABLE F.2-2

LIST OF ALPHA VALUES
CORRECTED FOR CELL EFFECTS

SERIES 20
GAS 1/GAS 2 = 50/50

MEAN PRESSURE (TORR.) GAS 1	 GAS 2	10.0	25.0	62.5	156.3	390.6
KR	KR	.1306	.1123	.1013	.0739	.0699
	XE	.1087	.1189	.0995	.0624	.0423
	AR	.1247	.1146	.1058	.0759	.0460
	NE	.1313	.1025	.0941	.0811	.0678
	HE	.1194	.1122	.1086	.0762	.0483
XE	KR	.0945	.0882	.0755	.0591	.0439
	XE	.0892	.0906	.0757	.0488	.0412
	AR	.1078	.0989	.0813	.0597	.0329
	NE	.1021	.1134	.0885	.0647	.0477
	HE	.1089	.0957	.0734	.0730	.0435

SERIES 30
GAS 1/GAS 2 = 75/25

GAS 1	GAS 2	10.0	25.0	62.5	156.3	390.6
KR	KR	.1182	.1071	.0875	.0699	.0500
	XE	.1084	.1098	.0927	.0707	.0497
	AR	.1234	.1157	.0957	.0775	.0433
	NE	.1292	.1399	.1044	.0627	.0489
	HE	.1294	.1078	.0765	.0767	.0664

TABLE F.2-2 (CONT.)

MEAN PRESSURE (TORR.)		10.0	25.0	62.5	156.3	390.6
GAS 1	GAS 2					
XE	KR	.1031	.0796	.0791	.0500	.0543
	XE	.0879	.0947	.0745	.0534	.0337
	AR	.1173	.0871	.0864	.0599	.0358
	NE	.0972	.0866	.0765	.0604	.0370
	HE	.1103	.0998	.0781	.0570	.0348

SERIES 40
GAS 1/GAS 2 = 25/75

GAS 1	GAS 2	10.0	25.0	62.5	156.3	390.6
KR	KR	.1331	.1012	.1003	.0706	.0660
	XE	.1077	.0970	.0917	.0573	.0444
	AR	.1222	.1187	.1057	.0778	.0431
	NE	.1229	.1114	.1142	.0771	.0579
	HE	.1293	.1195	.1003	.0761	.0709
XE	KR	.1110	.0960	.0824	.0626	.0398
	XE	.0992	.0958	.0668	.0511	.0417
	AR	.1091	.0988	.0835	.0732	.0403
	NE	.1107	.1021	.0842	.0725	.0532
	HE	.1151	.1025	.0866	.0697	.0564

F.3 Latin Square Analysis of α'

The 25 values of $\alpha' = \log_{10}(100\ )$ in each L_{ht} together with the corresponding analysis of variance are presented in the six Tables below.

```
                        TABLE F.3-1
                     ANALYSIS OF L(1,1)

                           L(1,1)

MEAN PRESSURE
  (TORR.) 10.0        25.0        62.5        156.3        390.6

 GAS 2
   KR     1.14364    1.10105    1.03382      .79796       .71349

   XE      .95665    1.10550    1.05462      .84011       .49415

   AR     1.14178    1.08421     .97635      .76118       .73719

   NE     1.07989     .92583    1.01157      .97772       .87274

   HE     1.10105    1.00474     .95617      .92840       .79379

                            TOTALS
                     GAS 2       CELLS     PRESSURES

                    4.78996     4.92630     5.42301

                    4.45103     5.06896     5.22133

                    4.70071     4.93193     5.03253

                    4.86775     4.35309     4.30537

                    4.78415     4.31332     3.61136

GRAND TOTAL 23.59360

                     ANALYSIS OF VARIANCE

VARIATIONS DUE TO    D.F.      S.S.        M.S.        V.R.

 CELLS                 4    .1018501    .0254625     6.92**
 GAS 2                 4    .0207097    .0051774     1.41 NS
 PRESSURES             4    .4488445    .1122111    30.48***
 ERROR                12    .0441837    .0036820

 TOTAL                24    .6155879
```

```
                        TABLE F.3-2
                     ANALYSIS OF L(2,1)

                           L(2,1)

MEAN PRESSURE

 GAS 2
   KR    1.00085     .97818     .88252     .72509     .56229

   XE     .91275     .98363     .91698     .69548     .54654

   AR    1.05960     .99870     .87679     .71850     .58659

   NE     .98272    1.02531     .97405     .85491     .68574

   HE    1.04026     .95279     .81954     .89597     .70243

                           TOTALS
                    GAS 2      CELLS    PRESSURES

                   4.14893    4.44109    4.99618

                   4.05538    4.51210    4.93861

                   4.24018    4.30270    4.46988

                   4.52273    4.08393    3.88995

                   4.41099    4.03839    3.08359

GRAND TOTAL 21.37821

                     ANALYSIS OF VARIANCE

VARIATIONS DUE TO    D.F.     S.S.       M.S.        V.R.

 CELLS                 4   .0354119   .0088530     5.81**
 GAS 2                 4   .0290401   .0072600     4.76*
 PRESSURES             4   .5132353   .1283088    84.20***
 ERROR                12   .0182867   .0015239

 TOTAL                24   .5959740
```

TABLE F.3-3
ANALYSIS OF L(1,2)

```
                                  L(1,2)

MEAN PRESSURE
  (TORR.) 10.0         25.0        62.5        156.3        390.6

 GAS 2
   KR    1.10105     1.05806      .98000      .80209       .52244

   XE     .96237     1.07115      .99957      .89597       .63548

   AR    1.11591     1.09239      .95036      .78390       .71012

   NE    1.08884     1.09062     1.05076      .84448       .75511

   HE    1.13798     1.00559      .77670      .92788       .86688

                                TOTALS
                        GAS 2       CELLS     PRESSURES

                       4.46364     4.86096     5.40615

                       4.56454     4.88490     5.31781

                       4.65268     4.86145     4.75739

                       4.82981     4.48236     4.25432

                       4.71503     4.13603     3.49003

GRAND TOTAL 23.22570

                         ANALYSIS OF VARIANCE

VARIATIONS DUE TO     D.F.      S.S.        M.S.        V.R.

 CELLS                  4     .0873087    .0218272     5.69**
 GAS 2                  4     .0156966    .0039242     1.02 NS
 PRESSURES              4     .5062481    .1265620    32.97***
 ERROR                 12     .0460689    .0038390

 TOTAL                 24     .6553223
```

TABLE F.3-4
ANALYSIS OF L(2,2)

L(2,2)

MEAN PRESSURE (TORR.)	10.0	25.0	62.5	156.3	390.6
GAS 2					
KR	1.05540	.93247	.90795	.69020	.56820
XE	.84880	1.02200	.90580	.74194	.51455
AR	1.09097	.94890	.93146	.62941	.66558
NE	.98318	.84073	.93952	.82217	.58883
HE	1.04959	.99476	.78390	.82930	.61066

TOTALS

GAS 2	CELLS	PRESSURES
4.15422	4.51180	5.02794
4.03309	4.36207	4.73886
4.26632	4.23721	4.46863
4.17443	4.11415	3.71302
4.26821	3.67104	2.94782

GRAND TOTAL 20.89627

ANALYSIS OF VARIANCE

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0819775	.0204944	13.09***
GAS 2	4	.0075015	.0018754	- NS
PRESSURES	4	.5701938	.1425485	70.20***
ERROR	12	.0243690	.0020307	
TOTAL	24	.6840418		

```
                         TABLE F.3-5
                       ANALYSIS OF L(1,3)

                            L(1,3)

MEAN PRESSURE
  (TORR.) 10.0        25.0       62.5       156.3       390.6

 GAS 2
   KR     1.18640    1.05656    1.02402     .77960      .57749

   XE      .90037    1.07004    1.01873     .79727      .53148

   AR     1.13005    1.09378     .97909     .69548      .80346

   NE     1.05115     .92012    1.12939     .95328      .80140

   HE     1.12939    1.03783     .85794     .98498      .92221

                            TOTALS
                     GAS 2      CELLS    PRESSURES

                    4.62407    5.17427    5.39736

                    4.31789    5.08083    5.17833

                    4.70186    4.84586    5.00917

                    4.85534    4.37915    4.21061

                    4.93235    3.95140    3.63604

GRAND TOTAL 23.43151

                     ANALYSIS OF VARIANCE

VARIATIONS DUE TO    D.F.     S.S.       M.S.       V.R.

 CELLS                 4    .2107294   .0526824   32.05***
 GAS 2                 4    .0457911   .0114478    6.97**
 PRESSURES             4    .4362544   .1090636   66.36***
 ERROR                12    .0197232   .0016436

 TOTAL                24    .7124981
```

TABLE F.3-6
ANALYSIS OF L(2,3)

L(2,3)

MEAN PRESSURE (TORR.)	10.0	25.0	62.5	156.3	390.6
GAS 2					
KR	1.10584	1.03180	.95328	.73957	.07555
XE	.85309	1.05076	.89432	.76716	.53148
AR	1.08166	1.02612	.87967	.65610	.75511
NE	1.01284	.87040	1.00339	.92480	.78247
HE	1.08813	.97681	.76864	.93601	.83251

TOTALS

GAS 2	CELLS	PRESSURES
3.90604	4.85111	5.14156
4.09681	4.76509	4.95589
4.39866	4.61716	4.49930
4.59390	4.14037	4.02364
4.60210	3.22378	2.97712

GRAND TOTAL 21.59751

ANALYSIS OF VARIANCE

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.3604902	.0901225	9.89***
GAS 2	4	.0763929	.0190982	2.10 NS
PRESSURES	4	.6005240	.1501310	16.47***
ERROR	12	.1093907	.0091159	
TOTAL	24	1.1467978		

L_{23} contains the dubious run referred to in Sections 7.2.3 and 8.2. This run is represented by α'_{15} = 0.07555. The missing value corresponding to α'_{15} is 0.52979. The analysis of L_{23} using the dummy value is given below in Table F.3-7.

```
                          TABLE F.3-7

              ANALYSIS OF L(2,3) WITH MISSING VALUE

                            TOTALS
                      GAS 2      CELLS     PRESSURES

                     4.36028    4.85111    5.14156

                     4.09681    4.76509    4.95589

                     4.39866    4.61716    4.49930

                     4.59390    4.14037    4.02364

                     4.60210    3.67802    3.43136

GRAND TOTAL 22.05175

                       ANALYSIS OF VARIANCE

VARIATIONS DUE TO    D.F.     S.S.       M.S.        V.R.

 CELLS                 4    .1944153   .0486038    51.66***
 GAS 2                 4    .0342819   .0085705     9.11**
 PRESSURES             4    .3896320   .0974080   103.54***
 ERROR                11    .0103486   .0009408

 TOTAL                23    .6286779
```

F.4 Regression of α'_c on Pressure

The values of α' corrected for cell effects (denoted by α'_c) are given in Table F.4-1.

TABLE F.4-1

LIST OF TRANSFORMED ALPHA VALUES
CORRECTED FOR CELL EFFECTS

SERIES 29
GAS 1/GAS 2 = 50/50

MEAN PRESSURE (TORR.)		10.0	25.0	62.5	156.3	390.6
GAS 1	GAS 2					
KR	KR	1.10212	1.03100	.99118	.87109	.79457
	XE	1.03773	1.06398	.98457	.79747	.56728
	AR	1.07173	1.04157	1.04948	.84226	.69567
	NE	1.15302	1.00691	.97005	.90767	.83010
	HE	1.05841	1.07787	1.03725	.88689	.72374
XE	KR	.96776	.93089	.87711	.76343	.60974
	XE	.96020	.95054	.86969	.69007	.58488
	AR	1.01231	.99329	.91513	.76595	.55350
	NE	1.02106	1.07276	.94096	.80762	.68033
	HE	1.03485	.99113	.86699	.86288	.65514

SERIES 30
GAS 1/GAS 2 = 75/25

KR	KR	1.05788	1.01011	.93674	.83465	.62426
	XE	1.06419	1.02798	.95162	.85271	.66804
	AR	1.06796	1.04913	.98292	.88572	.66695
	NE	1.12140	1.19244	1.00759	.79653	.71185
	HE	1.09472	1.03815	.87852	.88471	.91893

TABLE F.4-1 (CONT.)

MEAN PRESSURE (TORR.)		10.0	25.0	62.5	156.3	390.6
GAS 1	GAS 2					
XE	KR	.98889	.89591	.89636	.70322	.66984
	XE	.95044	.95549	.86924	.73035	.52757
	AR	1.05441	.93731	.94448	.73105	.59907
	NE	.99620	.94237	.87301	.78561	.57724
	HE	1.03800	1.00778	.88554	.76279	.57410

SERIES 40
GAS 1/GAS 2 = 25/75

GAS 1	GAS 2	10.0	25.0	62.5	156.3	390.6
KR	KR	1.08881	.97765	.99211	.84103	.72447
	XE	1.04735	.97245	.93982	.76536	.59291
	AR	1.05114	1.06187	1.04052	.84246	.70587
	NE	1.11258	1.06710	1.03180	.87437	.76949
	HE	1.09748	1.09926	1.00492	.88739	.84330
XE	KR	1.01769	.96085	.91192	.79357	.67626
	XE	.99956	.96261	.82337	.72580	.58548
	AR	1.01071	.98476	.93367	.80257	.66696
	NE	1.06684	1.01687	.91524	.85385	.74111
	HE	1.04677	1.03081	.91511	.84786	.76156

The Latin square analyses of α', with the pressure and error S.S. replaced by regression and deviations from regression S.S. using log p as the determining variate, are presented in Table F.4-2. A similar set of analyses of regressions on log(p + 60) is given in Table F.4-3.

TABLE F.4-2
ANALYSIS OF VARIANCE OF THE SQUARES FOR THE REGRESSIONS ON LOG P

ANALYSIS OF L(1,1)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.1018501		
GAS 2	4	.0207097		
COMMON REGRN	1	.4120976		
BETWEEN REGRNS	4	.0138034	.0034509	– NS
REGRESSIONS	5	.4259010		
DEVIATIONS	11	.0671271	.0061025	
TOTAL	24	.6155879		

ANALYSIS OF L(2,1)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0354119		
GAS 2	4	.0290401		
COMMON REGRNS	1	.4750863		
BETWEEN REGRNS	4	.0046995	.0011749	– NS
REGRESSIONS	5	.4797859		
DEVIATIONS	11	.0517361	.0047033	
TOTAL	24	.5959740		

ANALYSIS OF L(1,2)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0873087		
GAS 2	4	.0156966		
COMMON REGRN	1	.4793634		
BETWEEN REGRNS	4	.0135138	.0033785	– NS
REGRESSIONS	5	.4928773		
DEVIATIONS	11	.0594397	.0054036	
TOTAL	24	.6553223		

TABLE F.4-2 (CONT.)

ANALYSIS OF L(2,2)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0819775		
GAS 2	4	.0075015		
COMMON REGRN	1	.5379085		
BETWEEN REGRNS	4	.0070291	.0017573	– NS
REGRESSIONS	5	.5449376		
DEVIATIONS	11	.0496252	.0045114	
TOTAL	24	.6840418		

ANALYSIS OF L(1,3)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.2107294		
GAS 2	4	.0457911		
COMMON REGRN	1	.4032667		
BETWEEN REGRNS	4	.0080690	.0020172	– NS
REGRESSIONS	5	.4113356		
DEVIATIONS	11	.0446419	.0040584	
TOTAL	24	.7124981		

ANALYSIS OF L(2,3)

CELLS	4	.1944153	
GAS 2	4	.0342819	
COMMON REGRN	1	.3799336	
BETWEEN REGRNS	4	.0053714	.0013429
REGRESSIONS	5	.3853050	
DEVIATIONS	10	.0146756	.0014676
TOTAL	23	.6286779	

TABLE F.4-3
ANALYSIS OF VARIANCE OF THE SQUARES FOR THE REGESSIONS ON LOG (P + 60)

ANALYSIS OF L(1,1)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.1018501		
GAS 2	4	.0207097		
COMMON REGRN	1	.444659		
BETWEEN REGRNS	4	.0215008	.0053752	2.20 NS
REGRESSIONS	5	.4661597		
DEVIATIONS	11	.0268685	.0024426	
TOTAL	24	.6155879		

ANALYSIS OF L(2,1)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0354119		
GAS 2	4	.0290401		
COMMON REGRN	1	.5109524		
BETWEEN REGRNS	4	.0058632	.0014658	- NS
REGRESSIONS	5	.5168155		
DEVIATIONS	11	.0208404	.0018946	
TOTAL	24	.5959740		

ANALYSIS OF L(1,2)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0873087		
GAS 2	4	.0156966		
COMMON REGRES				
COMMON REGRN	1	.5029472		
BETWEEN REGRNS	4	.0186489	.0046622	1.67 NS
REGRESSIONS	5	.5215961		
DEVIATIONS	11	.0307209	.002443	
TOTAL	24	.6553223		

TABLE F.4-3 (CONT.)

ANALYSIS OF L(2,2)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.0819775		
GAS 2	4	.0075015		
COMMON REGRN	1	.5678441		
BETWEEN REGRNS	4	.0087581	.0021895	1.34 NS
REGRESSIONS	5	.5766021		
DEVIATIONS	11	.0179607	.0016328	
TOTAL	24	.6840418		

ANALYSIS OF L(1,3)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.2107294		
GAS 2	4	.0457911		
COMMON REGRN	1	.4294136		
BETWEEN REGRN	4	.0097554	.0024389	1.60 NS
REGRESSIONS	5	.4391690		
DEVIATIONS	11	.0168085	.0015281	
TOTAL	24	.7124981		

ANALYSIS OF L(2,3)

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
CELLS	4	.1944153		
GAS 2	4	.0342819		
COMMON REGRN	1	.3859260		
BETWEEN REGRNS	4	.0058026	.0014506	1.76 NS
REGRESSIONS	5	.3917286		
DEVIATIONS	10	.0082520	.0008252	
TOTAL	23	.6286779		

F.5 Instrument Effects

The instrument effects were separated from the g_1 effects by substituting the g_{1h} and the I_r sums into the regression model (Eq. 8.5-1) and solving the resultant equations simultaneously, remembering that

$$g_{11} + g_{12} = 0 \qquad \ldots\ldots \text{(F.5-1)}$$

$$\text{and} \qquad I_1 + I_2 = 0 \qquad \ldots\ldots \text{(F.5-2)}$$

The regression model equations were

$$(\Sigma\alpha')_{I_r} = 75m + \left[36 + 3(r-1) \right] g_{12} + \left[39 - 3(r-1) \right] g_{11}$$

$$+ 75\, I_r \quad r=1,2 \qquad \ldots\ldots \text{(F.5-3)}$$

$$\text{and } (\Sigma\alpha')_{g_{1h}} = 75m + 75g_{1h} + 3I_h \quad h=1,2 \qquad \ldots\ldots \text{(F.5-4)}$$

The value of $\Sigma\alpha'$ and the corresponding values of the g_{1h} and I_r effects, found from the solution of the above equations, are given in Table F.5-1.

Table F.5-1

Instrument and g_1 Effects

	$\Sigma\alpha'$	Effect
I_1	67.19491	-0.002833
I_2	67.38213	0.002833
g_{11}	70.25081	0.0396105
g_{12}	64.32623	-0.0396105

The values of $(\Sigma\alpha')_{I_r}$ adjusted for g_1 effects were calculated from

$$(\Sigma\alpha')_{I_r} = 75(m + I_r) \qquad \ldots\ldots \text{(F.5-5)}$$

where m = 0.89718.

The corrected sums, the corrected instrument S.S. on 1 d.f. and variance ratio are given in Table F.5-2.

Table F.5-2

Instrument Effects - Variance Analysis

	Corrected Sums	d.f.	S.S.	V.R.
I_1:	67.076-45			
I_2:	67.500995	1	0.001204	<1 N.S.

The corrected g_1 S.S. were 0.235355 (c.f. 0.234004 in Table 8.4-2).

F.6 Numerical Values for the Terms in the Regression Model

Constants

$m = 0.89718$

$p = 2.1703$

Log (p + 60)

1.8451

1.9294

2.0881

2.3351

2.6538

g_1 Effects

$g_{11} = -g_{12} = 0.039497$

g_2 Effects

$g_{21} = -0.012477$

$g_{22} = -0.046556$

$g_{23} = 0.001500$

$g_{24} = 0.030952$

$g_{25} = 0.026581$

Series Effects

$S_1 = 0.002256$

$S_2 = -0.014741$

$S_3 = 0.012485$

Regression Coefficients

$b_m = -0.46769$

$d_{g1} = 0.039250$

$d_{g2} = -0.069289$

$d_{g3} = -0.034449$

$d_{g4} = 0.011410$

$d_{g5} = 0.053078$

$d_{s1} = -0.002637$

$d_{s2} = -0.030246$

$d_{s3} = -0.032882$

Cell Effects

Cell	1	2	3	4	5
L_{11}	.04152	.07005	.04264	-.07313	-.08108
L_{21}	.03309	.04729	.00541	-.03834	-.04745
L_{12}	.04317	.04795	.04326	-.03256	-.10182
L_{22}	.06651	.03656	.01159	-.01302	-.10164
L_{13}	.09759	.07891	.03191	-.06143	-.14698
L_{23}	.08815	.07095	.04136	-.05400	-.14647

APPENDIX G

ANALYSIS OF SOME PUBLISHED VALUES OF D_{eff}

G.1 Some Results of Scott and Cox

Some values of D_{eff} published by Scott and Cox (85) for the counter-diffusion of N_2 and H_2 through several porous materials are presented in Fig. 4.4-1. Values of log (100 D_{eff}) and log (100 p) for Celite read from Fig. 4.4-1 are presented below in Table G.1-1. The mean of the log (100 D_{eff}) values was adjusted so that it lay on the mean regression line defined by Eq. 8.5-3. The individual values were then adjusted by multiplying them by ratio of the adjusted mean to the original mean. The adjusted values and the values of log (p + 60) corresponding to them are also presented in Table G.1-1.

Table G.1-1

Scott's Data for Celite

Log (100p), atm (from Fig. 4.4-1)	Log (p + 60) torr.	Log (100 D_{eff}) (from Fig. 4.4-1)	Log (100 D_{eff}) (adjusted)
.711	1.996	1.69	1.015
1.025	2.148	1.605	.964
1.132	2.212	1.555	.934
1.395	2.396	1.432	.860
1.642	2.594	1.185	.712
1.87	2.788	1.000	.601
2.00	2.914	.853	.513

G.2 Results of Evans et al

Values of log (D_{eff} x 10^5) for the counter-diffusion of He and Ar in a fine-pored graphite were calculated from the concentration data published by Evans et al (84). These values, together with the corresponding values of p, p + H, log p and log (p + H) are presented below in Table G.2-1.

Table G.2-1

Log(D_{eff} x 10^5) Calculated from the Data of Evans et al

p (atm)	p + 0.8 (atm)	log p	log (p + 0.8)	log(D_{eff} x 10^5)
1.16	1.24	.06446	.09342	1.25427
1.30	1.38	.11394	.13988	1.19053
1.64	1.72	.21485	.23553	1.13005
1.76	1.84	.24551	.26482	1.12795
1.96	2.04	.29226	.30963	1.11420
2.30	2.38	.36173	.37658	1.03221
2.98	3.06	.47422	.48572	.97557
4.98	5.06	.69723	.70415	.74398
7.20	7.28	.85733	.86213	.64708

Regressions of log (D_{eff} x 10^5) on log p and log (p + 0.8) were calculated. The analyses of variance and regression coefficients corresponding to them are presented in Table G.2-2.

TABLE G.2-2
ANALYSIS OF EVANS' RESULTS

REGRESSION ON LOG P

	COEFF.	STD. ERROR	T
A	1.307		
B	-.7675	.03165	24.25***

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
REGRESSION	1	.3299111	.3299111	588.15***
DEVIATIONS	7	.0039265	.0005609	
TOTAL	8	.333838		

REGRESSION ON LOG (P + H)

	COEFF.	STD. ERROR	T
A	1.329		
B	-.7913	.03144	25.17***

VARIATIONS DUE TO	D.F.	S.S.	M.S.	V.R.
REGRESSION	1	.3301910	.3301910	633.26***
DEVIATIONS	7	.0036466	.0005209	
TOTAL	8	.3338376		

APPENDIX H

THE COMPUTED RESULTS

The punched card output from the negative exponential regression programme for all the runs in the second experimental plan is listed below. A discussion of this output is given in Section 4.5 of the main text, however the output listed here has two minor errors.

(1) The value for the standard error in α(SEC) is incorrect. The correct value for SEC can be found by multiplying the listed value by the regression constant B1.

(2) The background count P was not subtracted from the data points. Since all the converted data points for each run were in error by a constant factor, this mistake did not alter the value of α. In fact, the only values noticably affected were the constant A and the deviation sum of squares. The true value of A can be obtained simply by subtracting the background count from the listed value of A. The programme listed in Appendix E gives the correct results.

The computed results follow.

```
                         THE COMPUTED RESULTS

                          RUN    18 20 PRESS=  11.37     33

 13.7453E-02
   4
      DF       SS             MS             VR
REGN   2  2.7281E+05  1.3640E+05  8.6265E+05
DEVN  96  1.5180E+01  1.5812E-01
TOTL  98  2.7283E+05

  A= 35.637E+01 B1=-3.6207E+02   B2=-1.5810E-03   C= 1.3918E-01
                SEB1= 2.8813E-01 SEB2= 2.2555E-01 SEC= 1.7165E-06

  A= 35.637E+01 B1=-3.6207E+02   B2=
REGSS= 2.7281E+05 D= 3.6592E-03
                          RUN    28 20 PRESS=  24.73     31

 13.1756E-02
   5
      DF       SS             MS             VR
REGN   2  3.8406E+05  1.9203E+05  2.9032E+05
DEVN  90  5.9530E+01  6.6144E-01
TOTL  92  3.8412E+05

  A= 42.374E+01 B1=-4.2751E+02   B2= 1.7400E-03   C= 1.2622E-01
                SEB1= 1.0490E-00 SEB2= 4.8250E-01 SEC= 2.6399E-06

  A= 42.374E+01 B1=-4.2751E+02   B2=
REGSS= 3.8406E+05 D= 3.2552E-03
                          RUN    38 20 PRESS=  61.64     35

 11.3245E-02
   6
      DF       SS             MS             VR
REGN   2  3.0336E+05  1.5168E+05  3.6283E+05
DEVN 102  4.2640E+01  4.1803E-01
TOTL 104  3.0340E+05

  A= 37.736E+01 B1=-3.9830E+02   B2= 7.8000E-04   C= 1.0813E-01
                SEB1= 6.9030E-01 SEB2= 3.5545E-01 SEC= 2.2404E-06

  A= 37.736E+01 B1=-3.9830E+02   B2=
REGSS= 3.0336E+05 D= 2.4158E-03
                          RUN    48 20 PRESS= 157.24     36

 68.3657E-03
   2
      DF       SS             MS             VR
REGN   2  1.9724E+05  9.8622E+04  2.0336E+05
```

```
DEVN 105  5.0920E+01  4.8495E-01
TOTL 107  1.9729E+05

  A= 32.491E+01 B1=-3.2520E+02   B2= 5.5000E-04   C= 6.2801E-02
              SEB1= 9.8556E-01 SEB2= 2.4732E-01 SEC= 2.3386E-06

  A= 32.491E+01 B1=-3.2520E+02   B2=
REGSS= 1.9724E+05 D= 1.6768E-03
                    RUN   58 20 PRESS= 390.07    37

 46.0064E-03
   3
     DF      SS          MS          VR
REGN   2  3.1359E+05  1.5679E+05  6.6674E+04
DEVN 108  2.5398E+02  2.3516E-00
TOTL 110  3.1384E+05

  A= 38.887E+01 B1=-4.0178E+02   B2=-5.2000E-04   C= 5.1718E-02
              SEB1= 1.4553E-00 SEB2= 3.9591E-01 SEC= 2.4525E-06

  A= 38.886E+01 B1=-4.0178E+02   B2=
REGSS= 3.1359E+05 D= 2.0283E-03
                    RUN  189 20 PRESS=  25.22    32

 12.8262E-02
   3
     DF      SS          MS          VR
REGN   2  3.5223E+05  1.7611E+05  2.5834E+06
DEVN  93  6.3400E-00  6.8172E-02
TOTL  95  3.5223E+05

  A= 40.452E+01 B1=-4.1648E+02   B2= 1.9000E-03   C= 1.2754E-01
              SEB1= 2.6586E-01 SEB2= 1.5307E-01 SEC= 8.8245E-07

  A= 40.452E+01 B1=-4.1648E+02   B2=
REGSS= 3.5223E+05 D= 3.3531E-03
                    RUN  289 20 PRESS=  62.95    20

 11.7659E-02
   3
     DF      SS          MS          VR
REGN   2  2.2335E+05  1.1167E+05  1.1727E+05
DEVN  57  5.4280E+01  9.5228E-01
TOTL  59  2.2340E+05

  A= 38.179E+01 B1=-4.1958E+02   B2=-1.9800E-03   C= 1.1339E-01
              SEB1= 9.3049E-01 SEB2= 5.8399E-01 SEC= 3.3171E-06

  A= 38.178E+01 B1=-4.1958E+02   B2=
REGSS= 2.2335E+05 D= 2.9245E-03
```

```
                    RUN   389 20 PRESS= 155.79     33

 78.8531E-03
   4
       DF      SS            MS            VR
REGN    2  2.0493E+05  1.0246E+05  2.4762E+04
DEVN   96  3.9725E+02  4.1380E-00
TOTL   98  2.0532E+05

  A= 30.497E+01 B1=-3.2272E+02   B2= 6.0100E-04   C= 6.9157E-02
                SEB1= 1.4717E-00 SEB2= 5.9254E-01 SEC= 5.6892E-06

  A= 30.497E+01 B1=-3.2272E+02   B2=
REGSS= 2.0493E+05 D= 1.5449E-03
                    RUN   489 20 PRESS= 391.97     31

 33.3470E-03
   3
       DF      SS            MS            VR
REGN    2  4.3446E+06  2.1723E+06  8.6615E+04
DEVN   90  2.2572E+03  2.5080E+01
TOTL   92  4.3469E+06

  A= 14.075E+02 B1=-1.4419E+03   B2= 2.4300E-03   C= 3.1181E-02
                SEB1= 6.6951E-00 SEB2= 7.4450E-01 SEC= 3.5806E-07

  A= 14.075E+02 B1=-1.4419E+03   B2=
REGSS= 4.3446E+06 D= 8.3254E-04
                    RUN   589 20 PRESS=  10.69     45

 92.6439E-03
   2
       DF      SS            MS            VR
REGN    2  2.9165E+05  1.4582E+05  5.4762E+05
DEVN  132  3.5150E+01  2.6628E-01
TOTL  134  2.9168E+05

  A= 32.043E+01 B1=-3.3642E+02   B2=-5.4000E-04   C= 9.0521E-02
                SEB1= 3.9770E-01 SEB2= 1.9097E-01 SEC= 1.6873E-06

  A= 32.043E+01 B1=-3.3642E+02   B2=
REGSS= 2.9165E+05 D= 2.5502E-03
                    RUN   187 21 PRESS= 393.68     26

 53.6714E-03
   2
       DF      SS            MS            VR
REGN    2  1.1604E+06  5.8021E+05  4.4179E+05
DEVN   75  9.8500E+01  1.3133E-00
TOTL   77  1.1605E+06
```

```
   A= 94.347E+01 B1=-9.6249E+02   B2=-3.2940E-03   C= 5.4601E-02
                SEB1= 1.0287E-00 SEB2= 3.5214E-01 SEC= 3.8012E-07

   A= 94.345E+01 B1=-9.6249E+02   B2=
REGSS= 1.1604E+06 D= 1.4354E-03
                         RUN  287 21 PRESS=   9.92     26

 14.3164E-02
   6
       DF      SS            MS           VR
REGN    2  2.0630E+05  1.0315E+05  3.5374E+05
DEVN   75  2.1870E+01  2.9160E-01
TOTL   77  2.0632E+05

   A= 33.109E+01 B1=-3.4014E+02   B2=-1.5470E-03   C= 1.3861E-01
                SEB1= 4.1562E-01 SEB2= 2.8438E-01 SEC= 2.4580E-06

   A= 33.109E+01 B1=-3.4014E+02   B2=
REGSS= 2.0630E+05 D= 3.5748E-03
                         RUN  387 21 PRESS=  24.96     28

 11.8552E-02
   3
       DF      SS            MS           VR
REGN    2  2.8799E+05  1.4399E+05  2.7567E+05
DEVN   81  4.2310E+01  5.2234E-01
TOTL   83  2.8803E+05

   A= 35.954E+01 B1=-3.7635E+02   B2=-9.6000E-05   C= 1.2138E-01
                SEB1= 5.1403E-01 SEB2= 3.2884E-01 SEC= 2.3216E-06

   A= 35.954E+01 B1=-3.7636E+02   B2=
REGSS= 2.8799E+05 D= 2.7116E-03
                         RUN  487 21 PRESS=  62.61     26

 95.4783E-03
   2
       DF      SS            MS           VR
REGN    2  2.1575E+05  1.0787E+05  1.3949E+06
DEVN   75  5.8000E-00  7.7333E-02
TOTL   77  2.1575E+05

   A= 34.093E+01 B1=-3.4112E+02   B2= 5.3000E-04   C= 9.4689E-02
                SEB1= 2.1260E-01 SEB2= 1.0665E-01 SEC= 9.1653E-07

   A= 34.093E+01 B1=-3.4112E+02   B2=
REGSS= 2.1575E+05 D= 2.5281E-03
                         RUN  587 21 PRESS= 156.58     28
```

```
 50.2972E-03
   3
       DF      SS            MS            VR
REGN    2  2.8825E+05  1.4412E+05  5.7897E+04
DEVN   81  2.0164E+02  2.4893E-00
TOTL   83  2.8846E+05

  A= 37.228E+01 B1=-3.7752E+02   B2=-1.3300E-03   C= 5.7705E-02
                 SEB1= 1.1973E-00 SEB2= 3.5813E-01 SEC= 2.5128E-06

  A= 37.227E+01 B1=-3.7752E+02   B2=
REGSS= 2.8826E+05 D= 2.2632E-03
                           RUN  186 20 PRESS=  63.91     31

 11.0097E-02
   7
       DF      SS            MS            VR
REGN    2  3.3304E+05  1.6652E+05  5.7492E+04
DEVN   90  2.6068E+02  2.8964E-00
TOTL   92  3.3330E+05

  A= 37.962E+01 B1=-3.8556E+02   B2=-1.5000E-03   C= 1.0271E-01
                 SEB1= 1.2639E-00 SEB2= 6.6203E-01 SEC= 4.4532E-06

  A= 37.962E+01 B1=-3.8556E+02   B2=
REGSS= 3.3304E+05 D= 2.7003E-03
                           RUN  286 20 PRESS= 157.00     31

 96.4974E-03
   3
       DF      SS            MS            VR
REGN    2  3.6081E+05  1.8040E+05  4.2516E+05
DEVN   90  3.8190E+01  4.2433E-01
TOTL   92  3.6085E+05

  A= 39.585E+01 B1=-4.1668E+02   B2=-1.9100E-03   C= 9.4985E-02
                 SEB1= 5.5499E-01 SEB2= 2.6135E-01 SEC= 1.5052E-06

  A= 39.585E+01 B1=-4.1668E+02   B2=
REGSS= 3.6081E+05 D= 2.4496E-03
                           RUN  386 20 PRESS= 390.86     30

 79.3084E-03
   4
       DF      SS            MS            VR
REGN    2  1.3881E+06  6.9406E+05  2.4890E+05
DEVN   87  2.4260E+02  2.7885E-00
TOTL   89  1.3883E+06

  A= 91.728E+01 B1=-9.8860E+02   B2= 1.3100E-03   C= 7.4560E-02
```

```
              SEB1= 1.5146E-00 SEB2= 6.2877E-01 SEC= 6.4336E-07

  A= 91.728E+01 B1=-9.8859E+02   B2=
REGSS= 1.3881E+06 D= 1.6656E-03
                    RUN  486 20 PRESS=  10.13    22

 12.1788E-02
   3
      DF      SS          MS          VR
REGN   2  1.4986E+05  7.4933E+04  2.1245E+05
DEVN  63  2.2220E+01  3.5269E-01
TOTL  65  1.4988E+05

  A= 31.041E+01 B1=-3.1492E+02   B2=-1.2820E-03   C= 1.2021E-01
              SEB1= 4.8801E-01 SEB2= 3.0044E-01 SEC= 3.0294E-06

  A= 31.041E+01 B1=-3.1492E+02   B2=
REGSS= 1.4986E+05 D= 3.2097E-03
                    RUN  586 20 PRESS=  24.26    37

 82.7713E-03
   2
      DF      SS          MS          VR
REGN   2  3.4363E+05  1.7181E+05  7.3026E+05
DEVN 108  2.5410E+01  2.3527E-01
TOTL 110  3.4365E+05

  A= 36.834E+01 B1=-3.6761E+02   B2=-1.0880E-03   C= 8.4333E-02
              SEB1= 3.3377E-01 SEB2= 1.4811E-01 SEC= 1.0960E-06

  A= 36.833E+01 B1=-3.6761E+02   B2=
REGSS= 3.4363E+05 D= 3.3075E-03
                    RUN  185 20 PRESS= 155.84    37

 84.4184E-03
   2
      DF      SS          MS          VR
REGN   2  3.0206E+05  1.5103E+05  5.8548E+05
DEVN 108  2.7860E+01  2.5796E-01
TOTL 110  3.0209E+05

  A= 35.159E+01 B1=-3.4450E+02   B2=-4.2600E-04   C= 8.4826E-02
              SEB1= 3.4560E-01 SEB2= 1.5510E-01 SEC= 1.3068E-06

  A= 35.159E+01 B1=-3.4451E+02   B2=
REGSS= 3.0206E+05 D= 2.2300E-03
                    RUN  285 20 PRESS= 390.04    32

 62.5179E-03
   2
```

```
      DF      SS           MS          VR
REGN   2  5.9043E+06  2.9521E+06  5.9711E+05
DEVN  93  4.5980E+02  4.9440E-00
TOTL  95  5.9048E+06

  A= 18.127E+02 B1=-1.8538E+03   B2=-6.4000E-03   C= 6.2244E-02
              SEB1= 5.7363E-00 SEB2= 9.2991E-01 SEC= 2.7058E-07

  A= 18.127E+02 B1=-1.8538E+03   B2=
REGSS= 5.9043E+06 D= 1.6052E-03
                    RUN  385 20 PRESS=  11.08    35

 11.0725E-02
   4
      DF      SS           MS          VR
REGN   2  1.5820E+05  7.9101E+04  8.3024E+04
DEVN 102  9.7180E+01  9.5274E-01
TOTL 104  1.5830E+05

  A= 29.299E+01 B1=-2.8352E+02   B2= 8.4500E-04   C= 1.2617E-01
              SEB1= 7.0671E-01 SEB2= 5.3457E-01 SEC= 6.6498E-06

  A= 29.299E+01 B1=-2.8352E+02   B2=
REGSS= 1.5820E+05 D= 2.8188E-03
                    RUN  485 20 PRESS=  24.92    33

 98.7566E-03
   2
      DF      SS           MS          VR
REGN   2  1.5738E+05  7.8693E+04  7.1606E+05
DEVN  96  1.0550E+01  1.0989E-01
TOTL  98  1.5739E+05

  A= 28.250E+01 B1=-2.7883E+02   B2= 1.7100E-04   C= 1.0106E-01
              SEB1= 2.3756E-01 SEB2= 1.2800E-01 SEC= 1.6463E-06

  A= 28.250E+01 B1=-2.7884E+02   B2=
REGSS= 1.5738E+05 D= 2.6984E-03
                    RUN  585 20 PRESS=  61.20    39

 91.2814E-03
   4
      DF      SS           MS          VR
REGN   2  2.2817E+05  1.1408E+05  1.8633E+06
DEVN 114  6.9800E-00  6.1228E-02
TOTL 116  2.2818E+05

  A= 30.454E+01 B1=-3.1762E+02   B2= 1.1000E-03   C= 9.0386E-02
              SEB1= 1.9016E-01 SEB2= 7.6934E-02 SEC= 7.6259E-07
```

```
  A= 30.454E+01 B1=-3.1762E+02    B2=
REGSS= 2.2817E+05 D= 3.5449E-03
                         RUN  198 20 PRESS=   9.79     33

 10.1692E-02
   2
      DF      SS            MS            VR
REGN   2  1.4232E+05  7.1160E+04  1.7516E+06
DEVN  96  3.9000E-00  4.0625E-02
TOTL  98  1.4232E+05

  A= 27.437E+01 B1=-2.6910E+02    B2= 1.2600E-04    C= 1.0023E-01
               SEB1= 1.4793E-01 SEB2= 7.8922E-02 SEC= 1.0898E-06

  A= 27.437E+01 B1=-2.6910E+02    B2=
REGSS= 1.4232E+05 D= 2.6351E-03
                         RUN  298 20 PRESS=  25.00     31

 93.7707E-03
   3
      DF      SS            MS            VR
REGN   2  2.0054E+05  1.0027E+05  3.2300E+05
DEVN  90  2.7940E+01  3.1044E-01
TOTL  92  2.0057E+05

  A= 31.954E+01 B1=-3.1061E+02    B2= 4.4000E-04    C= 9.5083E-02
               SEB1= 4.7333E-01 SEB2= 2.2354E-01 SEC= 2.3169E-06

  A= 31.955E+01 B1=-3.1061E+02    B2=
REGSS= 2.0054E+05 D= 2.4522E-03
                         RUN  398 20 PRESS=  61.49     41

 78.7870E-03
   3
      DF      SS            MS            VR
REGN   2  4.1051E+05  2.0525E+05  3.0475E+05
DEVN 120  8.0820E+01  6.7350E-01
TOTL 122  4.1059E+05

  A= 37.925E+01 B1=-3.7737E+02    B2= 7.8500E-04    C= 7.6331E-02
               SEB1= 5.4058E-01 SEB2= 2.1246E-01 SEC= 1.4919E-06

  A= 37.925E+01 B1=-3.7737E+02    B2=
REGSS= 4.1051E+05 D= 1.7052E-03
                         RUN  498 20 PRESS= 156.26     29

 54.1969E-03
   3
      DF      SS            MS            VR
REGN   2  8.8476E+04  4.4238E+04  2.8781E+05
```

```
DEVN  84  1.2911E+01  1.5370E-01
TOTL  86  8.8489E+04

   A= 24.279E+01 B1=-2.3940E+02   B2=-8.5600E-04   C= 5.3141E-02
                 SEB1= 3.2347E-01 SEB2= 9.7922E-02 SEC= 1.7085E-06

   A= 24.279E+01 B1=-2.3940E+02   B2=
REGSS= 8.8476E+04 D= 1.4188E-03
                          RUN  598 20 PRESS= 391.00    22

 36.2264E-03
   2
       DF       SS          MS          VR
REGN    2  4.0436E+05  2.0218E+05  3.0090E+05
DEVN   63  4.2330E+01  6.7190E-01
TOTL   65  4.0440E+05

   A= 66.631E+01 B1=-6.8826E+02   B2=-3.9000E-04   C= 3.6455E-02
                 SEB1= 1.4592E-00 SEB2= 1.8216E-01 SEC= 3.8454E-07

   A= 66.630E+01 B1=-6.8827E+02   B2=
REGSS= 4.0436E+05 D= 1.4297E-03
                          RUN   19 20 PRESS=  25.48    34

 97.2454E-03
   3
       DF       SS          MS          VR
REGN    2  1.1020E+05  5.5100E+04  3.6857E+05
DEVN   99  1.4800E+01  1.4949E-01
TOTL  101  1.1021E+05

   A= 24.190E+01 B1=-2.3695E+02   B2= 9.5600E-04   C= 9.6336E-02
                 SEB1= 2.8687E-01 SEB2= 1.4690E-01 SEC= 2.6164E-06

   A= 24.191E+01 B1=-2.3695E+02   B2=
REGSS= 1.1020E+05 D= 2.5326E-03
                          RUN   29 20 PRESS=  62.69    44

 86.2086E-03
   3
       DF       SS          MS          VR
REGN    2  2.3636E+05  1.1818E+05  1.0904E+05
DEVN  129  1.3981E+02  1.0837E-00
TOTL  131  2.3650E+05

   A= 28.655E+01 B1=-2.9602E+02   B2= 2.9200E-04   C= 8.2621E-02
                 SEB1= 7.2496E-01 SEB2= 2.6363E-01 SEC= 3.0084E-06

   A= 28.655E+01 B1=-2.9602E+02   B2=
REGSS= 2.3636E+05 D= 2.1308E-03
```

```
                         RUN   39 20 PRESS= 156.26    36

 50.9185E-03
   9
      DF      SS           MS          VR
REGN   2  3.4744E+05  1.7372E+05  2.5497E+05
DEVN 105  7.1540E+01  6.8133E-01
TOTL 107  3.4751E+05

  A= 39.455E+01 B1=-3.9245E+02   B2=-1.7000E-03   C= 4.9572E-02
              SEB1= 1.2586E-00 SEB2= 2.0245E-01 SEC= 1.3144E-06

  A= 39.454E+01 B1=-3.9245E+02   B2=
REGSS= 3.4743E+05 D= 1.1074E-03
                         RUN   49 20 PRESS= 390.71    36

 35.5282E-03
   2
      DF      SS           MS          VR
REGN   2  2.7045E+06  1.3522E+06  6.8758E+05
DEVN 105  2.0650E+02  1.9666E-00
TOTL 107  2.7047E+06

  A= 10.289E+02 B1=-1.0379E+03   B2=-2.2950E-03   C= 3.5195E-02
              SEB1= 8.8856E-01 SEB2= 1.6737E-01 SEC= 1.5535E-07

  A= 10.289E+02 B1=-1.0379E+03   B2=
REGSS= 2.7045E+06 D= 9.3970E-04
                         RUN   59 20 PRESS=  10.10    32

 83.4188E-03
   3
      DF      SS           MS          VR
REGN   2  1.6953E+05  8.4768E+04  1.0979E+06
DEVN  93  7.1800E-00  7.7204E-02
TOTL  95  1.6954E+05

  A= 27.642E+01 B1=-2.8453E+02   B2= 1.2500E-04   C= 8.1801E-02
              SEB1= 1.9681E-01 SEB2= 8.1983E-02 SEC= 1.0126E-06

  A= 27.642E+01 B1=-2.8453E+02   B2=
REGSS= 1.6953E+05 D= 3.2082E-03
                         RUN  197 20 PRESS= 390.33    41

 35.5355E-03
   3
      DF      SS           MS          VR
REGN   2  3.2476E+05  1.6238E+05  1.2235E+05
DEVN 120  1.5926E+02  1.3271E-00
TOTL 122  3.2492E+05
```

```
   A= 33.704E+01 B1=-3.3536E+02   B2=-1.0760E-03   C= 3.8559E-02
               SEB1= 7.4346E-01 SEB2= 1.4912E-01 SEC= 1.3258E-06

   A= 33.704E+01 B1=-3.3537E+02   B2=
REGSS= 3.2476E+05 D= 1.0137E-03
                         RUN  297 20 PRESS=   9.93    30

  11.8390E-02
    3
       DF      SS           MS           VR
REGN    2  3.0181E+05  1.5090E+05  3.5283E+05
DEVN   87  3.7210E+01  4.2770E-01
TOTL   89  3.0185E+05

   A= 34.875E+01 B1=-3.5504E+02   B2=-6.6900E-04   C= 1.1468E-01
               SEB1= 4.4940E-01 SEB2= 2.5624E-01 SEC= 2.0327E-06

   A= 34.874E+01 B1=-3.5504E+02   B2=
REGSS= 3.0181E+05 D= 2.9576E-03
                         RUN  397 20 PRESS=  24.69    36

  10.5424E-02
    5
       DF      SS           MS           VR
REGN    2  2.8595E+05  1.4297E+05  1.6360E+05
DEVN  105  9.1760E+01  8.7390E-01
TOTL  107  2.8604E+05

   A= 32.403E+01 B1=-3.3269E+02   B2=-1.7500E-04   C= 9.9700E-02
               SEB1= 5.8482E-01 SEB2= 2.9520E-01 SEC= 2.6671E-06

   A= 32.403E+01 B1=-3.3269E+02   B2=
REGSS= 2.8595E+05 D= 2.2273E-03
                         RUN  497 20 PRESS=  67.77    43

  78.8981E-03
    3
       DF      SS           MS           VR
REGN    2  1.6636E+05  8.3182E+04  3.5159E+05
DEVN  126  2.9810E+01  2.3658E-01
TOTL  128  1.6639E+05

   A= 26.519E+01 B1=-2.6965E+02   B2=-5.9000E-04   C= 7.5269E-02
               SEB1= 3.5347E-01 SEB2= 1.3518E-01 SEC= 1.8590E-06

   A= 26.519E+01 B1=-2.6965E+02   B2=
REGSS= 1.6636E+05 D= 2.0097E-03
                         RUN  597 20 PRESS= 156.44    36
```

```
 54.5385E-03
   3
      DF      SS          MS          VR
REGN   2  1.1701E+05  5.8508E+04  3.6265E+05
DEVN 105  1.6940E+01  1.6133E-01
TOTL 107  1.1703E+05

  A= 24.220E+01 B1=-2.5341E+02   B2= 9.9100E-04   C= 5.2298E-02
             SEB1= 4.5323E-01 SEB2= 7.5958E-02 SEC= 1.1827E-06

  A= 24.221E+01 B1=-2.5341E+02   B2=
REGSS= 1.1701E+05 D= 2.0511E-03
                   RUN  196 20 PRESS=  62.11    30

 10.3890E-02
   4
      DF      SS          MS          VR
REGN   2  2.4062E+05  1.2031E+05  1.0552E+05
DEVN  87  9.9190E+01  1.1401E-00
TOTL  89  2.4071E+05

  A= 31.485E+01 B1=-3.3029E+02   B2=-1.1130E-03   C= 9.4172E-02
             SEB1= 7.3918E-01 SEB2= 3.3038E-01 SEC= 3.0283E-06

  A= 31.484E+01 B1=-3.3029E+02   B2=
REGSS= 2.4062E+05 D= 2.4757E-03
                   RUN  296 20 PRESS= 156.30    25

 69.2013E-03
   3
      DF      SS          MS          VR
REGN   2  2.5636E+05  1.2818E+05  1.2813E+05
DEVN  72  7.2030E+01  1.0004E-00
TOTL  74  2.5643E+05

  A= 35.743E+01 B1=-3.6833E+02   B2= 1.5150E-04   C= 7.1625E-02
             SEB1= 7.2809E-01 SEB2= 2.6590E-01 SEC= 1.9599E-06

  A= 35.743E+01 B1=-3.6833E+02   B2=
REGSS= 2.5636E+05 D= 1.8472E-03
                   RUN  396 20 PRESS= 391.59    31

 51.5838E-03
   3
      DF      SS          MS          VR
REGN   2  3.0967E+05  1.5483E+05  2.7909E+05
DEVN  90  4.9930E+01  5.5477E-01
TOTL  92  3.0972E+05

  A= 36.791E+01 B1=-3.8516E+02   B2= 1.0700E-03   C= 4.8467E-02
```

```
                  SEB1= 6.0247E-01 SEB2= 1.4934E-01 SEC= 1.0066E-06

  A= 36.792E+01 B1=-3.8516E+02   B2=
REGSS= 3.0967E+05 D= 1.0827E-03
                         RUN  496 20 PRESS=  10.32    35

 89.6190E-03
   3
      DF      SS            MS            VR
REGN   2  9.6444E+04  4.8222E+04  1.9032E+05
DEVN 102  2.5843E+01  2.5336E-01
TOTL 104  9.6470E+04

  A= 23.330E+01 B1=-2.2875E+02   B2= 1.0550E-03   C= 9.6078E-02
                  SEB1= 4.4174E-01 SEB2= 1.9222E-01 SEC= 3.6733E-06

  A= 23.331E+01 B1=-2.2875E+02   B2=
REGSS= 9.6444E+04 D= 2.5652E-03
                         RUN  596 20 PRESS=  24.75    36

 12.9294E-02
   4
      DF      SS            MS            VR
REGN   2  1.4546E+05  7.2730E+04  8.6589E+03
DEVN 105  8.8194E+02  8.3994E-00
TOTL 107  1.4634E+05

  A= 26.146E+01 B1=-3.0995E+02   B2=-1.2100E-03   C= 1.0600E-01
                  SEB1= 3.4139E-00 SEB2= 1.3102E-00 SEC= 1.3638E-05

  A= 26.145E+01 B1=-3.0995E+02   B2=
REGSS= 1.4546E+05 D= 4.1573E-03
                         RUN  195 20 PRESS= 156.00    33

 75.3897E-03
   3
      DF      SS            MS            VR
REGN   2  1.9670E+05  9.8353E+04  6.2695E+05
DEVN  96  1.5060E+01  1.5687E-01
TOTL  98  1.9672E+05

  A= 29.642E+01 B1=-3.0747E+02   B2= 1.4990E-03   C= 7.8656E-02
                  SEB1= 2.8567E-01 SEB2= 1.1358E-01 SEC= 1.2014E-06

  A= 29.643E+01 B1=-3.0747E+02   B2=
REGSS= 1.9670E+05 D= 2.0678E-03
                         RUN  295 20 PRESS= 391.31    27

 52.6545E-03
   3
```

```
      DF      SS           MS           VR
REGN   2  3.0373E+05  1.5186E+05  1.7997E+05
DEVN  78  6.5820E+01  8.4384E-01
TOTL  80  3.0380E+05

  A= 40.724E+01 B1=-4.2091E+02   B2=-1.4100E-03   C= 5.0418E-02
              SEB1= 1.0175E-00 SEB2= 2.3164E-01 SEC= 1.3074E-06

  A= 40.723E+01 B1=-4.2092E+02   B2=
REGSS= 3.0374E+05 D= 1.3002E-03
                    RUN  395 20 PRESS=  10.46    29

 10.9256E-02
   5
      DF      SS           MS           VR
REGN   2  7.4592E+04  3.7296E+04  2.5921E+05
DEVN  84  1.2086E+01  1.4388E-01
TOTL  86  7.4604E+04

  A= 22.590E+01 B1=-2.2019E+02   B2=-5.9000E-04   C= 1.0972E-01
              SEB1= 3.2797E-01 SEB2= 1.9032E-01 SEC= 3.9254E-06

  A= 22.590E+01 B1=-2.2019E+02   B2=
REGSS= 7.4591E+04 D= 2.4511E-03
                    RUN  495 20 PRESS=  25.14    34

 84.0581E-03
   3
      DF      SS           MS           VR
REGN   2  1.2365E+05  6.1828E+04  2.0498E+05
DEVN  99  2.9860E+01  3.0161E-01
TOTL 101  1.2368E+05

  A= 25.128E+01 B1=-2.5066E+02   B2=-1.0200E-03   C= 8.9659E-02
              SEB1= 3.9261E-01 SEB2= 2.0703E-01 SEC= 3.2950E-06

  A= 25.127E+01 B1=-2.5066E+02   B2=
REGSS= 1.2365E+05 D= 2.3939E-03
                    RUN  595 20 PRESS=  62.52    37

 65.5392E-03
   2
      DF      SS           MS           VR
REGN   2  2.5421E+05  1.2710E+05  5.1414E+05
DEVN 108  2.6700E+01  2.4722E-01
TOTL 110  2.5424E+05

  A= 31.090E+01 B1=-3.1536E+02   B2= 8.2200E-04   C= 6.5989E-02
              SEB1= 3.2004E-01 SEB2= 1.1402E-01 SEC= 1.1464E-06
```

```
  A= 31.091E+01 B1=-3.1536E+02   B2=
REGSS= 2.5421E+05 D= 2.5881F-03
                        RUN   18 30 PRESS=   9.96    26

 13.2255E-02
   3
      DF      SS           MS           VR
REGN   2  1.9818E+05  9.9090E+04  2.7959E+05
DEVN  75  2.6580E+01  3.5440E-01
TOTL  77  1.9820E+05

  A= 32.882E+01 B1=-3.3319E+02   B2= 3.1700E-04   C= 1.2619E-01
             SEB1= 4.5331E-01 SEB2= 3.1023E-01 SEC= 2.7944F-06

  A= 32.882E+01 B1=-3.3319E+02   B2=
REGSS= 1.9817E+05 D= 3.3175E-03
                        RUN   28 30 PRESS=  24.46    26

 11.3617E-02
   2
      DF      SS           MS           VR
REGN   2  2.3482E+05  1.1741E+05  1.1403E+05
DEVN  75  7.7220E+01  1.0296F-00
TOTL  77  2.3490E+05

  A= 36.714E+01 B1=-3.6534E+02   B2=-2.1000E-04   C= 1.1434E-01
             SEB1= 9.2650E-01 SEB2= 5.2797E-01 SEC= 3.9554E-06

  A= 36.714E+01 B1=-3.6534E+02   B2=
REGSS= 2.3482E+05 D= 2.9489E-03
                        RUN   38 30 PRESS=  63.16    25

 10.1222E-02
   3
      DF      SS           MS           VR
REGN   2  2.5768E+05  1.2884E+05  2.5408E+05
DEVN  72  3.6510E+01  5.0708E-01
TOTL  74  2.5772F+05

  A= 36.555E+01 B1=-3.6463E+02   B2=-1.0100E-03   C= 9.5533E-02
             SEB1= 6.1973E-01 SEB2= 2.7701E-01 SEC= 2.0834E-06

  A= 36.554E+01 B1=-3.6463E+02   B2=
REGSS= 2.5768E+05 D= 2.1342E-03
                        RUN   48 30 PRESS= 156.18    30

 63.2252E-03
   2
      DF      SS           MS           VR
REGN   2  2.9593E+05  1.4796E+05  6.3384E+05
```

```
DEVN   87   2.0310E+01   2.3344E-01
TOTL   89   2.9595E+05

   A= 35.251E+01 B1=-3.5959E+02    B2= 2.7100E-04    C= 6.3398E-02
                 SEB1= 3.2488E-01 SEB2= 9.7963E-02 SEC= 7.5761E-07

   A= 35.251E+01 B1=-3.5958E+02    B2=
REGSS= 2.9593E+05 D= 1.6927E-03
                           RUN    58 30 PRESS= 391.13     32

 33.4926E-03
   2
       DF      SS            MS            VR
REGN    2   3.7954E+06   1.8977E+06   2.2144E+06
DEVN   93   7.9700E+01   8.5698E-01
TOTL   95   3.7955E+06

   A= 12.803E+02 B1=-1.2970E+03    B2=-8.4000E-04    C= 3.3259E-02
                 SEB1= 9.1799E-01 SEB2= 1.2914E-01 SEC= 7.6764E-08

   A= 12.802E+02 B1=-1.2970E+03    B2=
REGSS= 3.7954E+06 D= 1.3044E-03
                           RUN   189 30 PRESS=  25.07     30

 12.4041E-02
   3
       DF      SS            MS            VR
REGN    2   2.5414E+05   1.2707E+05   2.9069E+05
DEVN   87   3.8030E+01   4.3712E-01
TOTL   89   2.5418E+05

   A= 32.471E+01 B1=-3.3305E+02    B2=-1.0990E-03    C= 1.1784E-01
                 SEB1= 4.3991E-01 SEB2= 2.6560E-01 SEC= 2.3945E-06

   A= 32.471E+01 B1=-3.3305E+02    B2=
REGSS= 2.5414E+05 D= 3.0982E-03
                           RUN   289 30 PRESS=  62.75     26

 10.7921E-02
   4
       DF      SS            MS            VR
REGN    2   2.9085E+05   1.4542E+05   1.4529E+05
DEVN   75   7.5070E+01   1.0009E-00
TOTL   77   2.9093E+05

   A= 40.840E+01 B1=-4.1574E+02    B2=-8.6000E-04    C= 9.9855E-02
                 SEB1= 1.3641E-00 SEB2= 5.2712E-01 SEC= 3.0497E-06

   A= 40.840E+01 B1=-4.1574E+02    B2=
REGSS= 2.9085E+05 D= 2.5752E-03
```

```
                         RUN  389 30 PRESS= 156.45    41

 86.5157E-03
   4
      DF      SS            MS            VR
REGN   2  1.2427E+06  6.2138E+05  8.2247E+04
DEVN 120  9.0660E+02  7.5550E-00
TOTL 122  1.2436E+06

   A= 73.366E+01 B1=-7.5479E+02   B2=-2.8600E-03   C= 7.8682E-02
                 SEB1= 2.0344E-00 SEB2= 8.2027E-01 SEC= 1.4398E-06

   A= 73.364E+01 B1=-7.5479E+02   B2=
REGSS= 1.2427E+06 D= 1.7577E-03
                         RUN  489 30 PRESS= 390.76    26

 45.2452E-03
   3
      DF      SS            MS            VR
REGN   2  4.6304E+06  2.3152E+06  5.3281E+05
DEVN  75  3.2590E+02  4.3453E-00
TOTL  77  4.6308E+06

   A= 16.838E+02 B1=-1.7455E+03   B2= 4.9000E-03   C= 4.3184E-02
                 SEB1= 4.2815E-00 SEB2= 5.7341E-01 SEC= 1.8818E-07

   A= 16.838E+02 B1=-1.7455E+03   B2=
REGSS= 4.6305E+06 D= 1.1530E-03
                         RUN  589 30 PRESS=  10.60    33

 94.4060E-03
   3
      DF      SS            MS            VR
REGN   2  1.7602E+05  8.8013E+04  2.2411E+05
DEVN  96  3.7700E+01  3.9270E-01
TOTL  98  1.7606E+05

   A= 30.284E+01 B1=-2.9914E+02   B2= 2.8300E-04   C= 9.1743E-02
                 SEB1= 4.5563E-01 SEB2= 2.4332E-01 SEC= 2.7190E-06

   A= 30.284E+01 B1=-2.9914E+02   B2=
REGSS= 1.7602E+05 D= 3.5981E-03
                         RUN  187 30 PRESS= 390.39    28

 51.5598E-03
   4
      DF      SS            MS            VR
REGN   2  1.7460E+06  8.7303E+05  9.6606E+05
DEVN  81  7.3200E+01  9.0370E-01
TOTL  83  1.7461E+06
```

```
  A= 10.267E+02 B1=-1.0493E+03   B2= 1.0300E-03   C= 5.1316E-02
              SEB1= 7.9721E-01 SEB2= 2.4127E-01 SEC= 2.1913E-07

  A= 10.267E+02 B1=-1.0492E+03   B2=
REGSS= 1.7460E+06 D= 1.3491E-03
                    RUN  287 30 PRESS=   9.72    34

 12.9325E-02
   3
      DF      SS          MS          VR
REGN   2  1.4832E+05  7.4163E+04  1.9756E+04
DEVN  99  3.7163E+02  3.7538E-00
TOTL 101  1.4869E+05

  A= 28.358E+01 B1=-2.7835E+02   B2= 2.9700E-04   C= 1.3055E-01
              SEB1= 1.4168E-00 SEB2= 1.1079E-00 SEC= 1.4299E-05

  A= 28.358E+01 B1=-2.7835E+02   B2=
REGSS= 1.4832E+05 D= 3.3669E-03
                    RUN  387 30 PRESS=  24.72    26

 13.0406E-02
   7
      DF      SS          MS          VR
REGN   2  2.4531E+05  1.2265E+05  2.1624E+05
DEVN  75  4.2540E+01  5.6720E-01
TOTL  77  2.4535E+05

  A= 36.510E+01 B1=-3.7100E+02   B2=-9.1700E-04   C= 1.2374E-01
              SEB1= 5.8610E-01 SEB2= 3.9205E-01 SEC= 2.8482E-06

  A= 36.509E+01 B1=-3.7100E+02   B2=
REGSS= 2.4531E+05 D= 2.7644E-03
                    RUN  487 30 PRESS=  62.58    34

 83.1508E-03
   3
      DF      SS          MS          VR
REGN   2  1.4366E+05  7.1834E+04  1.6824E+05
DEVN  99  4.2270E+01  4.2696E-01
TOTL 101  1.4371E+05

  A= 26.975E+01 B1=-2.7020E+02   B2=-3.4900E-04   C= 8.9159E-02
              SEB1= 4.6839E-01 SEB2= 2.4622E-01 SEC= 3.3723E-06

  A= 26.975E+01 B1=-2.7021E+02   B2=
REGSS= 1.4367E+05 D= 2.3805E-03
                    RUN  587 30 PRESS= 156.24    26
```

```
 61.8053E-03
   3
      DF       SS             MS             VR
REGN   2  2.1570E+05  1.0785E+05  1.1791E+05
DEVN  75  6.8600E+01  9.1466E-01
TOTL  77  2.1577E+05

  A= 33.816E+01 B1=-3.4823E+02   B2=-7.5000E-05   C= 6.0833E-02
               SEB1= 7.6331E-01 SEB2= 2.4880E-01 SEC= 2.0517E-06

  A= 33.816E+01 B1=-3.4823E+02   B2=
REGSS= 2.1570E+05 D= 2.3859E-03
                     RUN  186 30 PRESS=  62.17    29

 10.9872E-02
   7
      DF       SS             MS             VR
REGN   2  1.4465E+05  7.2327E+04  1.9529E+05
DEVN  84  3.1110E+01  3.7035E-01
TOTL  86  1.4468E+05

  A= 29.255E+01 B1=-2.9703E+02   B2= 1.0920E-03   C= 1.1236E-01
               SEB1= 4.9871E-01 SEB2= 2.9645E-01 SEC= 3.3600E-06

  A= 29.255E+01 B1=-2.9703E+02   B2=
REGSS= 1.4465E+05 D= 2.9539E-03
                     RUN  286 30 PRESS= 156.87    35

 71.5500E-03
   3
      DF       SS             MS             VR
REGN   2  2.9213E+05  1.4606E+05  2.4500E+05
DEVN 102  6.0810E+01  5.9617E-01
TOTL 104  2.9219E+05

  A= 33.893E+01 B1=-3.3090E+02   B2=-1.2400E-03   C= 6.9905E-02
               SEB1= 5.2977E-01 SEB2= 1.8326E-01 SEC= 1.6736E-06

  A= 33.892E+01 B1=-3.3090E+02   B2=
REGSS= 2.9213E+05 D= 1.8028E-03
                     RUN  386 30 PRESS= 391.87    39

 58.9482E-03
   4
      DF       SS             MS             VR
REGN   2  3.0545E+06  1.5272E+06  6.3221E+05
DEVN 114  2.7540E+02  2.4157E-00
TOTL 116  3.0548E+06

  A= 10.955E+02 B1=-1.1426E+03   B2=-4.3900E-03   C= 5.6916E-02
```

```
                 SEB1= 1.0751E-00 SEB2= 3.5052E-01 SEC= 2.6845E-07

   A= 10.954E+02 B1=-1.1426E+03    B2=
REGSS= 3.0546E+06 D= 1.2715E-03
                          RUN  486 30 PRESS=   9.91     32

 12.8695E-02
   3
       DF      SS            MS            VR
REGN    2  1.6087E+05  8.0435E+04  1.5794E+05
DEVN   93  4.7360F+01  5.0924E-01
TOTL   95  1.6091E+05

   A= 26.417E+01 B1=-2.7523E+02    B2= 7.7000E-04    C= 1.2266E-01
                 SEB1= 5.7904E-01 SEB2= 2.8277E-01 SEC= 3.7328E-06

   A= 26.417E+01 B1=-2.7523E+02    B2=
REGSS= 1.6086E+05 D= 3.2751E-03
                          RUN  586 30 PRESS=  25.69     29

 14.1830E-02
   7
       DF      SS            MS            VR
REGN    2  1.6632E+05  8.3160E+04  3.2837E+04
DEVN   84  2.1273E+02  2.5325E-00
TOTL   86  1.6653E+05

   A= 29.443E+01 B1=-3.3355E+02    B2= 1.0200E-03    C= 1.2316E-01
                 SEB1= 1.7782E-00 SEB2= 8.1974E-01 SEC= 7.3677E-06

   A= 29.443E+01 B1=-3.3355E+02    B2=
REGSS= 1.6632E+05 D= 4.8304E-03
                          RUN  185 30 PRESS= 155.36     37

 82.0258E-03
   2
       DF      SS            MS            VR
REGN    2  2.9510E+05  1.4755E+05  1.0016E+06
DEVN  108  1.5910E+01  1.4731E-01
TOTL  110  2.9512E+05

   A= 34.184E+01 B1=-3.4932E+02    B2= 1.3500E-03    C= 8.4691E-02
                 SEB1= 2.5656E-01 SEB2= 1.2022E-01 SEC= 9.8526E-07

   A= 34.185E+01 B1=-3.4932E+02    B2=
REGSS= 2.9510E+05 D= 2.2265E-03
                          RUN  285 30 PRESS= 390.94     33

 75.7487E-03
   3
```

```
       DF       SS             MS            VR
REGN    2  3.0582E+06  1.5291E+06  1.0006E+06
DEVN   96  1.4670E+02  1.5281E-00
TOTL   98  3.0584E+06

   A= 11.093E+02 B1=-1.2103E+03    B2= 3.9970E-03    C= 7.3558E-02
                SEB1= 8.5588E-01 SEB2= 3.5153E-01 SEC= 2.3995E-07

   A= 11.093E+02 B1=-1.2103E+03    B2=
REGSS= 3.0582E+06 D= 1.8970E-03
                         RUN  385 30 PRESS=  10.05     37

 13.3039E-02
   3
       DF       SS             MS            VR
REGN    2  2.3590E+05  1.1795E+05  8.7551E+05
DEVN  108  1.4550E+01  1.3472E-01
TOTL  110  2.3591E+05

   A= 30.199E+01 B1=-3.0346E+02    B2=-1.2070E-03    C= 1.3739E-01
                SEB1= 2.2967E-01 SEB2= 1.6881E-01 SEC= 1.8330E-06

   A= 30.198E+01 B1=-3.0346E+02    B2=
REGSS= 2.3590E+05 D= 3.0693E-03
                         RUN  485 31 PRESS=  25.21     29

 98.5864E-03
   3
       DF       SS             MS            VR
REGN    2  1.0123E+05  5.0617E+04  1.6766E+05
DEVN   84  2.5360E+01  3.0190E-01
TOTL   86  1.0126E+05

   A= 26.031E+01 B1=-2.5587E+02    B2= 3.6170E-04    C= 1.0125E-01
                SEB1= 4.4208E-01 SEB2= 2.7312E-01 SEC= 4.1715E-06

   A= 26.031E+01 B1=-2.5587E+02    B2=
REGSS= 1.0123E+05 D= 2.7035E-03
                         RUN  585 30 PRESS=  62.78     26

 58.5917E-03
   3
       DF       SS             MS            VR
REGN    2  1.5883E+05  7.9417E+04  1.1808E+05
DEVN   75  5.0440E+01  6.7253E-01
TOTL   77  1.5888E+05

   A= 31.037E+01 B1=-3.0458E+02    B2= 6.2000E-04    C= 5.9845E-02
                SEB1= 6.6251E-01 SEB2= 2.1714E-01 SEC= 2.3406E-06
```

```
  A= 31.037E+01 B1=-2.9458E+02   B2=
REGSS= 1.5883E+05 D= 2.3471E-03
                       RUN  198 30 PRESS=  10.04    29

 11.2229E-02
   4
       DF      SS            MS            VR
REGN    2  1.3711E+05  6.8557E+04  5.4897E+05
DEVN   84  1.0490E+01  1.2488E-01
TOTL   86  1.3712E+05

  A= 29.047E+01 B1=-2.9436E+02   B2= 1.4090E-03   C= 1.1364E-01
               SEB1= 3.0995E-01 SEB2= 1.7543E-01 SEC= 2.0245E-06

  A= 29.047E+01 B1=-2.9436E+02   B2=
REGSS= 1.3711E+05 D= 2.9876E-03
                       RUN  298 30 PRESS=  24.89    31

 83.9494E-03
   4
       DF      SS            MS            VR
REGN    2  2.3788E+05  1.1894E+05  1.5493E+04
DEVN   90  6.9091E+02  7.6767E-00
TOTL   92  2.3857E+05

  A= 34.600E+01 B1=-3.4385E+02   B2= 6.7000E-04   C= 8.5623E-02
               SEB1= 3.2078E-00 SEB2= 1.1214E-00 SEC= 9.4841E-06

  A= 34.601E+01 B1=-3.4386E+02   B2=
REGSS= 2.3788E+05 D= 2.2082E-03
                       RUN  398 30 PRESS=  62.41    42

 78.7414E-03
   3
       DF      SS            MS            VR
REGN    2  2.6071E+05  1.3035E+05  1.5689E+06
DEVN  123  1.0220E+01  8.3089E-02
TOTL  125  2.6073E+05

  A= 30.735E+01 B1=-3.0046E+02   B2=-5.2370E-04   C= 8.0917E-02
               SEB1= 1.6966E-01 SEB2= 7.3357E-02 SEC= 8.1258E-07

  A= 30.734E+01 B1=-3.0046E+02   B2=
REGSS= 2.6071E+05 D= 1.8076E-03
                       RUN  498 30 PRESS= 155.48    30

 52.7623E-03
   3
       DF      SS            MS            VR
REGN    2  1.8983E+05  9.4915E+04  1.8548E+05
```

```
DEVN  87  4.4520E+01  5.1172E-01
TOTL  89  1.8987E+05

  A= 31.082E+01 B1=-2.9294E+02   B2= 8.4700E-04   C= 4.9039E-02
               SEB1= 6.8265E-01 SEB2= 1.4373E-01 SEC= 1.6748E-06

  A= 31.082E+01 B1=-2.9295E+02   B2=
REGSS= 1.8983E+05 D= 1.3093E-03
                         RUN  598 30 PRESS= 389.70    36

 37.6721E-03
   3
      DF      SS           MS          VR
REGN   2  1.0346E+06  5.1732E+05  1.8227E+05
DEVN 105  2.9800E+02  2.8380E-00
TOTL 107  1.0349E+06

  A= 82.580E+01 B1=-8.8963E+02   B2=-1.1000E-04   C= 3.7044E-02
               SEB1= 1.7737E-00 SEB2= 3.6427E-01 SEC= 4.6025E-07

  A= 82.580E+01 B1=-8.8963E+02   B2=
REGSS= 1.0346E+06 D= 1.4528E-03
                         RUN   19 30 PRESS=  25.63    33

 10.8268E-02
   3
      DF      SS           MS          VR
REGN   2  2.1105E+05  1.0552E+05  3.0652E+05
DEVN  96  3.3050E+01  3.4427E-01
TOTL  98  2.1108E+05

  A= 30.852E+01 B1=-3.2876E+02   B2= 3.4000E-05   C= 1.0522E-01
               SEB1= 4.6351E-01 SEB2= 2.3165E-01 SEC= 2.1431E-06

  A= 30.852E+01 B1=-3.2876E+02   B2=
REGSS= 2.1105E+05 D= 2.7664E-03
                         RUN   29 30 PRESS=  63.07    40

 79.8449E-03
   5
      DF      SS           MS          VR
REGN   2  1.6066E+05  8.0332E+04  1.9955E+06
DEVN 117  4.7100E-00  4.0256E-02
TOTL 119  1.6067E+05

  A= 26.996E+01 B1=-2.6498E+02   B2=-2.6000E-05   C= 8.0450E-02
               SEB1= 1.3602E-01 SEB2= 5.9910E-02 SEC= 8.5323E-07

  A= 26.996E+01 B1=-2.6498E+02   B2=
REGSS= 1.6066E+05 D= 2.0748E-03
```

```
                         RUN   39 30 PRESS= 156.68    26

 54.6225E-03
   3
       DF      SS            MS            VR
REGN    2  1.4314E+05  7.1571E+04  2.1540E+05
DEVN   75  2.4920E+01  3.3226E-01
TOTL   77  1.4316E+05

  A= 29.807E+01 B1=-2.8651E+02   B2= 4.8000E-04   C= 5.5206E-02
               SEB1= 5.7933E-01 SEB2= 1.5024E-01 SEC= 1.8302E-06

  A= 29.807E+01 B1=-2.8651E+02   B2=
REGSS= 1.4314E+05 D= 1.2333E-03
                         RUN   49 30 PRESS= 391.13    28

 31.9237E-03
   3
       DF      SS            MS            VR
REGN    2  1.1382E+05  5.6914E+04  8.2469E+05
DEVN   81  5.5900E-00  6.9012E-02
TOTL   83  1.1383E+05

  A= 30.138E+01 B1=-2.6615E+02   B2= 9.3300E-04   C= 3.2705E-02
               SEB1= 3.7648E-01 SEB2= 4.9150E-02 SEC= 6.9385E-07

  A= 30.139E+01 B1=-2.6615E+02   B2=
REGSS= 1.1382E+05 D= 8.7324E-04
                         RUN   59 30 PRESS=   9.96    30

 73.4978E-03
   3
       DF      SS            MS            VR
REGN    2  1.7134E+05  8.5671E+04  4.6759E+05
DEVN   87  1.5940E+01  1.8321E-01
TOTL   89  1.7135E+05

  A= 29.085E+01 B1=-2.9114E+02   B2= 1.0970E-04   C= 7.0563E-02
               SEB1= 3.0157E-01 SEB2= 1.0408E-01 SEC= 1.2278E-06

  A= 29.085E+01 B1=-2.9114E+02   B2=
REGSS= 1.7134E+05 D= 2.7675E-03
                         RUN  197 30 PRESS= 389.41    31

 49.3962E-03
   3
       DF      SS            MS            VR
REGN    2  2.4189E+05  1.2094E+05  9.4843E+04
DEVN   90  1.1477E+02  1.2752E-00
TOTL   92  2.4200E+05
```

```
  A= 31.102E+01 B1=-3.2801E+02   B2= 4.2400E-04   C= 4.6336E-02
              SEB1= 7.9421E-01 SEB2= 1.6781E-01 SEC= 1.5597E-06

  A= 31.102E+01 B1=-3.2801E+02   B2=
REGSS= 2.4189E+05 D= 1.2181E-03
                    RUN  297 30 PRESS=   9.97     30

 12.5190E-02
   3
      DF      SS           MS           VR
REGN   2  2.3735E+05  1.1867E+05  5.6358E+05
DEVN  87  1.8320E+01  2.1057E-01
TOTL  89  2.3737E+05

  A= 31.472E+01 B1=-3.2179E+02   B2=-1.0280E-03   C= 1.2329E-01
              SEB1= 3.0389E-01 SEB2= 1.8528E-01 SEC= 1.7892E-06

  A= 31.472E+01 B1=-3.2179E+02   B2=
REGSS= 2.3735E+05 D= 3.1798E-03
                    RUN  397 30 PRESS=  25.16     27

 89.7470E-03
   3
      DF      SS           MS           VR
REGN   2  3.2515E+05  1.6257E+05  3.0366E+05
DEVN  78  4.1760E+01  5.3538E-01
TOTL  80  3.2519E+05

  A= 43.999E+01 B1=-4.4695E+02   B2= 1.5700E-03   C= 8.8890E-02
              SEB1= 1.2018E-00 SEB2= 3.7575E-01 SEC= 1.8809E-06

  A= 44.000E+01 B1=-4.4695E+02   B2=
REGSS= 3.2515E+05 D= 1.9868E-03
                    RUN  497 30 PRESS=  62.77     41

 89.0094E-03
   4
      DF      SS           MS           VR
REGN   2  1.8596E+05  9.2981E+04  1.0207E+05
DEVN 120  1.0931E+02  9.1091E-01
TOTL 122  1.8607E+05

  A= 27.242E+01 B1=-2.8735E+02   B2=-3.7900E-04   C= 8.5375E-02
              SEB1= 7.7381E-01 SEB2= 2.8265E-01 SEC= 3.4230E-06

  A= 27.242E+01 B1=-2.8735E+02   B2=
REGSS= 1.8596E+05 D= 2.2795E-03
                    RUN  597 30 PRESS= 156.44     25
```

```
 43.5723E-03
   2
       DF       SS              MS             VR
REGN    2  1.2456E+05  6.2280E+04  3.1556E+05
DEVN   72  1.4210E+01  1.9736E-01
TOTL   74  1.2457E+05

  A= 28.826E+01 B1=-3.0126E+02   B2=-4.5600E-04   C= 4.2633E-02
                SEB1= 3.9130E-01 SEB2= 9.1935E-02 SEC= 1.0129E-06

  A= 28.825E+01 B1=-3.0126E+02   B2=
REGSS= 1.2456E+05 D= 1.6720E-03
                    RUN  196 30 PRESS=  62.71     26

 86.0230E-03
   5
       DF       SS              MS             VR
REGN    2  1.8650E+05  9.3251E+04  4.4264E+05
DEVN   75  1.5800E+01  2.1066E-01
TOTL   77  1.8651E+05

  A= 32.540E+01 B1=-3.2507E+02   B2= 6.2000E-04   C= 8.7039E-02
                SEB1= 4.0380E-01 SEB2= 1.7906E-01 SEC= 1.6944E-06

  A= 32.541E+01 B1=-3.2507E+02   B2=
REGSS= 1.8650E+05 D= 2.2882E-03
                    RUN  296 30 PRESS= 156.42     26

 66.4756E-03
   2
       DF       SS              MS             VR
REGN    2  2.4837E+05  1.2418E+05  1.7442E+06
DEVN   75  5.3400E-00  7.1200E-02
TOTL   77  2.4838E+05

  A= 35.930E+01 B1=-3.6541E+02   B2=-6.9300E-04   C= 6.6387E-02
                SEB1= 1.9596E-01 SEB2= 6.8470E-02 SEC= 5.1276E-07

  A= 35.930E+01 B1=-3.6542E+02   B2=
REGSS= 2.4837E+05 D= 1.7121E-03
                    RUN  396 30 PRESS= 391.12     28

 38.4551E-03
   2
       DF       SS              MS             VR
REGN    2  2.6114E+05  1.3057E+05  2.1847E+05
DEVN   81  4.8410E+01  5.9765E-01
TOTL   83  2.6118E+05

  A= 33.389E+01 B1=-3.1890E+02   B2= 2.9000E-04   C= 3.8791E-02
```

```
              SEB1= 5.3472E-01 SEB2= 9.4565E-02 SEC= 9.2981E-07

  A= 33.389E+01 B1=-3.1891E+02   B2=
REGSS= 2.6114E+05 D= 8.6659E-04
                    RUN  496 30 PRESS=   9.94     32

 92.5989E-03
   3
      DF      SS           MS          VR
REGN   2  6.8640E+04  3.4320E+04  2.8974E+05
DEVN  93  1.1016E+01  1.1845E-01
TOTL  95  6.8651E+04

  A= 21.953E+01 B1=-2.1558E+02   B2=-5.7300E-04   C= 9.6196E-02
              SEB1= 3.3573E-01 SEB2= 1.5926E-01 SEC= 3.4267E-06

  A= 21.953E+01 B1=-2.1558E+02   B2=
REGSS= 6.8640E+04 D= 2.5684E-03
                    RUN  596 30 PRESS=  25.54     26

 70.7850E-03
   3
      DF      SS           MS          VR
REGN   2  1.7981E+05  8.9906E+04  3.6646E+05
DEVN  75  1.8400E+01  2.4533E-01
TOTL  77  1.7983E+05

  A= 30.277E+01 B1=-3.1101E+02   B2=-3.2000E-05   C= 6.9254E-02
              SEB1= 3.6628E-01 SEB2= 1.2773E-01 SEC= 1.3205E-06

  A= 30.276E+01 B1=-3.1101E+02   B2=
REGSS= 1.7981E+05 D= 2.7161E-03
                    RUN  195 30 PRESS= 155.45     35

 68.2317E-03
   2
      DF      SS           MS          VR
REGN   2  3.9087E+05  1.9543E+05  6.7804E+05
DEVN 102  2.9400E+01  2.8823E-01
TOTL 104  3.9090E+05

  A= 37.247E+01 B1=-3.7901E+02   B2=-1.1000E-03   C= 6.7501E-02
              SEB1= 4.0745E-01 SEB2= 1.2577E-01 SEC= 8.7549E-07

  A= 37.246E+01 B1=-3.7901E+02   B2=
REGSS= 3.9087E+05 D= 1.7746E-03
                    RUN  295 30 PRESS= 390.12     31

 42.3088E-03
   5
```

```
        DF      SS             MS             VR
REGN    2  3.6486E+05  1.8243E+05  2.4723E+05
DEVN   90  6.6410E+01  7.3788E-01
TOTL   92  3.6493E+05

  A= 42.672E+01 B1=-4.2497E+02   B2= 1.3400E-03   C= 4.0801E-02
              SEB1= 1.1843E-00 SEB2= 1.7296E-01 SEC= 9.5769E-07

  A= 42.673E+01 B1=-4.2497E+02   B2=
REGSS= 3.6486E+05 D= 1.0522E-03
                     RUN  395 30 PRESS=  10.33    29

 11.2157E-02
   2
        DF      SS             MS             VR
REGN    2  1.3674E+05  6.8370E+04  7.5073E+05
DEVN   84  7.6500E-00  9.1071E-02
TOTL   86  1.3674E+05

  A= 28.678E+01 B1=-2.8875E+02   B2= 6.7800E-04   C= 1.1207E-01
              SEB1= 2.4641E-01 SEB2= 1.4695E-01 SEC= 1.7625E-06

  A= 28.678E+01 B1=-2.8875E+02   B2=
REGSS= 1.3674E+05 D= 2.5038E-03
                     RUN  495 30 PRESS=  24.37    28

 10.5045E-02
   3
        DF      SS             MS             VR
REGN    2  1.1331E+05  5.6657E+04  1.7787E+05
DEVN   81  2.5800E+01  3.1951E-01
TOTL   83  1.1334E+05

  A= 25.412E+01 B1=-2.6065E+02   B2= 9.0000E-06   C= 9.8813E-02
              SEB1= 5.2850E-01 SEB2= 2.1461E-01 SEC= 3.1587E-06

  A= 25.412E+01 B1=-2.6065E+02   B2=
REGSS= 1.1331E+05 D= 2.6383E-03
                     RUN  595 30 PRESS=  62.82    26

 62.9063E-03
   3
        DF      SS             MS             VR
REGN    2  1.8654E+05  9.3272E+04  1.0514E+05
DEVN   75  6.6530E+01  8.8706E-01
TOTL   77  1.8661E+05

  A= 31.798E+01 B1=-3.2982E+02   B2= 8.8100E-04   C= 6.0757E-02
              SEB1= 7.4438E-01 SEB2= 2.4952E-01 SEC= 2.2937E-06
```

```
  A= 31.799E+01 B1=-3.2982E+02   B2=
REGSS= 1.8654E+05 D= 2.3828E-03
                    RUN   18 40 PRESS=   9.70    41

 14.9765E-02
   4
      DF      SS          MS          VR
REGN   2  2.5374E+05  1.2687E+05  5.4902E+05
DEVN 120  2.7730E+01  2.3108E-01
TOTL 122  2.5376E+05

  A= 29.154E+01 B1=-3.0942E+02   B2=-5.2000E-04   C= 1.5384E-01
               SEB1= 3.9701E-01 SEB2= 2.0159E-01 SEC= 2.1054E-06

  A= 29.154E+01 B1=-3.0942E+02   B2=
REGSS= 2.5374E+05 D= 4.0447E-03
                    RUN   28 40 PRESS=  24.83    26

 10.9320E-02
   3
      DF      SS          MS          VR
REGN   2  2.8152E+05  1.4076E+05  3.5272E+05
DEVN  75  2.9930E+01  3.9906E-01
TOTL  77  2.8155E+05

  A= 40.618E+01 B1=-4.0019E+02   B2= 3.6000E-04   C= 1.1392E-01
               SEB1= 5.8238E-01 SEB2= 3.2875E-01 SEC= 2.0526E-06

  A= 40.618E+01 B1=-4.0020E+02   B2=
REGSS= 2.8152E+05 D= 2.9380E-03
                    RUN   38 40 PRESS=  63.41    31

 11.0904E-02
   3
      DF      SS          MS          VR
REGN   2  2.4649E+05  1.2324E+05  4.0946E+05
DEVN  90  2.7090E+01  3.0100E-01
TOTL  92  2.4652E+05

  A= 32.594E+01 B1=-3.3099E+02   B2=-7.2600E-04   C= 1.0571E-01
               SEB1= 3.8709E-01 SEB2= 2.1354E-01 SEC= 1.9491E-06

  A= 32.594E+01 B1=-3.3099E+02   B2=
REGSS= 2.4649E+05 D= 2.3616E-03
                    RUN   48 40 PRESS= 156.29    27

 59.7121E-03
   2
      DF      SS          MS          VR
REGN   2  1.7906E+05  8.9531E+04  3.1613E+05
```

```
DEVN  78  2.2090E+01  2.8320E-01
TOTL  80  1.7908E+05

  A= 32.289E+01 B1=-3.2969E+02   B2=-6.9900E-04   C= 6.0213E-02
              SEB1= 4.1652E-01 SEB2= 1.3888E-01 SEC= 1.2777E-06

  A= 32.289E+01 B1=-3.2969E+02   B2=
REGSS= 1.7906E+05 D= 1.6077E-03
                    RUN   58 40 PRESS= 391.08    26

 39.7897E-03
   3
      DF      SS          MS          VR
REGN   2  3.1072E+05  1.5536E+05  1.0032E+05
DEVN  75  1.1615E+02  1.5486E-00
TOTL  77  3.1084E+05

  A= 37.823E+01 B1=-4.0940E+02   B2=-3.4000E-05   C= 3.7815E-02
              SEB1= 9.5348E-01 SEB2= 1.9091E-01 SEC= 1.1389E-06

  A= 37.823E+01 B1=-4.0941E+02   B2=
REGSS= 3.1072E+05 D= 1.4831E-03
                    RUN  189 40 PRESS=  25.01    30

 12.0842E-02
   3
      DF      SS          MS          VR
REGN   2  2.5211E+05  1.2605E+05  3.5781E+05
DEVN  87  3.0650E+01  3.5229E-01
TOTL  89  2.5214E+05

  A= 32.749E+01 B1=-3.3174E+02   B2= 1.6290E-03   C= 1.1749E-01
              SEB1= 3.9558E-01 SEB2= 2.3838E-01 SEC= 2.1660E-06

  A= 32.749E+01 B1=-3.3174E+02   B2=
REGSS= 2.5211E+05 D= 3.0888E-03
                    RUN  289 40 PRESS=  62.26    35

 10.7250E-02
   4
      DF      SS          MS          VR
REGN   2  4.1176E+05  2.0588E+05  9.8351E+05
DEVN 105  2.1980E+01  2.0933E-01
TOTL 107  4.1178E+05

  A= 41.444E+01 B1=-4.2155E+02   B2=-7.9000E-04   C= 1.0438E-01
              SEB1= 5.9802E-01 SEB2= 2.2204E-01 SEC= 1.2495E-06

  A= 41.444E+01 B1=-4.2155E+02   B2=
REGSS= 4.1176E+05 D= 2.6921E-03
```

```
                    RUN  389 40 PRESS= 156.36    26

 62.7514E-03
   2
      DF     SS          MS          VR
REGN   2  2.0199E+05  1.0099E+05  8.4920E+05
DEVN  75  8.9200E-00  1.1893E-01
TOTL  77  2.0200E+05

  A= 33.225E+01 B1=-3.3020E+02   B2=-2.1100E-04   C= 6.2670E-02
              SEB1= 2.6635E-01 SEB2= 8.8157E-02 SEC= 8.0854E-07

  A= 33.225E+01 B1=-3.3020E+02   B2=
REGSS= 2.0199E+05 D= 1.4000E-03
                    RUN  489 40 PRESS= 390.52    29

 34.4915E-03
   3
      DF     SS          MS          VR
REGN   2  1.7818E+06  8.9091E+05  5.3956E+05
DEVN  84  1.3870E+02  1.6511E-00
TOTL  86  1.7819E+06

  A= 10.137E+02 B1=-1.0411E+03   B2= 1.3520E-03   C= 3.3965E-02
              SEB1= 1.0187E-00 SEB2= 2.0663E-01 SEC= 1.9062E-07

  A= 10.137E+02 B1=-1.0411E+03   B2=
REGSS= 1.7818E+06 D= 9.0686E-04
                    RUN  589 40 PRESS=  10.12    40

 79.7951E-03
   4
      DF     SS          MS          VR
REGN   2  2.2075E+05  1.1037E+05  5.7962E+05
DEVN 117  2.2280E+01  1.9042E-01
TOTL 119  2.2077E+05

  A= 30.124E+01 B1=-3.1047E+02   B2= 3.3200E-04   C= 7.9537E-02
              SEB1= 2.9254E-01 SEB2= 1.3010E-01 SEC= 1.3497E-06

  A= 30.124E+01 B1=-3.1048E+02   B2=
REGSS= 2.2075E+05 D= 3.1194E-03
                    RUN  187 40 PRESS= 390.77    24

 66.4184E-03
   3
      DF     SS          MS          VR
REGN   2  1.6755E+06  8.3775E+05  1.4560E+05
DEVN  69  3.9700E+02  5.7536E-00
TOTL  71  1.6759E+06
```

```
  A= 10.495E+02 B1=-1.1467E+03   B2= 5.7700E-04   C= 6.3585E-02
               SEB1= 2.1610E-00 SEB2= 7.9630E-01 SEC= 6.0553E-07

  A= 10.495E+02 B1=-1.1467E+03   B2=
REGSS= 1.6755E+06 D= 1.6716E-03
                          RUN  287 40 PRESS=   9.90    25

 13.2197E-02
   8
       DF      SS            MS           VR
REGN   2  1.6666E+05  8.3332E+04  3.8960E+05
DEVN  72  1.5400E+01  2.1388E-01
TOTL  74  1.6667E+05

  A= 31.456E+01 B1=-3.1617E+02   B2=-2.3810E-04   C= 1.3485E-01
               SEB1= 3.5826E-01 SEB2= 2.6007E-01 SEC= 2.6016E-06

  A= 31.456E+01 B1=-3.1617E+02   B2=
REGSS= 1.6666E+05 D= 3.4780E-03
                          RUN  387 40 PRESS=  25.06    26

 12.5089E-02
   2
       DF      SS            MS           VR
REGN   2  1.6644E+05  8.3222E+04  7.0847E+05
DEVN  75  8.8100E-00  1.1746E-01
TOTL  77  1.6645E+05

  A= 30.528E+01 B1=-3.0555E+02   B2=-1.[illegible]E-0   C= 1.[illegible]E-0
               SEB1= 2.6564E-01 SEB2= 1.7844E-01 SEC= 1.9112E-06

  A= 30.528E+01 B1=-3.0555E+02   B2=
REGSS= 1.6644E+05 D= 2.7732E-03
                          RUN  487 40 PRESS=  62.67    27

 94.7927E-03
   2
       DF      SS            MS           VR
REGN   2  2.5002E+05  1.2501E+05  2.5640E+05
DEVN  78  3.8030E+01  4.8756E-01
TOTL  80  2.5006E+05

  A= 34.473E+01 B1=-3.4826E+02   B2=-1.6090E-03   C= 9.5252E-02
               SEB1= 5.0252E-01 SEB2= 2.4564E-01 SEC= 2.0253E-06

  A= 34.473E+01 B1=-3.4826E+02   B2=
REGSS= 2.5002E+05 D= 2.5432E-03
                          RUN  587 40 PRESS= 156.53    25
```

```
 50.2226E-03
   2
       DF        SS            MS           VR
REGN    2   2.9558E+05  1.4779E+05  2.4184E+05
DEVN   72   4.4000E+01  6.1111E-01
TOTL   74   2.9563E+05

   A= 41.994E+01 B1=-4.2402E+02   B2= 2.1100E-03   C= 4.9570E-02
                SEB1= 1.3008E-00 SEB2= 2.1612E-01 SEC= 1.2020E-06

   A= 41.995E+01 B1=-4.2402E+02   B2=
REGSS= 2.9558E+05 D= 1.9441E-03
                        RUN  186 40 PRESS=  62.09     26

 13.4312E-02
   3
       DF        SS            MS           VR
REGN    2   1.5641E+05  7.8208E+04  5.0349E+05
DEVN   75   1.1650E+01  1.5533E-01
TOTL   77   1.5642E+05

   A= 30.191E+01 B1=-3.1437E+02   B2= 1.2600E-04   C= 1.3469E-01
                SEB1= 3.4075E-01 SEB2= 2.1961E-01 SEC= 2.2220E-06

   A= 30.191E+01 B1=-3.1437E+02   B2=
REGSS= 1.5641E+05 D= 3.5411E-03
                        RUN  286 40 PRESS= 156.13     26

 93.8053E-03
  13
       DF        SS            MS           VR
REGN    2   2.8518E+05  1.4259E+05  3.5109E+05
DEVN   75   3.0460E+01  4.0613E-01
TOTL   77   2.8521E+05

   A= 42.286E+01 B1=-4.2265E+02   B2=-1.3000E-03   C= 8.9841E-02
                SEB1= 1.1957E-00 SEB2= 3.4267E-01 SEC= 1.9182E-06

   A= 42.286E+01 B1=-4.2265E+02   B2=
REGSS= 2.8518E+05 D= 2.3170E-03
                        RUN  386 40 PRESS= 390.42     25

 65.3750E-03
   5
       DF        SS            MS           VR
REGN    2   3.3126E+05  1.6563E+05  1.4663E+05
DEVN   72   8.1330E+01  1.1295E-00
TOTL   74   3.3134E+05

   A= 41.216E+01 B1=-4.2170E+02   B2= 4.6500E-04   C= 6.3250E-02
```

```
              SEB1= 9.1198E-01 SEB2= 2.8100E-01 SEC= 1.5801E-06

  A= 41.216E+01 B1=-4.2170E+02   B2=
REGSS= 3.3126E+05 D= 1.4130E-03
                    RUN  486 40 PRESS=  10.01    27

 10.9111E-02
   4
      DF      SS          MS          VR
REGN   2  1.4850E+05  7.4252E+04  4.7629E+05
DEVN  78  1.2160E+01  1.5589E-01
TOTL  80  1.4851E+05

  A= 29.994E+01 B1=-2.9546E+02   B2= 3.9000E-05   C= 1.1252E-01
              SEB1= 3.2022E-01 SEB2= 2.0155E-01 SEC= 2.3087E-06

  A= 29.994E+01 B1=-2.9547E+02   B2=
REGSS= 1.4850E+05 D= 3.0043E-03
                    RUN  586 40 PRESS=  25.41    41

 87.4474E-03
   3
      DF      SS          MS          VR
REGN   2  4.4294E+05  2.2147E+05  3.3509E+05
DEVN 120  7.9310E+01  6.6091E-01
TOTL 122  4.4302E+05

  A= 37.696E+01 B1=-3.9023E+02   B2= 9.2300E-04   C= 8.3195E-02
              SEB1= 4.7858E-01 SEB2= 2.1127E-01 SEC= 1.3873E-06

  A= 37.696E+01 B1=-3.9023E+02   B2=
REGSS= 4.4294E+05 D= 3.2629E-03
                    RUN  185 40 PRESS= 156.68    35

 94.9532E-03
   2
      DF      SS          MS          VR
REGN   2  4.0077E+05  2.0038E+05  1.5626E+06
DEVN 102  1.3080E+01  1.2823E-01
TOTL 104  4.0078E+05

  A= 38.143E+01 B1=-3.8094E+02   B2=-1.4850E-03   C= 9.6614E-02
              SEB1= 2.3338E-01 SEB2= 1.1177E-01 SEC= 7.7023E-07

  A= 38.142E+01 B1=-3.8094E+02   B2=
REGSS= 4.0077E+05 D= 2.5399E-03
                    RUN  285 40 PRESS= 390.15    35

 85.0127E-03
   6
```

```
        DF       SS              MS            VR
REGN     2   2.1880E+06   1.0940E+06   7.2508E+05
DEVN   102   1.5390E+02   1.5088E-00
TOTL   104   2.1882E+06

  A= 10.178E+02 B1=-1.0546E+03    B2= 3.2400E-03    C= 8.3637E-02
                SEB1= 8.9470E-01 SEB2= 4.4844E-01 SEC= 4.0319E-07

  A= 10.178E+02 B1=-1.0546E+03    B2=
REGSS= 2.1880E+06 D= 2.1570E-03
                         RUN   385 40 PRESS=  10.01     37

 13.6566E-02
   7
        DF       SS              MS            VR
REGN     2   2.4009E+05   1.2004E+05   1.5427E+05
DEVN   108   8.4040E+01   7.7814E-01
TOTL   110   2.4017E+05

  A= 30.964E+01 B1=-3.0626E+02    B2= 8.5000E-04    C= 1.3472E-01
                SEB1= 5.5713E-01 SEB2= 4.0506E-01 SEC= 4.3185E-06

  A= 30.964E+01 B1=-3.0626E+02    B2=
REGSS= 2.4009E+05 D= 3.0098E-03
                         RUN   485 40 PRESS=  25.24     31

 10.4590E-02
   3
        DF       SS              MS            VR
REGN     2   2.3053E+05   1.1526E+05   4.2291E+05
DEVN    90   2.4530E+01   2.7255E-01
TOTL    92   2.3056E+05

  A= 32.741E+01 B1=-3.2487E+02    B2=-3.0800E-04    C= 1.0911E-01
                SEB1= 3.5539E-01 SEB2= 2.0688E-01 SEC= 1.9601E-06

  A= 32.741E+01 B1=-3.2487E+02    B2=
REGSS= 2.3053E+05 D= 2.9133E-03
                         RUN   585 40 PRESS=  63.02     24

 72.3162E-03
   2
        DF       SS              MS            VR
REGN     2   3.0676E+05   1.5338E+05   1.7418E+05
DEVN    69   6.0760E+01   8.8057E-01
TOTL    71   3.0682E+05

  A= 39.112E+01 B1=-3.9121E+02    B2=-1.5560E-03    C= 7.2096E-02
                SEB1= 7.2766E-01 SEB2= 2.5137E-01 SEC= 1.6424E-06
```

```
   A= 39.111E+01 B1=-3.9121E+02   B2=
REGSS= 3.0676E+05 D= 2.8276E-03
                      RUN  198 40 PRESS=  10.31    31

 14.4968E-02
   4
      DF      SS           MS           VR
REGN   2  3.3072E+05  1.6536E+05  2.8819E+04
DEVN  90  5.1642E+02  5.7380E-00
TOTL  92  3.3124E+05

   A= 35.084E+01 B1=-3.8456E+02   B2=-8.6000E-04   C= 1.2757E-01
                SEB1= 1.7631E-00 SEB2= 9.5579E-01 SEC= 6.4627E-06

   A= 35.084E+01 B1=-3.8457E+02   B2=
REGSS= 3.3073E+05 D= 3.3538E-03
                      RUN  198 40 PRESS=  10.31    27

 13.3706E-02
  10
      DF      SS           MS           VR
REGN   2  2.5052E+05  1.2526E+05  4.3424E+04
DEVN  78  2.2500E+02  2.8846E-00
TOTL  80  2.5075E+05

   A= 36.107E+01 B1=-3.8994E+02   B2= 7.9900E-04   C= 1.1987E-01
                SEB1= 1.3267E-00 SEB2= 8.8600E-01 SEC= 5.8266E-06

   A= 36.107E+01 B1=-3.8994E+02   B2=
REGSS= 2.5052E+05 D= 3.1513E-03
                      RUN  298 40 PRESS=  25.19    35

 10.7422E-02
   3
      DF      SS           MS           VR
REGN   2  3.9948E+05  1.9974E+05  2.2001E+06
DEVN 102  9.2600E-00  9.0784E-02
TOTL 104  3.9948E+05

   A= 41.079E+01 B1=-4.1076E+02   B2= 3.9000E-04   C= 1.0759E-01
                SEB1= 4.1670E-01 SEB2= 1.4880E-01 SEC= 8.8194E-07

   A= 41.079E+01 B1=-4.1076E+02   B2=
REGSS= 3.9947E+05 D= 2.7748E-03
                      RUN  398 40 PRESS=  62.67    40

 99.2744E-03
   6
      DF      SS           MS           VR
REGN   2  4.5440E+05  2.2720E+05  9.9086E+04
```

```
DEVN 117  2.6828E+02  2.2929E-00
TOTL 119  4.5467E+05

  A= 37.005E+01 B1=-3.8297E+02   B2= 5.5600E-04   C= 8.9770E-02
              SEB1= 8.6353E-01 SEB2= 3.9301E-01 SEC= 2.6796E-06

  A= 37.005E+01 B1=-3.8297E+02   B2=
REGSS= 4.5440E+05 D= 2.0054E-03
                    RUN  498 40 PRESS= 155.79    30

 55.2986E-03
   2
      DF     SS          MS          VR
REGN   2  2.1293E+05  1.0646E+05  7.0013E+05
DEVN  87  1.3230E+01  1.5206E-01
TOTL  89  2.1295E+05

  A= 31.835E+01 B1=-3.1105E+02   B2= 4.4800E-04   C= 5.4904E-02
              SEB1= 2.7843E-01 SEB2= 7.9341E-02 SEC= 8.2000E-07

  A= 31.835E+01 B1=-3.1105E+02   B2=
REGSS= 2.1293E+05 D= 1.4659E-03
                    RUN  598 40 PRESS= 388.29    31

 64.2108E-04
  21
      DF     SS          MS          VR
REGN   2  4.3975E+05  2.1987E+05  5.0225E+05
DEVN  90  3.9400E+01  4.3777E-01
TOTL  92  4.3979E+05

  A= 16.671E+02 B1=-1.6433E+03   B2=-1.0600E-00   C= 1.1933E-02
              SEB1= 6.0107E+01 SEB2= 7.8012E-01 SEC= 2.8888E-07

  A= 16.568E+02 B1=-1.6436E+03   B2=
REGSS= 4.3969E+05 D= 4.6801E-04
                    RUN   19 40 PRESS=  25.50    31

 11.4804E-02
   7
      DF     SS          MS          VR
REGN   2  1.3838E+05  6.9194E+04  9.8380E+05
DEVN  90  6.3300E-00  7.0333E-02
TOTL  92  1.3839E+05

  A= 27.739E+01 B1=-2.9291E+02   B2=-8.3000E-04   C= 1.1247E-01
              SEB1= 2.7001E-01 SEB2= 1.2269E-01 SEC= 1.4300E-06

  A= 27.738E+01 B1=-2.9290E+02   B2=
REGSS= 1.3838E+05 D= 2.9570E-03
```

```
                    RUN    29 40 PRESS=  62.16     31

 78.0396E-03
   6
      DF       SS             MS             VR
REGN   2  3.7864E+05  1.8932E+05  1.3414E+05
DEVN  90  1.2702E+02  1.4113E-00
TOTL  92  3.7877E+05

  A= 44.100E+01 B1=-4.4246E+02   B2=-6.5000E-04   C= 7.8440E-02
                SEB1= 1.8011E-00 SEB2= 4.8782E-01 SEC= 2.4917E-06

  A= 44.100E+01 B1=-4.4246E+02   B2=
REGSS= 3.7864E+05 D= 2.0229E-03
                    RUN    39 40 PRESS= 156.68     31

 59.7436E-03
   3
      DF       SS             MS             VR
REGN   2  2.0059E+05  1.0029E+05  5.2849E+05
DEVN  90  1.7080E+01  1.8977E-01
TOTL  92  2.0060E+05

  A= 29.425E+01 B1=-2.9795E+02   B2=-6.2770E-04   C= 5.8512E-02
                SEB1= 2.9157E-01 SEB2= 8.5530E-02 SEC= 9.6340E-07

  A= 29.425E+01 B1=-2.9795E+02   B2=
REGSS= 2.0059E+05 D= 1.3071E-03
                    RUN    49 40 PRESS= 389.34     35

 33.5053E-03
   2
      DF       SS             MS             VR
REGN   2  1.3019E+06  6.5095E+05  1.9357E+06
DEVN 102  3.4300E+01  3.3627E-01
TOTL 104  1.3019E+06

  A= 79.348E+01 B1=-8.2468E+02   B2= 2.8910E-03   C= 3.3969E-02
                SEB1= 4.3578E-01 SEB2= 8.1025E-02 SEC= 1.1913E-07

  A= 79.350E+01 B1=-8.2467E+02   B2=
REGSS= 1.3019E+06 D= 9.0698E-04
                    RUN    59 40 PRESS=  10.35     34

 69.4937E-03
   4
      DF       SS             MS             VR
REGN   2  1.4701E+05  7.3505E+04  3.6826E+05
DEVN  99  1.9760E+01  1.9959E-01
TOTL 101  1.4702E+05
```

```
  A= 26.648E+01 B1=-2.6964E+02   B2= 1.0820E-03   C= 7.1272E-02
              SEB1= 3.1715E-01 SEB2= 1.2527E-01 SEC= 1.7229E-06

  A= 26.649E+01 B1=-2.6964E+02   B2=
REGSS= 1.4700E+05 D= 2.7953E-03
                    RUN  197 40 PRESS= 390.29    29

 60.1467E-03
   3
      DF     SS          MS          VR
REGN   2  9.3990E+05  4.6995E+05  6.6770E+04
DEVN  84  5.9122E+02  7.0383E-00
TOTL  86  9.4050E+05

  A= 71.588E+01 B1=-7.5775E+02   B2= 2.7360E-03   C= 5.6899E-02
              SEB1= 2.2177E-00 SEB2= 6.4760E-01 SEC= 1.1278E-06

  A= 71.589E+01 B1=-7.5775E+02   B2=
REGSS= 9.3991E+05 D= 1.4958E-03
                    RUN  297 40 PRESS=   9.73    28

 12.4621E-02
   3
      DF     SS          MS          VR
REGN   2  1.6922E+05  8.4610E+04  2.2867E+05
DEVN  81  2.9970E+01  3.7000E-01
TOTL  83  1.6925E+05

  A= 29.762E+01 B1=-2.9918E+02   B2= 5.5291E-04   C= 1.2073E-01
              SEB1= 4.4240E-01 SEB2= 2.8687E-01 SEC= 3.2048E-06

  A= 29.762E+01 B1=-2.9918E+02   B2=
REGSS= 1.6922E+05 D= 3.1138E-03
                    RUN  397 40 PRESS=  25.41    33

 11.3783E-02
   3
      DF     SS          MS          VR
REGN   2  1.6016E+05  8.0083E+04  2.1474E+05
DEVN  96  3.5800E+01  3.7291E-01
TOTL  98  1.6020E+05

  A= 28.272E+01 B1=-2.8664E+02   B2= 1.0020E-03   C= 1.0618E-01
              SEB1= 4.9061E-01 SEB2= 2.4153E-01 SEC= 2.9396E-06

  A= 28.273E+01 B1=-2.8664E+02   B2=
REGSS= 1.6016E+05 D= 2.3720E-03
                    RUN  497 40 PRESS=  62.72    24
```

```
 76.7748E-03
    2
      DF       SS            MS            VR
REGN   2  1.7806E+05  8.9033E+04  7.1767E+05
DEVN  69  8.5600E-00  1.2405E-01
TOTL  71  1.7807E+05

  A= 31.819E+01 B1=-3.1804E+02   B2=-8.0800E-04   C= 7.5828E-02
               SEB1= 2.6701E-01 SEB2= 1.0125E-01 SEC= 1.0009E-06

  A= 31.819E+01 B1=-3.1804E+02   B2=
REGSS= 1.7806E+05 D= 2.0246E-03
                    RUN  597 40 PRESS= 156.58    26

 44.4480E-03
    2
      DF       SS            MS            VR
REGN   2  1.7967E+05  8.9838E+04  7.3477E+05
DEVN  75  9.1700E-00  1.2226E-01
TOTL  77  1.7968E+05

  A= 31.600E+01 B1=-3.2371E+02   B2=-1.4630E-03   C= 4.5273E-02
               SEB1= 2.7550E-01 SEB2= 6.2457E-02 SEC= 5.9600E-07

  A= 31.599E+01 B1=-3.2371E+02   B2=
REGSS= 1.7967E+05 D= 1.7756E-03
                    RUN  196 40 PRESS=  62.30    25

 98.8508E-03
    5
      DF       SS            MS            VR
REGN   2  1.7693E+05  8.8465E+04  4.2605E+05
DEVN  72  1.4950E+01  2.0763E-01
TOTL  74  1.7694E+05

  A= 31.216E+01 B1=-3.1289E+02   B2= 8.5800E-04   C= 1.0077E-01
               SEB1= 3.4652E-01 SEB2= 1.8452E-01 SEC= 1.8847E-06

  A= 31.217E+01 B1=-3.1289E+02   B2=
REGSS= 1.7693E+05 D= 2.6494E-03
                    RUN  296 40 PRESS= 156.37    21

 80.9436E-03
    3
      DF       SS            MS            VR
REGN   2  1.7003E+05  8.5018E+04  3.1237E+05
DEVN  60  1.6330E+01  2.7216E-01
TOTL  62  1.7005E+05

  A= 33.452E+01 B1=-3.4991E+02   B2= 1.3880E-03   C= 8.4075E-02
```

```
                    SEB1= 4.5600E-01 SEB2= 1.9232E-01 SEC= 1.5707E-06

  A= 33.452E+01 B1=-3.4991E+02   B2=
REGSS= 1.7003E+05 D= 2.1683E-03
                         RUN  396 40 PRESS= 390.37    40

 60.7334E-03
   2
       DF      SS           MS          VR
REGN   2  1.7931E+06  8.9655E+05  5.1044E+05
DEVN 117  2.0550E+02  1.7564E-00
TOTL 119  1.7933E+06

  A= 85.624E+01 B1=-8.9620E+02   B2= 1.6390E-03   C= 6.0622E-02
                    SEB1= 9.3083E-01 SEB2= 3.0061E-01 SEC= 3.7427E-07

  A= 85.625E+01 B1=-8.9620E+02   B2=
REGSS= 1.7931E+06 D= 1.3543E-03
                         RUN  496 40 PRESS=  10.57    34

 11.3473E-02
   6
       DF      SS           MS          VR
REGN   2  1.5976E+05  7.9882E+04  5.9407E+04
DEVN  99  1.3312E+02  1.3446E-00
TOTL 101  1.5989E+05

  A= 27.605E+01 B1=-2.8686E+02   B2=-9.1300E-04   C= 1.0295E-01
                    SEB1= 9.6721E-01 SEB2= 4.4602E-01 SEC= 5.4198E-06

  A= 27.604E+01 B1=-2.8686E+02   B2=
REGSS= 1.5976E+05 D= 2.7488E-03
                         RUN  596 40 PRESS=  25.36    37

 77.0281E-03
   3
       DF      SS           MS          VR
REGN   2  2.0589E+05  1.0294E+05  3.7448E+05
DEVN 108  2.9690E+01  2.7490E-01
TOTL 110  2.0592E+05

  A= 27.797E+01 B1=-2.8402E+02   B2= 9.0100E-04   C= 7.4220E-02
                    SEB1= 3.4137E-01 SEB2= 1.2184E-01 SEC= 1.5104E-06

  A= 27.797E+01 B1=-2.8401E+02   B2=
REGSS= 2.0589E+05 D= 2.9109E-03
                         RUN  195 40 PRESS= 156.06    29

 87.9883E-03
   3
```

```
      DF     SS           MS           VR
REGN   2  3.2605E+05  1.6302E+05  1.0242E+06
DEVN  84  1.3370E+01  1.5916E-01
TOTL  86  3.2606E+05

  A= 36.657E+01 B1=-3.6943E+02   B2= 8.7000E-04   C= 8.6300E-02
              SEB1= 3.0100E-01 SEB2= 1.2104E-01 SEC= 8.8689E-07

  A= 36.657E+01 B1=-3.6943E+02   B2=
REGSS= 3.2605E+05 D= 2.2688E-03
                    RUN  295 40 PRESS= 390.26    24

 67.8665E-03
   2
      DF     SS           MS           VR
REGN   2  7.4759E+05  3.7379E+05  2.0739E+05
DEVN  69  1.2436E+02  1.8023E-00
TOTL  71  7.4771E+05

  A= 76.776E+01 B1=-8.1782E+02   B2= 2.8100E-03   C= 6.8029E-02
              SEB1= 1.6787E-00 SEB2= 4.7876E-01 SEC= 7.1581E-07

  A= 76.778E+01 B1=-8.1782E+02   B2=
REGSS= 7.4758E+05 D= 1.7544E-03
                    RUN  395 40 PRESS=  10.35    29

 12.8095E-02
   6
      DF     SS           MS           VR
REGN   2  1.0797E+05  5.3987E+04  4.1339E+05
DEVN  84  1.0970E+01  1.3059E-01
TOTL  86  1.0798E+05

  A= 25.311E+01 B1=-2.5879E+02   B2= 6.1000E-04   C= 1.2246E-01
              SEB1= 3.5020E-01 SEB2= 1.7913E-01 SEC= 2.6746E-06

  A= 25.311E+01 B1=-2.5879E+02   B2=
REGSS= 1.0797E+05 D= 2.7359E-03
                    RUN  495 40 PRESS=  24.98    27

 98.5093E-03
   4
      DF     SS           MS           VR
REGN   2  1.4627E+05  7.3136E+04  1.4683E+05
DEVN  78  3.8850E+01  4.9807E-01
TOTL  80  1.4631E+05

  A= 28.537E+01 B1=-2.8743E+02   B2=-9.9700E-04   C= 9.4806E-02
              SEB1= 5.3437E-01 SEB2= 2.6777E-01 SEC= 3.2410E-06
```

```
  A= 28.537E+01 B1=-2.8743E+02   B2=
REGSS= 1.4627E+05 D= 2.5313E-03
                    RUN  595 40 PRESS=  62.44    31

 53.8967E-03
   3
      DF     SS          MS          VR
REGN   2  3.4115E+05  1.7057E+05  1.5721E+05
DEVN  90  9.7650E+01  1.0850E-00
TOTL  92  3.4125E+05

  A= 41.371E+01 B1=-4.1044E+02   B2= 5.9000E-04   C= 5.8717E-02
               SEB1= 1.6630E-00 SEB2= 3.1348E-01 SEC= 1.8608E-06

  A= 41.371E+01 B1=-4.1044E+02   B2=
REGSS= 3.4115E+05 D= 2.3028E-03
```

APPENDIX I
EXPERIMENTAL DATA

```
18 20   36       P= 11.37
    2800E1        1000E0        9945E0        616E-2        3080E1        8000E0
   2629E-1                      3700E1
 339     350    361     371    381     392    402     412    421     431    441     451
 460     469    477     485    493     501    508     516    524     532    539     547
 554     561    568     576    583     590    597     604    611     617    623     628
 583     597    611     623    634     646    658     670    682     693    703     713
 723     733    743     753    762     771    779     787    795     803    811     818
 825     831    837     843    848     854    860     866    872     878    884     889
28 20   36       P= 24.73
    2200E1        1000E0        9945E0        610E-2        3050E1        9000E0
   2579E-1                     -1200E1
 324     337    350     363    376     388    400     412    424     436    447     457
 468     478    489     499    509     519    529     538    547     556    565     574
 584     593    602     611    621     630    639     649    658     667    675     683
 565     584    602     621    639     658    675     692    709     725    739     752
 766     779    790     801    813     824    836     847    858     869    879     889
 900     910    920     930    940     949    959     968    976     983    990     998
38 20   36       P=61.64
    3400E1        1000E0        9983E0        616E-2        3080E1        7000E0
   2234E-1                      3700E1
 316     325    333     342    351     359    367     375    382     390    398     406
 413     421    428     436    444     451    459     467    474     482    490     497
 504     511    517     524    531     537    544     551    557     564    571     577
 571     583    595     607    620     632    644     656    666     675    685     694
 703     712    721     730    738     747    756     765    774     781    787     794
 800     807    814     820    827     834    841     848    854     860    866     872
48 20   36       P=157.24
    5500E1        1500E0        9980E0        610E-2        3050E1        1200E1
    2670-1                     -1200E1        5500E1
 311     318    324     331    338     344    351     357    363     370    376     382
 388     393    398     403    408     413    419     424    429     435    440     445
 450     455    461     466    472     477    483     488    493     499    504     509
```

```
    519    524    528    533    537    542    546    550    554    559    563    567
    571    576    580    584    588    592    596    600    604    608    612    617
    621    625    629    633    637    641    645    649    652    655    658    661
    666    669    672    675    677    679    682    685    688    691    694    697
    700    703    706    709    712    715    717    720    722    725    727    729
    732    734    737    739    742    745    747    750    752    755    758    760
  58 20   37        P=390.07
       7600E1        2000E0        9970E0        616E-2        3080E1        1000E1
     3922E-1                       3700E1
    352    361    370    379    388    397    406    415    424    433    442    451
    460    469    477    485    493    500    508    515    523    531    538    545
    551    557    563    569    576    582    588    594    600    606    612    618
    624    634    644    653    663    672    682    692    701    710    719    727
    736    745    754    763    771    779    786    794    801    809    816    824
    832    839    847    854    860    867    874    881    887    894    901    908
    915    921
 189 20   36        P= 25.22
       2600E1        1000E0        9945E0        616E-2        3080E1        7000E0
     2629E-1                       3700E1
    324    336    348    359    371    382    393    403    413    423    433    443
    454    464    474    484    494    503    512    521    530    539    548    556
    565    574    583    591    599    606    614    621    629    637    644    652
    583    599    614    629    644    660    674    688    701    714    727    740
    751    763    774    785    796    806    816    826    836    846    855    865
    873    881    889    896    904    912    920    928    936    943    949    955
 289 20   20        P= 62.95
       3400E1        2000E0        9945E0        616E-2        3080E1        9000E0
       2579-1                      3700E1        4000E1
    300    317    335    353    371    388    406    424    441    457    473    488
    503    508    533    548    562    576    590    603    617    629    641    653
    665    676    687    697    707    716    725    734    743    751    760    768
    776    784    792    800    807    815    822    829    836    843    850    856
    863    870    877    883    889    895    902    908    914    920    926    931
 389 20   36        P=155.79
       6000E1        2000E0        9983E0        610E-2        3050E1        9000E0
     2234E-1                      -1200E1
```

```
  312   320   327   334   342   350   357   364   371   379   386   393
  400   408   415   422   429   436   442   449   455   461   467   474
  480   486   492   499   505   511   516   521   527   532   538   544
  521   532   544   556   567   578   589   599   610   621   632   642
  652   662   671   679   687   694   701   708   714   720   726   731
  736   741   746   750   754   757   760   763   766   769   771   773
489 20  36     P=391.97
     8800E1      4000E0     9980E0     202E-1      1010E2      1400E1
    2670E-1                -2700E2
  323   334   344   355   367   379   390   400   410   419   429   438
  446   455   464   473   481   490   500   508   516   525   534   542
  550   557   564   571   578   586   593   601   609   616   623   630
  534   550   564   578   593   609   623   637   651   666   680   694
  706   718   730   741   750   758   766   775   784   793   802   811
  820   829   836   843   850   855   860   865   870   875   881   886
589 20  48     P= 10.69
     4200E1      1000E0     9970E0     610E-2      3050E1      1100E1
    3922E-1                -1200E1
  301   307   312   318   323   329   334   340   346   352   357   363
  368   374   379   385   390   396   401   407   412   417   422   428
  433   439   444   450   455   460   465   470   475   480   485   490
  495   500   505   510   514   519   523   528   532   537   541   546
  523   532   541   549   557   564   572   580   588   595   601   608
  614   621   628   635   642   649   655   662   669   676   682   688
  693   698   703   708   713   718   722   727   731   736   740   745
  749   754   758   762   766   771   775   779   783   787   790   793
187 21  26     P=393.68
     9000E1      3000E0     9945E0     201E-1      1005E2      9000E0
     2629-1                  1300E2     7800E1
  316   324   333   341   349   356   363   371   378   385   392   399
  406   412   419   425   432   439   445   451   456   462   468   473
  478   483   488   493   498   502   507   511   515   519   523   528
  532   536   540   545   549   553   557   561   565   569   573   577
  580   583   586   589   592   595   598   601   604   607   610   613
  616   619   621   624   626   628   630   633   635   638   640   643
  645   648   650   653   655   658
```

```
287 21  30      P=  9.92
     3000E1       1500E0       9945E0       630E-2       3150E1       1000E1
    2579E-1                    4500E1
   319    332   346    359   371    383   397    409   421    433   444    455
   466    477   488    498   508    518   527    536   545    554   563    572
   581    589   597    605   613    621   545    563   581    597   613    628
   642    656   670    684   698    708   718    728   737    746   754    763
   771    779   787    795   802    810   818    825   831    838   843    848
387 21  28      P=24.96
     3000E1       1500E0       9983E0       616E-2       3080E1       8000E0
     2234-1                    3700E1       4200E1
   303    317   330    343   357    370   383    396   409    422   434    446
   458    470   482    493   505    516   526    537   547    557   567    577
   586    595   603    612   620    629   637    644   651    659   666    673
   680    688   695    702   709    716   722    729   735    742   749    755
   762    768   775    781   787    793   798    803   808    813   818    822
   827    832   836    841   845    850   854    858   862    865   869    873
   877    880   883    886   889    892   895    897   900    902   905    907
487 21  30      P= 62.61
     3800E1       2000E0       9980E0       616E-2       3080E1       1100E1
     2670-1                    3700E1
   314    328   342    356   370    383   396    408   420    432   443    454
   465    476   486    496   507    517   527    536   545    554   563    572
   581    590   598    606   614    622   536    554   572    590   606    622
   638    654   668    682   695    707   719    730   741    751   761    771
   781    790   799    808   816    824   831    838   845    853   860    866
587 21  28      P=156.58
     6000E1       3000E0       9970E0       616E-2       3080E1       1100E1
     3922-1                    3700E1       8400E1
   315    329   344    359   373    388   402    415   428    442   455    468
   481    494   506    518   530    540   550    559   569    579   588    598
   607    616   624    632   639    647   654    661   668    674   681    687
   694    700   707    713   719    726   732    739   746    753   760    767
   774    781   787    794   800    807   813    819   824    829   834    838
   843    847   852    856   861    866   870    875   879    884   889    893
   897    901   904    907   910    913   917    920   924    927   930    932
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186 20  36      P= 63.91
      3300E1        1500E0        9945E0        630E-2        3150E1        8000E0
     2629E-1                      4500E1
   318     330    341     353    364     376    388     399    410     421    431     442
   452     462    472     482    492     501    510     519    528     537    545     554
   562     571    579     587    595     602    610     617    624     632    639     646
   545     562    579     595    610     624    639     654    668     683    698     712
   727     741    754     766    778     789    800     809    818     827    835     842
   849     854    860     867    873     879    886     892    898     904    910     916
286 20  36      P=157.00
      3600E1        1500E0        9945E0        616E-2        3080E1        1000E1
     2579E-1                      3700E1
   311     323    336     348    359     370    381     392    404     415    426     437
   448     458    468     478    489     499    509     519    530     540    550     560
   569     578    586     595    604     613    621     630    638     646    654     661
   569     586    604     621    638     654    668     682    696     710    724     737
   750     763    776     788    799     811    822     832    842     851    861     871
   880     888    895     902    909     917    924     930    937     944    951     957
386 20  30      P=390.86
      7000E1        2000E0        9983E0        201E-1        1005E2        9000E0
      2234-1                      1300E0        6000E1
   310     318    325     332    339     346    353     360    367     373    379     385
   391     397    403     408    414     419    424     430    436     441    446     451
   456     461    466     471    475     480    485     490    494     498    503     507
   512     516    521     525    529     533    537     541    545     548    552     555
   559     562    566     569    572     575    578     581    584     587    590     592
   595     597    600     602    605     607    610     612    615     617    619     621
   623     625    627     629    631     633    636     638    640     642    644     646
   648     650    652     653    655     657
486 20  22      P= 10.13
      3400E1        2000E0        9980E0        616E-2        3080E1        1100E1
      2670-1                      3700E1        4400E1
   312     328    343     357    370     384    397     410    422     434    446     458
   470     482    494     505    516     525    535     544    554     563    572     581
   589     598    606     615    623     632    640     647    653     660    666     673
   679     685    692     698    704     710    716     722    728     733    738     743
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  748    752    756    760    764    767    771    774    778    781    784    788
  791    794    798    801    804    808
 586 20  42       P= 24.26
     4200E1       1500E0       9970E0       630E-2       3150E1       1100E1
    3922E-1                    4500E1
  326    337    347    356    366    376    385    394    403    412    421    430
  438    447    455    463    471    479    487    495    503    511    519    526
  533    541    548    555    562    569    575    581    587    593    599    604    609
  609    615    620    626    631    637    562    575    587    599    609    620
  631    643    654    665    676    686    697    708    718    728    736    743
  751    760    768    776    783    790    797    804    811    818    824    831
  837    843    849    855    861    867    872    878    883    888    892    897
 185 20  42       P=155.84
     4200E1       1500E0       9945E0       630E-2       3150E1       8000E0
    2629E-1                    4500E1
  330    339    348    357    366    374    383    391    399    407    415    423
  431    438    446    453    461    468    476    483    490    497    504    512
  519    526    533    540    546    552    558    564    570    577    583    589
  595    601    607    612    617    621    546    558    570    583    595    607
  617    626    636    645    655    664    673    682    691    700    709    718
  727    735    743    751    759    766    773    779    785    791    796    801
  807    812    817    822    828    833    838    843    848    853    857    861
 285 20  36       P=390.04
     3900E1       1500E0       9945E0      2012E-2       1006E2       1200E1
    2579E-1                    4000E1
  329    341    352    364    376    387    398    408    419    429    440    450
  459    469    478    487    496    505    515    524    533    542    550    558
  566    575    583    591    599    607    615    623    631    639    646    653
  583    599    615    631    646    660    674    688    702    716    729    742
  755    768    780    792    803    814    825    836    846    856    865    874
  883    892    900    908    916    924    932    939    946    954    961    968
 385 20  36       P= 11.08
     3400E1       1000E0       9983E0       616E-2       3080E1       1100E1
    2234E-1                    3700E1
  324    332    340    349    357    364    371    379    386    393    401    408
  415    422    429    435    442    448    454    460    466    471    476    481
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   486   492   496   501   505   509   514   518   522   526   531   535
   531   539   547   555   563   571   578   586   594   601   608   615   622
   622   629   636   642   649   656   662   667   673   678   684   689
   695   700   704   709   714   719   723   727   731   735   739   743
 485 20  36       P= 24.92
      4350E1      1500E0       9980E0       630E-2       3150E1       1100E1
     2670E-1                   4500E1
   303   312   321   330   338   346   353   361   368   376   383   391
   398   404   410   417   423   430   436   443   449   454   460   465
   471   476   482   487   492   498   503   508   513   518   523   528
   498   508   518   528   537   546   554   563   571   579   587   595
   602   609   615   622   629   635   641   647   653   659   665   670
   675   680   685   690   694   698   701   704   708   711   714   718
 585 20  42       P= 61.20
      5400E1      1500E0       9970E0       630E-2       3150E1       1000E1
     3922E-1                   4500E1
   328   335   343   350   357   364   371   378   385   393   400   407
   414   421   428   435   442   449   455   461   467   473   478   484
   489   495   500   506   511   516   521   527   532   537   541   546
   550   555   560   564   569   573   550   560   569   579   588   597
   605   613   621   628   636   643   650   656   663   669   675   681
   687   693   699   704   709   714   719   723   728   732   737   741
   745   749   753   757   761   765   769   773   777   780   783   786
 198 20  36       P=  9.79
      4500E1      1500E0       9945E0       630E-2       3150E1       5700E1
     2629E-1    -8541E-3       4500E1
   307   315   323   331   339   346   353   360   367   374   381   388
   394   400   407   413   419   425   430   436   442   447   453   459
   465   471   476   482   487   493   498   503   508   513   517   522
   498   508   517   526   535   544   552   560   568   576   583   590
   597   605   612   618   624   630   636   641   647   652   657   662
   667   671   676   681   686   690   695   699   703   706   710   714
 298 20  36       P= 25.00
      3600E1      1500E0       9945E0       616E-2       3080E1       8700E1
      2579-1      -8541-3      3700E1
   300   311   322   332   342   352   362   372   381   390   399   407
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    415     422     430     438     446     453     461     468     475     482     489     496
    503     510     517     523     530     536     542     548     553     559     565     571
    503     517     530     542     553     565     577     588     599     610     621     632
    643     654     664     673     682     690     698     706     714     721     728     736
    743     750     757     763     769     774     780     785     790     795     799     804
 398 20   48         P= 61.49
        4500E1          1500E0          9983E0          630E-2          3150E1          4100E1
       2234E-1        -8541E-3          4500E1
    334     344     353     363     373     382     391     399     408     416     424     432
    440     447     454     462     469     477     484     492     500     507     514     520
    527     534     541     548     554     560     567     573     579     585     592     598
    604     610     616     621     627     633     639     645     650     656     661     667
    567     579     592     604     616     627     639     650     661     673     684     695
    706     717     727     737     746     755     763     771     779     787     795     803
    811     818     825     832     839     846     853     859     865     872     878     884
    889     894     899     903     908     912     916     920     925     929     933     937
 498 20   30         P=156.26
        9000E1          3000E0          9980E0          616E-2          3080E1          6700E1
        2670-1          -8541-3         3700E1
    291     298     306     313     320     327     334     340     347     354     361     368
    375     382     388     394     399     404     409     414     419     424     429     434
    439     444     449     454     459     464     469     479     489     498     507     515
    522     529     537     544     551     558     565     571     576     582     587     593
    599     605     611     617     622     626     630     634     637     640     644     649
 598 20   22         P=391.00
        1800E2          6000E0          9970E0          1994-2          9970E1          4400E1
        3922-1          -8541-3         8000E1          1320E2
    289     296     302     309     315     322     328     335     341     347     352     358
    364     369     374     380     385     390     395     400     404     408     412     416
    420     424     428     432     436     440     444     448     452     456     460     463
    466     469     472     475     478     481     484     487     490     493     496     498
    500     503     505     507     509     511     513     516     518     520     522     525
    527     529     531     533     535     537
  19 20   36         P= 25.48
        4800E1          1500E0          9945E0          612E-2          3060E1          2700E1
       2629E-1        -8541E-3          6000E1
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 279   286   293   300   306   312   318   324   330   336   342   348
 353   359   365   371   376   382   387   392   397   402   407   412
 417   422   427   431   436   441   445   450   454   459   463   468
 454   463   472   481   489   496   503   509   516   522   528   534
 539   545   551   557   562   567   572   577   582   587   592   597
 601   606   610   615   619   623   627   631   634   638   641   645
29 20  48        P= 62.69
    5700E1       1500E0       9945E0       612E-2       3060E1       4400E1
   2579E-1     -8541E-3       6000E1
 313   320   327   334   340   347   353   359   365   371   377   383
 388   394   399   405   411   417   422   428   433   438   443   449
 454   459   464   470   475   480   486   491   496   501   505   510
 515   520   525   529   534   538   543   547   552   556   560   564
 525   534   543   552   560   568   575   583   590   597   604   611
 618   624   631   638   644   651   658   664   671   677   682   687
 693   698   703   708   713   718   722   725   728   731   734   737
 740   743   745   748   751   754   757   760   763   766   768   770
39 20  42        P=156.26
    5400E1       2000E0       9983E0       600E-2       3000E1       2500E1
    2234-1       -8541-3
 314   324   333   342   351   360   369   378   386   394   402   410
 418   426   434   441   449   457   464   472   479   487   494   502
 510   518   525   533   541   549   556   563   570   577   584   591
 598   606   613   620   627   633   533   549   563   577   591   606
 620   633   645   657   669   681   693   704   714   724   734   744
 755   765   775   785   796   806   816   825   834   842   850   858
 865   872   879   886   892   899   906   913   919   925   931   937
49 20  42        P=390.71
    1080E2       4000E0       9980E0       494E-3       9880E1       3500E1
    2670-1       -8541-3      -7000E1
 336   346   356   366   375   384   392   401   410   419   428   437
 446   454   462   470   478   486   494   503   511   519   527   535
 543   551   558   566   573   580   587   594   601   608   615   622
 628   634   641   647   653   659   566   580   594   608   622   634
 647   659   670   681   692   703   714   724   734   744   753   763
 773   783   792   801   810   818   825   833   840   847   854   861
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   868   874   880   886   892   898   904   909   913   918   922   926
 59 20  36      P= 10.10
      5200E1      2000E0      9970E0      600E-2      3000E1      3400E1
      3922-1     -8541-3
   299   308   318   327   336   345   354   363   371   379   388   396
   404   412   420   427   435   443   450   457   464   471   477   484
   491   498   504   511   518   524   530   537   543   549   554   560
   504   518   530   543   554   565   576   587   596   605   614   622
   631   640   649   657   664   671   678   684   691   697   704   710
   716   723   729   734   740   745   750   754   759   763   768   772
197 20  48      P=390.33
      9000E1      3000E0      9945E0      600E-2      3000E1      2600E1
      2629-1     -8541-3
   326   335   344   354   363   372   381   389   398   406   414   423
   431   439   447   454   462   469   476   483   490   497   503   510
   516   523   530   536   543   549   556   562   568   574   579   585
   591   597   602   608   614   620   626   632   637   643   648   654
   556   568   579   591   602   614   626   637   648   657   666   675
   683   692   701   710   719   727   735   743   752   760   768   777
   785   794   802   811   819   827   834   840   846   852   858   864
   869   874   878   882   886   889   893   896   899   902   905   908
297 20  30      P=  9.93
      2800E1      1500E0      9945E0      600E-2      3000E1      4700E1
      2579-1     -8541-3                  4500E1
   302   316   329   342   355   368   381   394   406   418   430   442
   453   464   476   487   498   509   519   529   539   548   557   566
   574   583   592   600   609   617   626   634   642   651   659   667
   675   683   690   698   705   713   720   728   735   741   747   753
   759   766   772   778   784   789   794   800   805   810   815   819
   824   829   833   838   843   847   852   857   861   865   868   872
   876   879   883   887   891   894   898   902   906   909   912   915
   917   920   923   926   929   931
397 20  42      P= 24.69
      3900E1      1500E0      9983E0      612E-2      3060E1      2000E1
     2234E-1    -8541E-3      6000E1
   302   313   323   333   343   352   361   370   379   387   396   404
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  413   421   429   438   446   454   461   469   476   483   491   498
  506   514   521   528   535   543   550   556   563   569   575   582
  588   594   600   606   612   619   521   535   550   563   575   588
  600   612   625   637   648   659   669   679   689   699   708   716
  724   731   739   747   754   761   769   776   783   789   795   801
  806   811   816   820   825   829   834   838   842   846   849   852
497 20  44     P= 67.77
     6600E1      1500E0      9980E0      612E-2      3060E1      2500E1
    2670E-1    -8541E-3      6000E1
  310   316   322   327   332   337   342   347   352   357   362   367
  372   376   381   385   390   394   399   403   408   413   417   422
  426   431   435   440   444   449   453   458   462   467   471   475
  479   483   487   491   495   498   502   505   509   516   523   530
  537   543   550   557   563   569   575   580   586   591   596   601
  605   610   615   620   624   629   633   638   642   646   650   654
  658   661   665   668   671   675   678   681   685   688   691   694
  697   700   702   705
597 20  36     P=156.44
     1110E2      3000E0      9970E0      612E-2      3060E1      2300E1
    3922E-1    -8541E-3      6000E1
  307   314   321   328   335   341   347   353   359   364   370   376
  382   388   393   399   404   410   416   421   426   431   437   442
  447   452   457   461   466   471   476   480   484   488   492   496
  504   512   520   528   536   543   549   556   562   569   575   582
  588   594   600   605   610   614   618   622   626   630   634   639
  643   647   651   655   659   662   665   668   671   673   675   677
196 20  36     P= 62.11
     4200E1      2000E0      9945E0      600E-2      3000E1      1800E1
     2629-1     -8541-3
  312   324   335   347   359   371   382   393   404   414   424   434
  444   455   465   475   485   494   504   514   523   533   542   550
  558   567   576   584   592   600   608   616   624   632   640   647
  533   550   567   584   600   616   632   647   662   676   689   701
  713   724   735   746   756   765   773   780   787   795   802   809
  816   823   830   837   843   849   856   862   868   874   879   884
296 20  30     P=156.30
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      5100E1      3000E0      9945E0      612E-2      3060E1      1900E1
      2579-1     -8541-3      6000E1
  308   325   342   358   374   390   406   421   436   451   465   479
  491   503   516   528   541   553   565   577   589   601   613   625
  636   646   656   665   673   682   553   577   601   625   636   656
  673   691   708   725   743   760   776   789   802   815   828   841
  853   865   874   883   891   899   906   913   920   927   933   939
396 20  36     P=391.59
      7200E1      3000E0      9983E0      600E-2      3000E1      2200E1
      2234-1     -8541-3
  322   334   346   357   368   379   391   402   413   423   433   444
  454   465   475   485   495   506   516   525   535   544   553   562
  571   581   590   600   609   618   627   635   643   651   658   666
  571   590   609   627   643   658   674   688   702   716   730   744
  758   772   783   794   804   813   823   832   842   851   861   871
  880   889   898   907   915   923   931   939   947   954   961   968
496 20  36     P= 10.32
      5400E1      1500E0      9980E0      612E-2      3060E1      1900E1
     2670E-1    -8541E-3      6000E1
  292   299   305   311   317   323   328   334   340   345   351   356
  362   367   373   378   383   388   393   397   402   407   412   416
  420   424   429   433   438   442   446   450   454   458   462   465
  469   475   482   488   494   500   506   512   518   524   530   535
  541   547   552   557   562   567   572   577   582   586   590   594
  598   602   606   609   612   614   616   618   621   623   625   627
596 20  36     P= 24.75
      5600E1      1500E0      9970E0      600E-2      3000E1      2200E1
      3922-1     -8541-3                  4500E1
  310   317   324   331   338   345   351   358   364   371   378   384
  391   397   403   409   415   420   426   431   437   442   447   453
  458   463   468   474   479   484   490   495   500   506   511   517
  522   527   532   537   542   547   551   556   560   564   568   572
  575   579   583   586   590   593   596   599   602   605   607   610
  612   615   618   621   624   626   629   632   635   637   640   643
  646   649   651   654   657   659   661   663   666   668   670   673
  675   677   679   682   684   686   687   689   691   693   695   697
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   699   701   703   705   707   709   711   713   715   716   718   719
195 20  36     P=156.00
      5600E1      2000E0      9945E0      600E-2      3000E1      1900E1
      2629-1     -8541-3
   323   333   343   353   362   371   380   389   398   407   416   424
   433   441   449   457   466   474   482   489   497   504   511   519
   526   532   539   546   552   558   565   571   576   582   587   593
   552   565   576   587   598   608   619   629   639   649   659   669
   678   686   694   701   709   716   724   732   739   747   754   761
   768   774   779   784   789   794   799   804   809   813   818   823
295 20  30     P=391.31
      6600E1      3000E0      9945E0      612E-2      3060E1      2600E1
      2579-1     -8541-3      6000E1
   325   338   351   365   378   391   403   415   427   439   451   463
   475   487   499   511   523   534   545   556   567   578   589   598
   607   616   624   633   642   651   589   607   624   642   660   678
   696   714   732   750   767   782   796   810   824   836   848   860
   870   881   891   902   912   922   931   941   951   960   970   980
395 20  30     P= 10.46
      4500E1      1500E0      9983E0      612E-2      3060E1      1400E1
      2234-1     -8541-3      6000E1
   275   283   290   296   302   309   316   322   328   333   339   345
   351   356   362   368   374   380   385   391   397   402   407   411
   415   419   423   427   431   435   439   447   455   463   471   479
   487   494   501   508   515   521   527   533   538   543   548   552
   557   561   566   570   574   578   582   586   589   593   597   601
495 20  36     P= 25.14
      4800E1      1500E0      9980E0      600E-2      3000E1      1700E1
      2670-1     -8541-3
   289   296   303   310   317   323   330   337   343   350   356   362
   368   375   381   388   394   400   405   410   416   421   426   431
   436   442   447   452   457   462   467   472   476   481   486   490
   476   486   495   504   512   519   525   532   539   546   552   559
   565   572   578   584   591   597   603   610   616   621   627   632
   638   643   647   651   656   660   664   669   673   676   679   681
595 20  42     P= 62.52
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      5600E1      2000E0      9970E0       600E-2      3000E1      2700E1
      3922-1     -8541-3
   307   315   324   332   341   349   358   367   375   384   392   400
   408   416   424   433   441   449   456   463   471   478   484   491
   498   504   511   518   524   531   537   543   549   555   560   566
   571   576   582   587   592   597   524   537   549   560   571   582
   592   602   612   622   631   641   651   660   670   679   689   698
   707   715   723   730   736   743   750   756   762   768   774   779
   785   790   796   801   807   813   818   824   829   834   839   844
  18 30  30     P=  9.96
      3000E1      1500E0      9945E0       600E-2      3000E1      3100E1
      2629-1
   332   345   359   372   384   396   408   420   431   442   452   463
   473   484   495   505   515   525   534   543   552   562   571   580
   590   599   608   617   626   634   552   571   590   608   626   642
   656   669   683   696   708   721   733   744   756   766   776   786
   794   802   810   818   826   834   841   848   854   860   866   872
  28 30  30     P= 24.46
      3000E1      1500E0      9945E0       612E-2      3060E1      2300E1
      2579-1                  6000E1
   325   339   353   366   380   393   406   419   432   444   456   467
   477   488   498   508   517   527   536   545   554   564   573   582
   592   601   610   619   627   636   554   573   592   610   627   644
   659   674   689   703   718   732   746   758   770   782   794   805
   816   826   835   843   852   860   866   872   878   883   889   894
  38 30  30     P= 63.16
      3200E1      2000E0      9983E0       600E-2      3000E1      1200E1
      2234-1
   316   334   351   366   382   398   413   426   440   454   467   479
   491   503   515   526   538   549   560   571   582   593   604   614
   625   636   646   657   667   676   538   560   582   604   625   646
   667   685   702   719   737   752   768   783   797   809   820   831
   842   852   863   873   883   893   902   911   921   929   936   943
  48 30  36     P=156.18
      6000E1      3000E0      9980E0       612E-2      3060E1      1400E1
      2670-1                  6000E1
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  324   338   351   364   378   391   404   417   429   441   452   464
  476   488   500   511   522   532   542   552   562   572   582   592
  601   610   619   628   636   643   650   657   664   671   678   685
  562   582   601   619   636   650   664   678   692   706   719   733
  746   759   772   783   793   802   812   822   830   838   846   853
  861   869   877   884   890   897   903   908   913   917   922   927
 58 30  32     P=391.13
     9000E1      4000E0      9970E0      1976-2      9880E1      3200E1
     3922-1                              1280E2
  304   315   326   337   348   359   369   379   389   399   409   418
  427   436   444   453   462   470   479   487   496   504   512   520
  527   534   541   548   555   562   569   577   584   590   596   602
  609   616   622   628   634   641   647   653   658   663   668   673
  678   683   688   692   697   701   706   711   715   720   724   729
  733   737   742   746   751   755   759   763   766   769   773   777
  781   784   788   791   795   798   801   804   807   810   813   815
  818   821   824   827   830   833   836   839   842   845   847   850
189 30  36     P= 25.07
     3000E1      1500E0      9945E0      600E-2      3000E1      2900E1
     2629-1
  303   316   328   339   351   362   373   384   394   405   416   427
  438   448   459   469   479   488   497   506   515   524   533   542
  551   559   568   576   584   593   601   608   616   623   629   636
  515   533   551   568   584   601   616   629   644   658   673   685
  698   709   719   729   739   749   758   766   775   783   791   799
  807   815   822   828   834   841   847   853   858   863   868   873
289 30  30     P= 62.75
     3000E1      1500E0      9945E0      600E-2      3000E1      1500E1
     2579-1
  331   345   358   372   385   399   412   426   439   451   463   476
  488   500   511   522   533   544   555   566   577   587   598   608
  618   628   638   648   657   667   577   598   618   638   657   677
  696   714   732   749   764   781   795   808   821   834   846   857
  868   879   880   901   912   923   934   945   955   965   976   986
389 30  42     P=156.45
     6300E1      1500E0      9983E0      1994-2      9970E1      2300E1
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     2234-1                  8000E1
  254   259   264   269   273   278   283   287   291   295   299   303
  306   309   313   317   320   324   328   331   335   339   342   346
  350   353   357   361   364   367   370   374   377   380   383   387
  390   394   397   401   404   408   411   417   423   429   434   439
  444   448   453   457   461   465   468   471   475   478   481   484
  488   491   494   498   501   504   507   509   512   515   518   521
  524   527   530   533   536   539   542   545   548   550   552   554
489 30  30     P=390.76
     6300E1      3000E0      9980E0      1994-2      9970E1      1500E1
     2670-1                  8000E1
  327   341   356   370   383   396   409   422   435   448   460   472
  483   495   507   519   530   541   551   562   573   584   595   605
  614   623   632   642   651   660   584   605   623   642   660   679
  697   715   730   745   760   775   789   802   814   827   839   850
  861   872   882   892   902   912   922   931   941   951   960   968
589 30  36     P= 10.60
     4500E1      1500E0      9970E0      612E-2      3060E1      1400E1
     3922-1                  6000E1
  315   324   333   342   350   358   366   374   382   389   397   405
  413   421   427   433   439   445   451   457   463   469   475   481
  487   493   499   504   509   514   520   525   531   536   541   547
  520   531   541   552   562   573   583   593   603   612   621   629
  636   644   652   660   667   674   680   687   693   699   705   710
  715   720   725   730   734   739   743   748   752   757   761   765
187 30  30     P=390.39
     8100E1      3000E0      9945E0      1994-2      9970E1      2700E1
     2629-1                  8000E1
  308   317   326   334   342   350   359   367   375   384   392   400
  408   415   422   429   436   443   450   456   462   468   474   480
  486   492   498   503   509   515   503   515   527   538   548   558
  567   576   585   593   601   608   616   623   631   638   645   652
  658   664   670   675   680   685   689   694   699   703   708   712
287 30  36     P=  9.72
     3300E1      1000E0      9945E0      612E-2      3060E1      3100E1
     2579-1                  6000E1
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   311    318    326    333    340    347    353    360    366    373    380    386
   393    339    405    411    417    423    429    435    441    446    452    457
   462    467    473    478    483    489    494    499    503    507    512    516
   507    516    525    533    542    551    559    566    573    580    587    594
   601    608    614    620    626    632    637    643    649    654    660    666
   671    676    681    686    690    695    700    704    708    712    715    718
387 30   30        P= 24.72
     3000E1       1500E0       9983E0       600E-2       3000E1       1000E1
     2234-1
   359    373    389    403    417    430    443    457    469    481    493    504
   516    528    539    550    560    571    581    592    602    612    622    632
   641    650    660    669    679    689    602    622    641    660    679    698
   714    730    746    762    775    788    802    816    828    838    849    859
   869    879    888    897    905    912    921    928    935    942    948    954
487 30   36        P= 62.58
     4800E1       1500E0       9980E0       600E-2       3000E1       1300E1
     2670-1
   302    310    318    326    333    341    348    356    363    379    386    382
   389    395    402    409    416    422    429    434    440    446    451    457
   463    468    474    479    484    488    492    497    501    506    511    516
   501    511    520    528    536    544    552    560    568    576    583    590
   597    604    611    618    625    633    638    644    649    655    661    666
   671    675    680    685    689    694    698    701    705    709    713    716
587 30   30        P=156.24
     6000E1       3000E0       9970E0       600E-2       3000E1       2400E1
     3922-1
   318    332    345    358    371    384    396    408    421    424    446    457
   468    480    490    499    509    518    528    537    547    556    566    574
   583    592    600    608    617    625    547    566    583    600    617    633
   649    664    678    693    708    722    735    747    759    771    782    792
   801    810    818    826    834    842    848    854    860    866    872    878
186 30   30        P= 62.17
     4200E1       1500E0       9945E0       612E-2       3060E1       1000E1
     2629-1                    6000E1
   325    334    343    352    361    369    378    386    394    403    411    419
   427    436    444    452    459    466    474    482    489    496    503    510
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   517   524   530   536   542   548   542   553   564   575   585   595
   604   613   621   629   637   645   653   661   668   676   683   689
   696   702   709   715   721   727   732   738   743   749   754   760
286 30  42      P=156.87
       4600E1      2000E0      9945E0      600E-2      3000E1      1400E1
       2579-1
   320   331   342   353   364   374   385   395   406   416   426   435
   444   454   463   471   479   488   496   504   512   519   526   533
   540   547   554   560   567   574   580   586   593   599   606   612
   618   625   631   637   643   650   533   547   560   574   586   599
   612   625   637   650   663   676   687   699   710   720   729   738
   746   754   762   771   779   787   794   801   808   814   821   826
   833   839   845   851   857   863   869   876   882   888   894   900
386 30  42      P=391.87
       7000E1      2000E0      9983E0      1994-2      9970E1      9000E0
       2234-1                  8000E1
   303   311   318   325   332   339   346   353   360   367   373   379
   386   392   399   405   412   418   423   429   434   440   445   451
   456   462   467   472   477   482   487   492   497   502   507   512
   517   521   526   530   534   539   512   521   530   539   548   557
   565   574   583   591   600   607   613   619   625   631   637   643
   649   655   661   667   673   678   682   687   692   697   701   705
   709   713   718   722   726   730   734   737   741   744   748   751
486 30  36      P=  9.91
       3750E1      1500E0      9980E0      600E-2      3000E1      1100E1
       2670-1
   302   311   320   329   339   348   357   364   372   379   387   394
   402   409   417   425   433   440   447   455   462   470   477   484
   491   499   506   513   520   527   533   538   543   548   553   558
   499   513   527   538   548   558   568   578   588   597   606   614
   622   631   639   647   653   659   665   671   677   683   689   694
   698   703   707   712   717   721   725   729   733   737   742   746
586 30  30      P= 25.69
       4500E1      1500E0      9970E0      612E-2      3060E1      1500E1
       3922-1                  6000E1
   320   329   338   347   355   364   373   381   390   399   407   415
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    423   431   439   447   455   463   471   479   487   495   503   511
    518   525   532   540   547   554   562   578   591   604   617   627
    635   643   651   659   666   673   680   686   692   699   705   711
    718   724   731   737   743   750   756   762   768   773   778   782
185 30  42       P=155.36
       4500E1      1500E0      9945E0      612E-2      3060E1      1800E1
       2629-1                  6000E1
    312   321   330   339   348   357   366   374   382   391   399   407
    415   423   431   439   447   454   462   469   476   484   491   498
    505   512   520   527   534   541   547   554   560   566   572   577
    582   588   593   598   603   609   547   560   572   582   593   603
    614   624   635   645   655   664   673   682   691   699   708   716
    724   731   739   747   754   762   770   777   783   789   795   801
    806   811   816   821   826   831   836   841   846   851   855   859
285 30  36       P=390.94
       5600E1      2000E0      9945E0      1976-2      9880E1      2000E1
       2579-1                 -7000E1
    306   315   324   333   342   351   360   369   378   387   396   404
    412   421   429   437   445   453   461   468   476   483   491   498
    505   512   518   525   531   538   544   550   556   562   568   574
    531   544   556   568   579   590   601   612   622   631   640   649
    658   666   674   682   689   696   703   709   716   723   729   735
    740   746   751   756   761   766   771   776   780   785   789   794
385 30  42       P= 10.05
       2800E1      1000E0      9983E0      600E-2      3000E1      9000E0
       2234-1
    313   322   330   339   348   356   364   372   380   388   396   403
    411   418   426   433   441   448   456   463   471   477   484   491
    498   504   511   518   524   530   535   541   546   551   557   562
    567   573   578   583   587   592   524   535   546   557   567   578
    587   597   607   616   626   635   644   652   660   668   676   683
    689   696   703   710   717   724   730   737   743   749   755   760
    766   771   776   781   785   789   793   797   801   804   808   812
485 31  30       P= 25.21
       4500E1      1500E0      9980E0      628E-2      3140E1      1100E1
       2670-1                  6000E1
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  285   293   300   308   315   323   330   337   344   350   357   364
  370   376   382   388   394   400   406   411   417   423   429   435
  440   445   450   455   460   465   470   478   486   494   502   510
  517   524   532   539   546   553   560   566   572   578   583   588/
  593   599   604   610   615   620   626   631   636   641   645   649
585 30  30     P= 62.78
     6300E1      3000E0      9970E0      612E-2      3060E1      1100E1
     3922-1                  6000E1
  304   317   328   339   350   360   370   381   391   402   412   422
  431   441   450   459   468   477   485   493   502   510   518   526
  534   542   549   556   563   570   510   526   542   556   570   583
  596   608   619   630   640   649   658   667   675   684   693   702
  712   721   730   739   747   754   761   767   772   778   783   788
198 30  30     P= 10.04
     4350E1      1500E0      9945E0      628E-2      3140E1      2700E1
     2629-1     -8541-3      6000E1
  326   336   346   355   364   373   382   390   398   405   413   421
  429   437   444   451   458   465   472   480   487   494   501   507
  513   519   525   531   537   543   543   553   563   573   583   593
  602   611   620   629   637   644   651   658   665   672   678   684
  691   698   705   711   717   722   727   732   736   741   746   751
298 30  36     P= 24.89
     3600E1      1500E0      9945E0      600E-2      3000E1      7600E1
     2579-1     -8541-3
  315   324   333   342   351   360   369   378   388   397   406   414
  423   431   440   448   457   465   473   481   488   496   503   511
  518   526   533   539   545   551   558   564   570   577   583   590
  518   533   545   558   570   583   596   609   622   635   648   661
  674   687   700   713   725   737   748   759   769   778   787   796
  804   809   814   819   822   825   828   831   834   837   840   842
398 30  48     P= 62.41
     4800E1      1500E0      9983E0      628E-2      3140E1      2500E1
     2234-1     -8541-3      6000E1
  303   311   319   327   335   342   349   356   363   370   377   384
  391   398   404   410   417   423   429   435   441   447   453   458
  463   469   474   480   485   490   496   501   506   512   517   522
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  527   532   537   542   547   551   556   560   564   568   572   577
  506   517   527   537   547   556   564   572   581   589   597   604
  612   619   626   633   640   647   653   660   666   672   679   685
  690   696   702   708   713   718   723   728   733   738   743   748
  752   756   760   764   768   772   776   779   782   785   789   792
498 30  36     P=155.48
     6000E1      3000E0      9980E0      600E-2      3000E1      1900E2
     2670-1     -8541-3
  306   316   326   336   346   356   366   376   385   394   403   411
  419   428   436   444   452   459   466   474   481   489   496   503
  510   518   525   533   540   547   554   561   568   574   581   588
  481   496   510   525   540   554   568   581   594   608   621   633
  644   656   667   675   684   692   701   709   718   726   734   741
  749   757   764   772   779   786   793   800   806   812   818   823
598 30  36     P=389.70
     1620E2      3000E0      9970E0      2050-2      1025E2      4250E2
     3922-1     -8541-3      7000E1      1080E2
  309   313   317   321   325   330   334   338   342   347   351   355
  359   363   367   371   374   378   382   385   389   393   397   400   403
  403   407   410   414   418   421   425   429   432   435   438   441   462
  444   447   450   453   456   459   462   465   468   471   474   477
  479   482   485   488   490   493   496   498   500   503   505   508
  510   512   514   517   519   522   524   527   529   531   533   536
  538   540   542   544   546   548   549   551   552   554   556   558
  560   562   564   568   569   571   572   574   575   577   578   579
  580   581   582   583   585   586   587   588   589   590   591   592
 19 30  36     P= 25.63
     4500E1      1500E0      9945E0      628E-2      3140E1      2000E1
     2629-1     -8541-3      6000E1
  312   321   330   338   346   354   363   371   379   388   396   404
  413   421   428   435   443   451   458   465   472   480   487   494
  501   508   515   522   529   535   542   548   554   560   565   571
  542   554   565   576   587   598   608   618   628   637   646   654
  663   671   680   688   695   702   710   717   723   729   735   741
  747   752   757   762   766   771   775   780   784   788   792   796
 29 30  42     P= 63.07
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      5700E1      1500E0      9945E0      628E-2      3140E1      4700E1
      2579-1     -8541-3      6000E1
   302   308   315   321   327   333   339   344   350   356   361   367
   372   377   382   387   392   397   403   408   413   418   422   427
   431   436   441   446   450   454   458   463   467   472   476   480
   485   489   493   497   500   503   493   500   507   513   520   527
   534   541   548   554   561   567   573   579   584   590   596   601
   607   612   617   622   626   631   636   640   644   648   651   655
   659   663   667   670   674   677   680   683   687   690   693   696
39 30  30       P=156.68
      6000E1      3000E0      9983E0      600E-2      3000E1      7300E1
      2234-1     -8541-3
   300   312   324   335   346   356   367   377   387   396   406   416
   425   434   443   451   460   468   477   485   493   501   509   516
   524   531   538   544   551   558   493   509   524   538   551   565
   577   589   601   613   626   638   649   658   667   676   684   693
   702   711   720   729   738   746   754   762   770   777   783   788
49 30  30       P=391.13
      1000E2      4000E0      9980E0      600E-2      3000E1      3800E2
      2670-1     -8541-3
   359   367   376   384   392   400   408   415   422   429   437   444
   451   458   465   472   479   486   492   498   505   511   518   524
   531   536   542   548   554   559   536   548   559   571   580   590
   600   610   620   629   639   648   657   666   675   684   693   700
   707   714   720   727   735   742   749   756   763   769   775   780
59 30  30       P=  9.96
      5300E1      3000E0      9970E0      600E-2      3000E1      4600E1
      3922-1     -8541-3                  7100E1
   300   313   326   339   351   363   375   387   399   410   421   432
   443   453   463   473   482   492   501   510   519   528   537   546
   554   562   570   577   585   592   551   559   567   575   583   590
   598   605   612   619   627   634   641   648   654   660   666   671
   677   682   688   693   698   703   709   714   719   723   727   731
   707   712   717   722   726   730   734   738   742   746   750   753
   757   761   764   768   772   776   779   783   786   790   793   797
   801   804   807   810   813   816
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197 30  36        P=389.41
     8800E1        4000E0        9945E0        600E-2        3000E1        7600E1
     2629-1       -8541-3
  314     327     338     349     361     372     383     394     404     414     424     434
  445     455     464     474     483     492     502     511     521     529     538     547
  556     565     573     582     591     599     607     614     621     628     636     643
  538     556     573     591     607     621     636     650     664     677     689     702
  714     726     737     747     757     767     776     785     794     803     811     819
  826     833     838     843     849     854     860     866     871     875     879     883
297 30  36        P=  9.97
     3000E1        1500E0        9945E0        600E-2        3000E1        1800E1
     2579-1       -8541-3
  308     320     332     344     356     368     379     389     399     410     420     431
  442     452     463     474     484     494     503     513     522     531     541     550
  558     566     574     582     590     598     606     614     621     628     635     642
  522     541     558     574     590     606     621     635     649     661     673     684
  696     708     719     729     739     749     757     766     776     784     792     799
  807     815     822     828     834     839     845     851     857     863     869     874
397 30  30        P= 25.16
     3300E1        1500E0        9983E0        628E-2        3140E1        1600E1
     2234-1       -8541-3        6000E1
  318     331     344     357     370     383     395     406     417     428     439     451
  462     473     484     496     507     518     528     539     549     559     570     580
  590     600     609     619     629     638     570     590     609     629     647     664
  680     696     712     728     743     758     773     788     802     816     830     843
  855     866     877     887     898     908     918     927     936     944     953     962
497 30  42        P= 62.77
     6000E1        1500E0        9970E0        628E-2        3140E1        2500E1
     2670-1       -8541-3        6000E1
  300     307     313     319     325     331     337     343     349     354     360     366
  371     377     382     388     393     398     403     408     413     418     423     428
  433     437     442     447     452     457     461     466     471     475     479     484
  488     492     496     501     505     509     505     513     522     530     538     546
  553     560     567     574     581     588     594     599     604     609     614     619
  624     629     635     640     645     650     655     660     665     670     674     678
  681     684     687     689     692     694     696     698     700     702     704     706
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597 30  25     P=156.44
     1110E2      4500E0      9970E0      628E-2      3140E1      3900E1
     3922-1     -8541-3      6000E1      1110E2
  299   310   321   332   342   351   361   371   380   390   399   408
  417   425   434   443   451   459   468   476   484   492   500   508
  515   519   526   532   539   545   552   558   564   570   576   582
  588   593   599   605   611   616   622   627   632   636   641   645
  649   653   656   660   664   668   672   676   680   684   689   693
  697   702   706   710   714   718   722   724   727   729   731   734
  736   739   741
196 30  30     P= 62.71
     4000E1      2000E0      9945E0      600E-2      3000E1      5000E1
     2629-1     -8541-3
  315   328   341   353   365   376   387   399   410   421   432   443
  454   464   475   485   494   504   513   522   531   540   549   557
  566   574   582   590   598   605   531   549   566   582   598   613
  629   634   657   669   681   693   705   717   729   741   752   762
  771   780   788   796   804   812   820   828   835   843   850   856
296 30  30     P=156.42
     5700E1      3000E0      9945E0      628E-2      3140E1      2400E1
     2579-1     -8541-3      6000E1
  323   337   352   366   380   395   409   423   436   449   461   474
  487   498   509   520   531   542   552   562   572   582   592   601
  611   621   631   640   649   658   562   582   601   621   640   657
  673   689   704   718   733   747   759   772   784   796   807   818
  828   838   848   857   866   874   882   890   898   905   911   917
396 30  36     P=391.12
     7000E1      5000E0      9983E0      600E-2      3000E1      1640E2
     2234-1     -8541-3
  300   315   330   345   359   373   386   399   413   426   439   451
  464   476   487   499   510   521   531   541   551   561   571   581
  591   601   610   619   627   636   644   654   662   670   678   686
  487   510   531   551   571   591   610   627   644   662   678   695
  711   726   740   752   764   777   780   802   814   826   836   846
  856   865   874   882   889   896   902   909   916   922   928   934
496 30  32     P=  9.94
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        5700E1         1500E0         9980E0         628E-2         3140E1         1600E1
        2670-1        -8541-3         6000E1         4800E1
    278     283     289     295     300     306     311     317     322     327     332     336
    341     345     350     354     359     363     367     371     375     379     383     387
    392     396     400     404     408     412     415     419     422     426     429     433
    437     440     443     446     449     452     455     458     460     463     465     468
    471     473     476     478     481     483     486     488     491     493     496     498
    501     503     505     508     510     512     515     517     520     522     524     527
    529     531     533     535     537     539     541     543     545     547     548     550
    551     552     553     555     557     558     559     561     562     564     565     566
596 30   30         P= 25.54
        5700E1         3000E0         9970E0         600E-2         3000E1         3000E1
        3922-1        -8541-3
    309     321     335     348     360     373     386     398     410     422     434     446
    457     468     478     487     497     506     516     525     534     543     552     560
    569     578     587     595     603     610     525     543     560     578     595     610
    625     640     655     668     680     692     704     716     728     739     749     758
    768     775     783     790     797     804     811     818     824     831     838     845
195 30   42         P=155.45
        4400E1         2000E0         9945E0         600E-2         3000E1         6400E1
        2629-1        -8541-3
    304     314     325     336     347     358     369     380     381     402     413     424
    434     445     455     465     475     484     494     503     512     521     530     539
    547     556     565     574     582     591     599     606     614     622     629     637
    644     652     659     667     674     680     530     547     565     582     599     614
    629     644     659     674     687     700     712     725     737     750     762     774
    786     798     808     818     828     838     848     857     865     873     881     889
    898     906     913     919     926     932     939     946     953     960     966     972
295 30   36         P=390.12
        6900E1         3000E0         9945E0         628E-2         3140E1         1110E2
        2579-1        -8541-3         6000E1
    318     330     341     352     363     374     385     395     405     415     426     436
    446     457     467     477     487     498     508     518     527     536     545     554
    562     571     579     588     596     604     612     620     628     636     644     651
    554     571     588     604     620     636     651     667     682     698     714     729
    744     759     773     785     796     807     818     829     840     850     861     872
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  882   891   901   910   919   927   935   943   951   959   966   973
395 30   30    P= 10.33
     4200E1      1500E0      9983E0      628E-2      3140E1      1300E1
     2234-1     -8541-3      6000E1
  315   324   333   342   351   359   367   375   383   391   399   407
  414   421   428   436   443   450   457   464   471   478   484   490
  497   503   510   516   523   529   523   535   545   554   563   572
  582   591   600   609   618   626   634   641   648   655   662   669
  675   682   688   693   699   704   710   715   720   724   728   732
495 30   30    P= 24.37
     5000E1      2000E0      9980E0      600E-2      3000E1      2100E1
     2670-1     -8541-3
  314   324   333   343   352   362   371   379   387   395   404   412
  420   428   436   444   452   459   466   473   479   485   491   497
  504   509   515   521   527   533   509   521   533   545   556   567
  578   589   598   607   616   625   633   640   646   653   659   664
  669   675   680   686   691   696   701   707   712   717   722   727
595 30   30    P= 62.82
     6300E1      3000E0      9970E0      600E-2      3000E1      3400E1
     3922-1     -8541-3
  311   323   336   348   361   372   383   394   405   415   426   436
  446   455   465   475   485   494   504   514   524   533   543   552
  562   572   581   590   599   607   533   552   572   590   607   621
  636   648   661   673   685   697   710   722   735   746   757   767
  777   786   795   802   808   815   822   828   835   842   848   854
 18 40   36    P=  9.70
     3200E1      1000E0      9945E0      600E-2      3000E1      1600E1
     2629-1
  338   346   354   362   371   379   387   395   403   411   419   427
  435   442   449   456   464   471   478   485   493   500   507   514
  520   526   532   538   544   550   556   562   568   573   579   584
  568   579   589   600   610   620   629   637   646   654   662   670
  677   683   690   696   703   709   716   722   728   734   740   746
  751   757   762   767   772   777   782   786   790   794   798   802
 28 40   30    P= 24.83
     3000E1      1500E0      9945E0      628E-2      3140E1      9000E0
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     2579-1                 6000E1
  355   370   385   400   415   429   444   458   472   485   497   509
  522   534   544   554   565   575   586   596   606   615   625   635
  645   654   663   672   681   690   606   625   645   663   681   699
  715   731   745   760   774   788   801   813   826   839   851   862
  873   884   895   906   916   924   932   940   948   955   962   969
 38 40  36      P=63.41
     3300E1      1500E0      9983E0      600E-2      3000E1      8000E0
     2234-1
  306   317   329   340   350   360   370   380   390   400   410   420
  429   439   449   458   468   477   486   494   502   510   519   527
  535   543   551   559   567   574   581   588   596   603   610   617
  519   535   551   567   581   596   610   624   637   650   661   672
  683   694   705   716   725   734   743   751   759   766   774   781
  788   796   803   810   817   823   830   836   843   850   856   861
 48 40  30      P=156.29
     7200E1      3000E0      9980E0      628E-2      3140E1      9000E0
     2670-1                 6000E1
  325   335   346   356   366   376   386   396   406   415   425   435
  445   455   465   474   483   492   500   509   518   527   535   543
  550   558   565   572   578   584   550   565   578   590   602   613
  625   637   649   659   670   680   690   700   710   717   724   732
  740   748   755   762   770   776   782   788   793   799   804   808
 58 40  30      P=391.08
     9500E1      5000E0      9970E0      600E-2      3000E1      1100E1
     3922-1
  313   329   344   359   373   386   400   413   426   440   453   466
  480   493   507   521   534   548   561   573   584   595   606   617
  628   639   650   661   672   682   573   595   617   639   661   682
  701   720   738   755   772   787   800   814   827   839   851   864
  882   891   901   910   919   927   935   943   951   959   966   973
189 40  36      P= 25.01
     3000E1      1500E0      9945E0      600E-2      3000E1      1600E1
     2629-1
  310   324   338   350   362   373   385   395   406   417   428   438
  449   459   469   479   489   498   508   517   526   535   544   553
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  561    569    578    586    594    602    610    618    625    632    638    644
  526    544    561    578    594    610    625    638    651    664    678    691
  703    715    727    738    749    758    767    776    785    794    802    810
  817    824    830    836    842    848    854    860    866    871    875    879
289 40   42        P= 62.26
       2700E1        1000E0         9945E0         600E-2         3000E1         1500E0
       2579-1
  316    327    337    347    358    368    378    387    397    406    416    425
  434    443    452    461    469    478    486    495    503    512    521    529
  538    547    554    562    569    577    585    593    601    608    616    624
  631    638    644    651    657    663    562    577    593    608    624    638
  651    663    676    689    702    714    726    738    750    762    773    784
  794    804    814    823    832    841    850    858    867    876    885    893
  901    908    916    924    932    940    948    955    963    970    978    985
389 40   30        P=156.36
       5700E1        3000E0         9982E0         628E-2         3140E1         2300E1
       2234-1                       6000E1
  297    310    323    335    348    360    372    384    396    407    417    428
  438    449    459    468    477    486    496    505    514    523    532    541
  550    559    567    575    583    591    505    523    541    559    575    591
  605    618    631    643    654    666    678    689    700    712    721    730
  740    749    757    764    772    780    788    795    801    807    814    819
489 40   30        P=390.52
       1260E2        4500E0         9980E0         2050-2         1025E2         4000E1
       2670-1                       7000E1
  301    310    319    328    336    343    350    357    364    371    379    386
  394    401    408    414    420    427    433    440    446    453    460    466
  472    478    484    489    495    500    495    505    514    523    533    542
  551    560    568    576    583    590    598    605    612    619    626    631
  636    641    646    651    656    661    666    671    676    681    685    689
589 40   42        P= 10.12
       5700E1        1500E0         9970E0         628E-2         3140E1         1200E1
       3922-1                       6000E1
  307    314    320    327    334    340    347    353    359    365    372    378
  384    391    398    404    409    414    420    425    431    436    442    447
  453    459    464    469    474    479    483    488    493    498    503    517
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  512   517   522   527   532   537   522   532   541   550   558   565
  573   580   587   594   600   607   614   620   626   632   638   644
  650   656   662   668   673   678   682   687   691   696   700   705
  710   714   719   723   728   732   735   738   741   744   747   750
187 40  24     P=390.77
     7500E1      3000E0      9945E0      2050-2      1025E2      1100E1
     2629-1                  7000E1
  305   316   327   338   348   357   367   377   386   395   404   413
  422   431   439   447   454   462   470   478   485   492   499   507
  521   534   546   558   569   581   592   602   611   621   631   639
  647   654   661   667   673   680   686   691   696   701   705   710
287 40  28     P=  9.90
     3000E1      1500E0      9945E0      628E-2      3140E1      8000E0
     2579-1                  6000E1
  302   315   329   342   354   366   378   389   401   411   422   433
  442   451   461   470   479   489   498   508   517   526   534   542
  550   559   567   574   517   534   550   567   580   593   606   618
  629   640   651   663   674   684   695   705   713   721   729   737
  744   751   758   765   772   779   785   791
387 40  30     P= 25.06
     3000E1      1500E0      9983E0      600E-2      3000E1      8000E0
     2234-1
  309   322   334   346   358   370   381   393   404   414   425   435
  445   455   464   473   482   491   499   508   517   525   533   541
  549   557   565   573   580   587   517   533   549   565   580   594
  608   621   639   646   657   669   680   690   699   708   717   726
  735   744   752   761   768   775   782   788   795   801   806   811
487 40  33     P= 62.67
     3600E1      2000E0      9980E0      600E-2      3000E1      9000E0
     2670-1
  319   334   349   362   376   389   402   415   428   442   455   467
  479   491   502   514   526   537   548   558   568   578   589   598
  607   616   624   632   641   649   657   665   673   548   568   589
  607   624   641   657   673   689   704   718   733   746   758   769
  779   790   800   809   819   828   838   848   857   866   876   885
  893   900   907   912   917   922
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587 40  30     P=156.53
     5400E1      3000E0      9970E0      600E-2      3000E1      1300E1
     3922-1
  308   324   340   355   370   386   401   416   431   445   459   473
  484   496   508   519   530   542   553   564   576   587   598   609
  619   629   640   650   659   669   553   576   598   619   640   659
  678   697   715   732   750   767   784   800   814   828   841   853
  865   877   889   901   914   926   938   950   962   974   984   995
186 40  28     P= 62.09
     3450E1      1500E0      9945E0      628E-2      3140E1      4100E1
     2629-1                  6000E1
  305   317   329   341   353   364   375   386   397   407   416   426
  436   446   455   464   473   482   490   498   505   513   520   528
  535   542   549   555   528   542   555   569   582   595   607   618
  630   640   649   659   668   677   685   693   700   707   713   721
  728   735   742   749   755   760   765   770
286 40  30     P=156.13
     3000E1      1500E0      9945E0      600E-2      3000E1      9000E0
     2579-1
  327   341   355   369   382   395   408   421   433   445   456   468
  480   491   502   514   526   536   546   556   566   576   586   596
  606   615   624   634   643   652   566   586   606   624   643   662
  680   699   717   735   751   766   780   793   806   819   833   845
  856   868   879   890   901   912   923   935   946   956   966   975
386 40  30     P=390.42
     5100E1      3000E0      9983E0      628E-2      3140E1      8000E0
     2234-1                  6000E1
  318   335   351   368   384   399   414   429   445   458   472   486
  500   514   527   539   551   563   576   588   600   612   624   635
  645   656   666   677   686   695   563   588   612   635   656   677
  695   714   733   752   771   789   805   821   835   850   863   875
  887   899   910   920   929   938   946   954   962   970   978   987
486 40  30     P= 10.01
     3450E1      1500E0      9980E0      600E-2      3000E1      1000E1
     2670-1
  323   334   345   356   366   376   387   397   408   417   426   435
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  444   453   462   470   478   485   493   500   508   516   523   530
  536   542   549   556   562   568   530   542   556   568   581   593
  605   617   629   640   650   660   669   679   688   697   706   714
  722   729   736   742   749   755   762   768   774   779   784   789
586 40  48     P= 25.41
     4500E1      1500E0      9970E0      628E-2      3140E1      1700E1
     3922-1                  6000E1
  324   333   342   352   361   370   379   389   398   407   416   424
  433   441   449   458   466   474   482   490   498   505   512   519
  526   533   540   548   555   562   569   576   583   589   595   601
  607   613   618   624   630   636   642   648   654   660   666   672
  569   583   595   607   618   630   642   654   666   678   690   701
  712   723   733   743   752   761   770   778   786   792   800   807
  814   822   829   836   842   848   854   860   865   870   876   881
  886   891   896   900   905   910   915   920   925   930   934   938
185 40  42     P=156.68
     3300E1      1500E0      9945E0      628E-2      3140E1      1000E1
     2629-1                  6000E1
  304   317   330   342   354   366   377   389   400   411   421   431
  441   451   461   471   481   490   499   508   517   526   535   544
  553   561   569   577   584   591   599   606   614   621   629   636
  644   651   658   665   672   679   535   553   569   584   599   614
  629   644   658   672   684   696   708   719   730   741   751   761
  771   782   792   802   811   820   829   837   845   853   861   868
  875   882   888   894   900   906   912   918   923   928   933   938
285 40  36     P=390.15
     5100E1      1500E0      9945E0      1976-2      9880E1      1100E1
     2579-1                 -7000E1
  319   327   335   343   350   357   364   372   379   386   393   400
  407   413   418   424   429   434   440   445   450   456   461   467
  472   478   483   489   494   499   504   508   513   518   523   527
  523   532   541   550   558   566   574   582   590   598   605   612
  618   624   630   636   642   648   653   659   664   670   675   680
  684   689   694   698   702   706   710   713   716   720   723   727
385 40  42     P= 10.01
     2800E1      1000E0      9983E0      600E-2      3000E1      9000E0
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     2234-1
  325   334   343   351   360   369   377   385   394   402   410   418
  426   433   440   448   455   463   470   477   484   491   497   503
  509   516   522   528   534   541   547   553   559   565   570   575
  581   586   591   596   601   606   534   547   559   570   581   591
  601   611   621   630   639   649   658   667   676   685   692   699
  706   713   720   726   733   740   746   752   758   764   769   754
  779   784   789   794   800   805   810   815   820   825   829   833
485 40  36     P= 25.24
     3450E1      1500E0      9980E0      628E-2      3140E1      9000E0
     2670-1                  6000E1
  305   316   327   338   348   359   369   379   389   399   408   418
  428   437   446   455   464   472   481   490   498   505   512   520
  527   535   543   550   556   562   568   574   580   586   592   597
  520   535   550   562   574   586   597   608   619   630   641   652
  663   674   683   692   700   709   717   725   732   739   747   754
  762   769   775   780   786   792   798   803   808   813   818   822
585 40  30     P= 63.02
     4200E1      3000E0      9970E0      628E-2      3140E1      2200E1
     3922-1                  6000E1
  299   319   338   355   372   389   407   425   440   455   470   485
  500   514   528   542   556   569   582   593   603   614   625   635
  646   656   666   677   687   697   528   556   582   603   625   646
  666   687   707   726   744   762   780   797   814   829   842   854
  866   877   888   899   908   916   924   932   941   950   958   964
198 40  36     P= 10.31
     3300E1      1500E0      9945E0      628E-2      3140E1      1300E1
     2629-1     -8541-3      6000E1
  306   318   329   341   353   364   376   388   400   411   422   433
  443   453   464   474   484   493   503   513   523   532   542   552
  562   571   581   590   600   609   618   627   636   644   652   660
  542   562   581   600   618   636   652   668   683   698   713   727
  740   752   763   774   785   795   805   814   822   831   839   847
  854   861   867   873   878   882   885   889   892   895   898   901
198 40  30     P= 10.31
     3600E1      1500E0      9945E0      628E-2      3140E1      1300E1
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      2629-1     -8541-3      6000E1
   329   341   353   364   376   388   400   411   422   433   443   453
   464   474   484   493   503   513   523   532   542   552   562   571
   581   590   600   609   618   627   581   600   618   636   652   668
   683   700   713   727   740   752   763   774   785   795   805   814
   822   831   839   847   854   861   867   873   878   882   885   889
298 40  42      P= 25.19
      2400E1      1000E0      9945E0      600E-2      3000E1      1070E2
      2579-1     -8541-3
   310   320   330   340   350   360   370   380   390   400   410   419
   429   438   448   457   466   475   484   493   502   511   519   528
   536   545   553   562   570   578   586   593   601   608   615   623
   631   638   645   651   658   665   536   553   570   586   601   615
   631   645   658   672   686   699   711   723   735   747   759   770
   782   793   804   814   825   835   845   854   863   872   882   891
   900   908   916   924   931   939   946   953   959   966   973   979
398 40  48      P= 62.67
      3900E1      1500E0      9983E0      628E-2      3140E1      5800E1
      2234-1     -8541-3      6000E1
   302   312   322   332   342   352   362   372   381   391   401   410
   419   428   437   446   455   463   471   479   487   495   502   510
   518   526   533   541   548   556   563   569   576   583   590   597
   604   611   617   624   630   637   643   650   656   662   668   674
   533   548   563   576   590   604   617   630   643   656   668   680
   692   704   716   728   740   751   762   772   782   792   801   809
   816   823   829   835   841   847   853   859   865   872   877   883
   888   894   900   905   910   915   919   924   928   932   936   940
498 40  36      P=155.79
      6300E1      3000E0      9980E0      600E-2      3000E1      1400E2
      2670-1     -8541-3
   324   335   346   356   367   378   388   399   410   420   431   441
   451   462   472   481   490   499   507   515   523   530   538   546
   553   561   569   576   584   592   600   607   614   620   626   633
   530   546   561   576   592   607   620   633   645   657   670   682
   694   705   716   726   736   746   755   764   773   781   789   796
   803   810   817   825   831   838   845   852   859   866   872   879
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598 40   31       P=388.29
      4800E1       1500E0         9970E0        628E-2        3140E1        1350E2
      3922-1      -8541-3         6000E1
   306     316     325     334     343     352     360     369     378     386     394     403
   411     420     428     437     445     454     462     471     479     487     495     503
   511     519     527     534     542     549     556     572     587     602     616     631
   646     661     676     691     706     721     737     752     767     782     797     812
   827     842     857     872     887     902     917     931     946     959     973     986
   999    1012
 19 40   32       P= 25.50
      4800E1       1500E0         9945E0        628E-2        3140E1        2500E1
      2629-1      -8541-3         6000E1
   316     325     334     342     350     358     366     374     381     389     396     403
   410     417     424     431     437     443     450     456     463     469     476     482
   488     494     500     506     511     517     523     528     533     542     552     561
   571     580     588     596     603     611     619     627     634     640     647     653
   659     664     670     675     681     686     691     695     700     704     708     712
   716     721     725     729
 29 40   36       P= 62.16
      3600E1       1500E0         9945E0        628E-2        3140E1        5100E1
      2579-1      -8541-3         6000E1
   319     331     343     354     365     376     387     399     410     421     432     442
   452     462     472     482     491     500     509     519     528     537     546     555
   564     573     581     589     597     605     613     621     630     638     646     654
   564     581     597     613     630     646     662     677     691     705     720     735
   749     762     776     790     803     816     829     841     852     862     873     882
   891     900     908     916     924     932     939     947     954     961     968     976
 39 40   36       P=156.68
      6600E1       3000E0         9983E0        600E-2        3000E1        2900E1
      2234-1      -8541-3
   302     314     326     337     348     359     370     380     390     399     408     417
   426     434     443     451     459     468     477     486     494     502     510     518
   525     532     540     548     555     563     570     578     585     592     599     605
   510     525     540     555     570     585     599     611     622     633     644     654
   664     674     684     694     702     711     720     727     735     744     751     759
   766     773     779     785     791     797     803     808     813     817     822     827
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 49 40  36    P=389.34
      1400E2      4000E0      9980E0      1976-2      9880E1      3800E1
      2670-1     -8541-3     -7000E1
   280   286   293   299   305   311   317   323   329   334   339   344
   349   354   360   365   371   376   381   386   391   396   401   405
   410   414   419   423   427   432   436   441   445   449   453   456
   456   464   470   477   484   491   498   504   511   518   524   529
   535   540   545   550   556   561   566   572   576   580   584   589
   593   596   600   603   607   611   615   618   621   624   627   630
 59 40  36    P= 10.35
      6200E1      2000E0      9970E0      600E-2      3000E1      5100E1
      3922-1     -8541-3
   306   314   322   330   338   345   353   360   367   374   380   387
   394   400   407   414   420   427   433   439   445   451   457   463
   469   474   480   486   492   497   502   508   513   519   524   529
   508   519   529   539   548   556   565   573   580   587   594   602
   609   616   622   629   635   642   649   655   662   668   674   680
   685   691   696   701   706   711   715   719   723   727   731   734
197 40  30    P=390.29
      8400E1      3000E0      9945E0      1976-2      9880E1      2200E1
      2629-1     -8541-3     -7000E1
   250   257   263   270   276   282   269   296   302   308   314   320
   325   331   336   342   347   353   359  -365   370   375   380   384
   388   393   397   401   405   410   405   414   423   431   440   448
   456   463   470   478   485   492   499   504   509   514   519   524
   529   533   537   541   545   548   551   554   557   560   563   565
297 40  32    P=  9.73
      3300E1      1500E0      9945E0      600E-2      3000E1      4500E1
      2579-1     -8541-3
   320   331   342   352   363   373   384   394   403   412   422   432
   442   451   460   469   478   487   496   504   512   520   527   535
   542   549   557   564   572   579   587   594   527   542   557   572
   587   601   615   629   640   650   659   669   678   687   696   705
   714   722   730   738   746   754   761   768   774   781   788   794
   800   807   813   819
397 40  36    P= 25.41
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        4500E1      1500E0       9983E0        628E-2       3140E1       2100E1
        2234-1     -8541-3       6000E1
    313     321     329     337     345     353     361     369     377     384     390     397
    403     410     416     423     430     436     443     449     455     462     468     474
    480     486     492     498     503     509     514     519     524     529     535     540
    514     524     535     545     555     565     575     584     593     602     610     618
    626     632     639     645     651     656     662     667     673     679     684     689
    694     699     704     708     713     717     721     725     729     733     737     741
497 40   28        P= 62.72
        5100E1      3000E0       9980E0        628E-2       3140E1       2400E1
        2670-1     -8541-3       6000E1
    301     316     330     345     358     372     385     399     413     426     438     449
    461     472     483     493     502     512     522     532     541     550     559     568
    578     587     595     603     512     532     550     568     587     603     620     636
    650     664     677     689     701     713     723     733     743     752     762     771
    780     788     796     804     811     817     823     828
597 40   30        P=156.58
        9450E1      4500E0       9970E0        628E-2       3140E1       4100E1
        3922-1     -8541-3       6000E1
    312     324     336     349     361     373     386     398     410     421     432     442
    452     462     473     483     493     502     511     521     530     540     549     557
    565     573     581     589     596     603     540     557     573     589     603     615
    628     642     655     669     681     693     703     713     723     733     743     752
    761     770     779     786     793     800     807     813     820     826     833     840
196 40   30        P= 62.30
        3600E1      2000E0       9945E0        600E-2       3000E1       2000E1
        2629-1     -8541-3
    310     324     338     351     363     376     388     401     414     426     437     449
    460     471     482     493     504     514     523     533     542     551     560     569
    578     587     595     603     611     619     523     542     560     578     595     611
    627     642     656     668     680     692     704     715     726     737     747     757
    768     778     787     796     804     812     820     828     834     840     846     852
296 40   24        P=156.37
        5100E1      3000E0       9945E0        628E-2       3140E1       2700E1
        2579-1     -8541-3       6000E1
    316     332     348     365     381     396     411     426     441     456     470     485
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   499   512   524   536   548   559   570   581   592   602   612   621
   559   581   602   621   639   656   672   688   703   718   733   747
   760   772   784   795   806   817   826   834   842   850   857   863
396 40  42     P=390.37
      7800E1      2000E0      9983E0      1976-2      9880E1      2300E1
      2234-1     -8541-3     -7000E1
   294   300   306   312   318   324   329   334   340   345   350   355
   361   366   371   376   382   387   392   397   402   406   411   415
   420   424   429   433   437   441   444   448   452   456   460   464
   467   471   474   478   482   486   478   486   494   501   508   515
   522   528   534   540   545   550   555   559   564   569   574   578
   583   587   592   596   600   605   609   614   618   623   627   631
   634   637   640   643   646   648   650   653   656   659   662   664
496 40  36     P= 10.57
      4800E1      1500E0      9980E0      628E-2      3140E1      2300E1
      2670-1     -8541-3      6000E1
   303   311   319   326   333   339   346   353   360   367   374   381
   388   395   401   408   414   420   426   433   439   445   452   457
   462   467   472   477   482   487   492   497   502   507   511   516
   502   511   521   531   541   551   560   569   578   587   595   603
   611   619   627   634   640   645   650   655   660   664   668   672
   676   680   684   688   692   696   700   704   708   712   715   718
596 40  42     P= 25.36
      5600E1      2000E0      9970E0      600E-2      3000E1      7000E1
      3922-1     -8541-3
   301   310   318   326   334   342   350   358   366   374   382   389
   397   405   413   420   427   433   439   445   452   458   464   471
   477   483   489   495   501   507   513   519   525   531   537   542
   547   552   557   562   566   571   501   513   525   537   547   557
   566   576   586   596   605   614   623   631   640   649   656   663
   670   677   684   690   696   702   708   714   719   724   729   734
   739   744   748   752   756   760   764   768   772   775   779   782
195 40  36     P=156.06
      3400E1      2000E0      9945E0      600E-2      3000E1      1700E1
      2629-1     -8541-3
   301   316   330   344   358   372   386   400   413   427   440   453
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  465   477   489   501   512   523   534   544   555   565   575   585
  595   605   615   624   634   643   652   661   671   680   689   698
  523   544   565   585   605   624   643   661   680   698   714   730
  744   758   772   786   798   810   821   833   844   855   865   876
  886   896   906   914   922   931   939   947   954   960   967   974
295 40  24     P=390.26
     8400E1      3000E0      9945E0      2050-2      1025E2      2400E1
     2579-1     -8541-3      7000E1      7200E1
  278   286   294   302   309   316   322   329   336   342   349   356
  362   368   375   381   387   393   398   404   410   415   420   425
  430   434   439   443   447   452   456   460   464   468   473   477
  481   485   488   492   495   498   502   505   509   512   515   519
  522   525   528   531   534   536   539   541   543   545   548   550
  552   554   556   558   560   561   563   565   567   569   571   573
395 40  30     P= 10.35
     4200E1      1500E0      9983E0      628E-2      3140E1      2200E1
     2234-1     -8541-3      6000E1
  291   299   307   315   323   331   339   347   354   362   369   377
  384   391   397   403   409   415   422   428   435   441   447   452
  457   462   468   473   478   484   478   489   500   510   519   528
  537   545   552   561   568   575   582   588   594   600   605   610
  615   620   625   630   635   640   645   649   653   658   663   667
495 40  30     P= 24.98
     4400E1      2000E0      9980E0      600E-2      3000E1      2100E1
     2670-1     -8541-3
  318   329   340   351   362   372   382   392   401   410   419   429
  438   447   456   465   474   482   489   497   504   512   519   527
  534   542   549   556   563   570   519   534   549   563   577   591
  603   615   627   638   649   659   669   679   688   697   705   713
  721   728   735   743   750   756   761   765   769   773   778   783
595 40  36     P= 62.44
     4400E1      2000E0      9970E0      600E-2      3000E1      2900E1
     3922-1     -8541-3
  313   325   338   350   362   373   385   397   408   420   430   441
  452   463   473   484   495   505   515   524   533   542   551   561
  570   579   587   595   604   612   621   629   638   646   653   660
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551	570	587	604	621	638	653	668	682	696	701	726
738	751	763	776	789	791	803	824	836	848	859	871
882	892	901	910	920	929	938	947	956	964	973	982

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