PART I

THE SOLUBILITY OF GASES IN WATER-METHANOL MIXTURES

AND DERIVED THERMODYNAMIC PROPERTIES

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THERMODYNAMICS OF SOLUTION

The present investigation was carried out as part of a wider plan to determine the effect of methanol in breaking down the water structure in water-methanol mixtures and the possibility of preferential orientation of one or other of the constituent molecules of the solvent in the neighbourhood of the solute molecules.

Work on the solution process of ions in water-methanol mixtures by Perrin[96] seemed to indicate preferential orientation of water molecules round the ion. This was shown by Debye and McAuley[97] who stated that an ion in a mixture of polar molecules will tend to sift out the dipoles so that the more polar molecules congregate round the ion. Uncharged gas molecules however should not, and in fact do not, show any tendency to cause preferential orientation.

The measurement of the solubility of a gas over a temperature range makes possible the calculation of the thermodynamic quantities $\Delta G_{Solv.}$ $\Delta S_{Solv.}$ $\Delta H_{Solv.}$, that is the free energy, entropy and heat of solution.

If γ is the Ostwald Coefficient, which is the ratio of the volume of gas absorbed at any pressure and temperature, to the volume of the absorbing liquid, then

$$\Delta G_{solv.} = -RT \ln \gamma + RT \ln \frac{82.1 \times T}{V_1}$$

The last term corrects to the standard state used by Frank and Evans for the solution (i.e. $N_2 = 1$). As will be seen later this quantity varies from author to author.

$$\Delta S_{solv.} = -\frac{\partial}{\partial T}(\Delta G_{solv.}) = R \ln \gamma + RT \frac{\partial}{\partial T} \ln \gamma -$$
$$R \ln \frac{82.1 \times T}{V_1} + RT \frac{\partial}{\partial T} \ln V_1.$$

$$\Delta H_{solv.} = \Delta G_{solv.} + T\Delta S_{solv.}$$

The considerable amount of work which has been done on the theoretical evaluation of the entropy of solution may be divided into two types:

(i) Those postulating a mechanism; such as Eley's cavity formation.

(ii) Those postulating no definite mechanism; e.g. Frank and Evans.

A. ENTROPY OF SOLUTION FROM CAVITY FORMATION

A number of attempts have been made to calculate the entropy of solvation of gaseous ions[1,2,3.] and molecules[4,5,6,7.], but in practically all except that of Frank and Evans some mechanism has been postulated.

Eley splits the process of solution of gas molecules into two steps with the following energy changes:

1. Formation of a cavity in the liquid involving a positive internal energy change $\frac{\Delta E_C}{N}$.

2. The gas molecule is then placed in this cavity $-\frac{\Delta E_A}{N}$ calories of energy being liberated.

The internal energy change for the solution of a mole of gas is then

$$\Delta E^O = \Delta E_C + \Delta E_A$$

The idea of the formation of a cavity in the liquid was first put forward by Sisskind and Kassarnowsky[7] and Eley's treatment differs only in the method of calculating ΔE_C.

If $-\Delta E_A > \Delta E_C$ the temperature coefficient of solubility will be negative and if $\Delta E_C > -\Delta E_A$ it will be positive.

Korosy[8] has shown that in general the temperature coefficient is positive for gases with a critical temperature T_C under $180^O K$ and negative for those with T_C above 180°. Because the solvent-solute interaction term $-\Delta E_A$ would be expected to increase with increasing T_C such

a relation should arise for a series of gases in an organic solvent if ΔE_C is constant over the series in comparison with ΔE_A. These regularities break down in water where the temperature coefficient of solubility is nearly always negative at ordinary temperatures, i.e. $0 - 50°C$.

In calculating ΔE^O from Eley's model we have

$$\Delta E_{A,T} = \Delta E_{A,0} + kT^2 \frac{\partial}{\partial T} \ln \frac{Q_S}{Q_G}$$

$$\Delta E_{C,T} = \Delta E_{C,0} + kT^2 \frac{\partial}{\partial T} \ln \frac{Q'_W}{Q_W}$$

Q_S Partition function for the gas in solution.

Q_G "   "   for the gas.

Q'_W "   "   for water molecules in solution.

Q_W "   "   for pure water.

If we assume that there is no change in water structure from $0°K$ to $273°K$ we may write

$$\Delta E_{A,273} = \Delta E_{A,0}.$$

When a mole of gas dissolves in an infinite volume of solution at a concentration of 1 mole per litre a dilatation of V c.c. occurs.

For solvent $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$

α thermal expansion, β compressibility.

This is only true for small volume changes, and if we assume α and β are the same for the solution as for the

solvent we may write

$$\Delta S_C = \int_{V_1}^{V_2} \frac{\alpha}{\beta}\, dV = \frac{\alpha}{\beta} V = \cdot 0241 \frac{\alpha}{\beta} V \text{ cal. mole}^{-1} \text{ deg}^{-1}$$

Now $\left(\frac{\partial E}{\partial V}\right)_T = p + T\left(\frac{\partial S}{\partial V}\right)_T$ and as p is negligible

$$\Delta E_C = T \frac{\alpha}{\beta} V = \cdot 0241 \; T \frac{\alpha}{\beta} V \text{ cal. mole}^{-1}$$

ΔE_C and ΔS_C are found to be negligible at room temperature but to increase rapidly with T.

ΔE_A can be shown to vary only slightly with temperature:-

$$\Delta E_{A,T_2} = \Delta E_{A,T_1} + k \left(T_2^2 - T_1^2\right) \frac{\partial}{\partial T} \ln \frac{Q_S}{Q_G}$$

Now roughly $\frac{\partial}{\partial T} \ln \frac{Q_S}{Q_G} \approx N \frac{\partial}{\partial T} \ln \frac{N_H - N_G}{N_G} \approx -\cdot 008$

so that the maximum correction at $353^\circ K$ to the above values will be only 0·5 Kcal, i.e. small compared with ΔE_C.

Thus the temperature variation of ΔE° may be represented by variation in ΔE_C. Assuming this, the values listed below were calculated. These are somewhat larger than the observed differences but show the same general variation.

$$\delta E = \Delta E_T^\circ - \Delta E^\circ_{273}$$

Gas	$293^\circ K.$		$293^\circ K.$	
	δE	ΔE_C	δS	ΔS_C
He	0·11	0·61	0·4	2·0
Ne	0·5	0·65	1·7	2·2
A	0·7	1·23	2·1	4·3
K_r	1·07	1·51	4·6	5·2

The calculated values of E^O are obtained from

$$\Delta E_T^O = \Delta E_{A277} + \Delta E_{C,T}.$$

i.e. the value of ΔE_A used is that at $4^O C$.

Calculation of ΔE_C.

The energy of cavity formation may be estimated by any one of three available methods:

(a)   That used by Eley for most of his calculations:-

i.e. $\Delta E_C = T \frac{\alpha}{\beta} V$

(b)   If we assume a similar structure for the internal spherical surfaces as for the macroscopic solvent surface we may calculate ΔE_C from σ the surface free energy in ergs/cm^2.

$$\Delta E_C \approx \Delta H_C = 45 \cdot 4 \left(\sigma - T \frac{\partial \sigma}{\partial T} \right)$$

For $N_v = 10$ c.c. i.e. cavity radius = $1 \cdot 58$ $\overset{O}{A}$

This is comparable to Uhligs[11] $\Delta G_C = 4 \pi r^2 \sigma$

(c)   Lange and Marten[9] suggest

$$\Delta E_C = \Delta E_{vap} \left\{ \frac{r}{r_S} \right\}^2$$

where r_S is molecular radius of the solvent and r the radius of the cavity.   This ΔE_C is approximately the energy required to put a solute molecule onto a quasi lattice point of the solvent. The three methods give comparable results for

organic solvents.

$$\Delta E_C \text{ Kcal/mole } 20^{\circ}C.$$

Solvent	$r_S(\overset{\circ}{A})$	a	b^{10}	c
Water	1·4	0·32	5·31	13·1
EtOH	2·0	0·86	2·01	6·0
Hexane	3·2	--	2·25	1·69
Acetone	2·4	1·05	2·67	3·08
Ether	2·7	0·62	1·92	1·96
CCl_4	3·0	0·94	2·92	2·05
C_6H_6	2·5	1·01	3·4	3·01

For close packed liquids of little structure (i.e. organic liquids) it is to be expected that gas molecules will share quasi lattice points. For water, however, special kinds of cavity formation are possible and the discrepancies between the three methods for water are probably due to the fact that here quasi lattice points are not occupied.

In fact at high temperatures methods (a) and (c) yield comparable values for ΔE_C for water.

Calculation of ΔE_A

If we consider an inert gas atom as just touching a water molecule, i.e. with separation of centres cf

$r_G + r_W$ there are three forces operative:

    (i)   London Forces (attraction)

    (ii) Polarisation of gas atoms in the field of the solvent dipole (attraction)

    (iii) Repulsion Forces

$$\text{Thus}\,\Delta E_A = -\frac{\alpha_G \mu_W^2}{(r_G + r_W)^6} - \frac{3}{2}\frac{\alpha_G \alpha_W}{(r_G + r_W)^6}\frac{I_G I_W}{I_G + I_W} + \frac{b}{(r_G + r_W)^9}$$

α polarisability;   I ionisation potential.

Using values of μ_W and r_W from Bernal and Fowler[12] and α and I from London[13], we find that to obtain exact agreement with experiment for the rare gases about 10 water molecules must be packed round each solute molecule.

Gas	$r_G(\overset{o}{A})$	$-E_A$(kcal)	$\frac{\Delta E^O 277}{E_A}$
He	·93	·256	1·6
Ne	1·12	·166	10·9
A	1·54	·416	7·3
Kr	1·69	·436	9·8

Calculation of ΔS^O

If ΔS^O_{298} is plotted against $\frac{3}{2} R \ln \frac{m_G}{m}$ (where m_G is the reduced mass of the gas molecule against a water molecule), a straight line is obtained for the inert gases.

This is to be expected as no appreciable restriction of water in the field of the gas molecule occurs and the main change in entropy is due to loss of translational motion.

For gases of increasing complexity the ΔS° values are more negative indicating the presence of additional factors, e.g. some loss of rotation on solution.

Considering only loss of translational motion to contribute to ΔS° we find:-

$$\Delta S^{\circ} = \Delta S_C + R\left[\ln \frac{N_S + N_G}{N_G} + \frac{3}{2}\ln \frac{m_G}{m} + \ln \frac{V_G N}{V} + T\frac{\partial}{\partial T}\ln V_G - 1\right]$$

This equation can be derived as follows.

The entropy of 1 mole of gas at 1 atms. pressure in a volume V is

$$S_G^{\circ} = Nk\left[\ln \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\frac{V}{N} + \frac{5}{2}\right]$$

In solution, if we regard the N_S solvent molecules and N_G gas molecules as perfectly interchangeable, on $N_S + N_G$ quasi lattice points without seriously increasing the energy of the system, then the partition function $Q(T)$ for the system is given by the formula of Guggenheim.[14]

$$Q(T) = Q_S(T)\,Q_G(T)$$

$$= \frac{N_S + N_G}{N_S!\,N_G!}\left\{V_S\,\frac{(2\pi m_S kT)^{3/2}}{h^3}J_S\right\}^{N_S}\left\{V_G\,\frac{(2\pi m_G kT)^{3/2}}{h^3}J_G\right\}^{N_G}e^{-\frac{(N_S\varepsilon_S + N_G\varepsilon_G)}{kT}}$$

where V is the free volume of the molecule.

J is the partition function for the internal energy of the molecule.

ε, the contribution of 1 molecule to the configuration-
al potential energy of the solution, may be neglected for
purposes of entropy. So

$$Q(T) = \frac{N_S + N_G}{N_S! \; N_G!} \; \phi_S^{N_S} \; \phi_G^{N_G}$$

The entropy of solution is

$$S(T) = k\left[\ln Q(T) + T \frac{\partial}{\partial T} \ln Q(T)\right]$$

The partial molal entropy of the gas in a solution of
concentration n_G moles in n_S moles of solvent,

$$\bar{S}_S = \left(\frac{\partial S(T)}{\partial n_G}\right)_{n_S,T,p} = N\left(\frac{\partial S(T)}{\partial N_G}\right)_{n_S,T,p.}$$

Therefore,

$$\bar{S}_S = Nk\left[\ln \frac{N_S + N_G}{N_G} + \ln \phi_G + T \frac{\partial}{\partial T} \ln \phi_G\right] + N_S k\left[\left\{\frac{\partial \ln \phi_S}{\partial n_G}\right\}_{n_S,T}\right.$$

$$\left. + \left\{\frac{\partial}{\partial n_G} (T \frac{\partial}{\partial T} \ln \phi_S)\right\}_{n_S T}\right]$$

so substituting for ϕ we get

$$\Delta S^O = \Delta S_C + R\left[\ln \frac{N_S + N_G}{N_G} + \frac{3}{2} \ln \frac{m_G}{m} + \ln \frac{V_G N}{V} + T \frac{\partial}{\partial T} \ln V_G - 1\right]$$

This will only hold for organic solvents with a minimum
of structure, i.e. where quasi lattice points are occupied.
For water, where the solute molecules will occupy cavities
already present we must add a further term,

$$\Delta S^O = \Delta S_C + R\left[\ln \frac{N_H - N_G}{N_G} + \frac{3}{2} \ln \frac{m_G}{m} + \ln \frac{V_G N}{V} + T \frac{\partial}{\partial T} \ln V_G + \right.$$

$$\left. T \frac{\partial}{\partial T} \ln \frac{N_H - N_G}{N_G} - 1\right]$$

where N_H is the number of cavities or available sites in
the water solvent.

B.   **FREE VOLUME ASPECTS OF $\Delta S_{Solv.}$**

The work of Frank and Evans[5] on the free
volume aspect of solutions has eliminated one of the major
weaknesses of earlier theories, i.e. the necessity to
postulate some definite mechanism.

Their basic equation,

$$\Delta S = R \ln \frac{V_g}{\delta_3 V_f}$$

(V_g free volume of gas, δ_3 free angle ratio of liquid, V_f
free volume of liquid)
may be derived quite generally as follows:

The statistical definition of entropy is

$$S = R \ln w$$

where w is the total number of possible states of the
system compatible with the prescribed total energy.

When the motions are classical w is the volume
of phase space within which the representative point may
be found without violating the assumed conditions.

i.e. $w = \dfrac{1}{N_1! \ N_2! \ \ldots \ N_S! \ h^{3t}} \ .x \displaystyle\int_{region}^{accessible} \int dp_1 \ .. \ dq_t$

N_1, N_2 etc. are the numbers of the different kinds of atoms
present.

3t is total number of degrees of freedom of the system as
$t = N_1 + N_2 \ldots N_S$.

We may choose the q's as the Cartesian co-ordinates of the

individual atoms x_1 y_1 z_1 x_2 y_2 ......the p's being
the co-ordinates of momentum.

Then the energy E is given by

$$E = E_q + E_{int} + \sum_{i=1}^{i=t} \frac{1}{2m_i} (p_{xi}^2 + p_{y_i}^2 + p_{z_i}^2)$$

E_q is the potential energy.

E_{int} is the sum of the internal energies of all the part-
icles.

By the principle of equipartition of energy[15]
the sum of the p^2 terms is $\frac{3}{2}$ tkT which will be correct for
any state of the system in which all the external motions
of the atom are classical. The integral over the p's
is then the hypervolume of the hyperellipsoid which is
defined by

$$\sum_{i=1}^{i=t} \frac{1}{2m_i} (p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2) = \frac{3}{2} tkT.$$

This is equal to $\prod_{j=1}^{j=s} (2\pi m_j kTe)^{3\,Nj/2}$

(s = number of kinds of atoms present.)

So $w = \prod_{j=1}^{j=s} \frac{(2\pi m_j kTe)^{3Nj/2}}{N_j! \, h^{3N_j}} \times \int_{\substack{\text{all xyz} \\ \text{compatible} \\ \text{with E}}} \int dx_1 \cdots \cdot dz_{Ns}$

$$= \prod_{j=1}^{j=s} \frac{2\pi m_j kTe)^{3N_j/2}}{N_j! \, h^{3N_j}} \quad V_{f_j}^{N_j} \qquad \text{--- (A)}$$

where $V_{f_1} = \int dx_1 dy_1 dz_1$ (over all configurations compatible
with E).

(A) defines the free volume of any atomic species as the geometrical mean of the extensions of real space accessible to each of the N_j atoms of the kind in question.

Now for any isothermal system,

$$\Delta S = S_B - S_A = k \ln \frac{w_B}{w_A}$$

$$= N_1 k \ln \left\{\frac{V_{f_B}}{V_{f_A}}\right\}_1 + N_2 k \ln\left\{\frac{V_{f_B}}{V_{f_A}}\right\}_2 + \cdots$$

These results hold only for a classically excited system.

For polyatomic liquids the free volume must include a term for the degree of freedom of rotation of the molecule,

i.e. Complete free volume $=\delta_3 V_f$

δ_3 is the "free angle ratio" of Kincaid and Eyring[16].

This is defined as the average fraction of the free rotational motion which the molecule is able to execute after condensation, and is equal to $\frac{sa}{8\pi^2}$. It obviously must always be less than or equal to unity.

s is the solid angle subtended at the centre of the molecule by the restricted atom after condensation.

a is the angle subtended at the centre through which the restricted atom is free to move.

The equation $\Delta S = R \ln \frac{\delta_3 V_{f_{liq.}}}{V_{f_{gas}}}$ is rigorous provided that,

(i) The internal vibrational motions are separable

from the translation and rotation of the molecule.

(ii) The internal vibrational motions of the molecule are not changed by the presence of neighbours.

(iii) The oscillations which have replaced rotation in the liquid are effectively classical.

It is obvious from the above discussion that one of the major advantages of Frank and Evans' theory is that it does not postulate any mechanism for the process of solution, dealing only with the initial and final states of the gas molecule. This appears to be a step in the right direction as theories such as Eley's can at the best be only semi-quantitative.

FREE VOLUME AND FREE ANGLE RATIOS

We will now consider the meaning of free volume and methods of calculating it.

As we saw above Frank and Evans define it as the geometrical mean of the extensions of real space accessible to each of the atoms or molecules in question.

Kincaid and Eyring[16] define it as the total integral over that part of the potential energy of the molecule in the liquid which is due to thermal displacements of the centre of gravity of the molecule from its equilibrium position. The free angle is the corresponding integral over angular displacements of the molecule about its centre of gravity.

These workers assume that each molecule is trapped in a cell whose boundary potential is infinite. Because the potential energy tends to infinity the idea of communal entropy has to be introduced to account for the possibility of a molecule moving from one cell to another. Hill[17] avoids this by assuming that as a molecule moves out from the cell centre the potential energy increases and before it can pass into another cell it must pass over a _finite_ potential barrier.

For a classical perfect gas,

$$-A/NkT = \ln\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} v \; j(T) + 1$$

$v = V/N$ and $j(T)$ is the internal partition function.

In passing to the free volume model of a liquid Hill replaces v (the volume per molecule) by an effective free volume v_f. $- X$ is the potential energy of interaction, calculated when the molecule is in the centre of its cell. Neglecting the dependence of X on T we have:-

$$-A/NkT = \ln\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} v_f (v,T) \; j(T) + 1 + \frac{X(v)}{kT}.$$

Now assuming both v_f and X are functions of v only. From this equation and

$$\frac{p}{kT} = \frac{\partial}{\partial v}\left(-\frac{A}{NkT}\right)$$

we have

$$\frac{pv}{kT} = \phi\left(\frac{v}{v^*} \; \frac{\wedge}{kT}\right) + \frac{\wedge}{kT} B\left(\frac{v}{v^*}\right)$$

where $\wedge = z\epsilon$ (z is average number of nearest neighbours)

$\wedge \psi(v) = X(v)$

$v_f(v,T) = v_f(v,T)$

$\quad v^* = r^{*3}/\gamma^* \quad \gamma^*$ depends on type of packing.

(These follow Fowler and Guggenheim[15])

$$\phi = \frac{\partial \ln v_f}{\partial \ln (v/v^*)} = 1 + \frac{\partial \ln f}{\partial \ln (v/v^*)}$$

$$B = \frac{d\psi}{d \ln (v/v^*)}$$

From these Hill calculates values of f and v_f for the gases Ne, N_2 and A. $f(v,T)$ is the fraction of the actual volume

that is effectively free.

Eyring[16] defines $\delta_3 V_f$ by

$$\delta_3 v_f = \frac{RT}{p} e^{-\Delta H/RT}$$

where δ_3 the free angle ratio =

Partition function for restricted rotation in liquid
Partition function for free rotation in gas
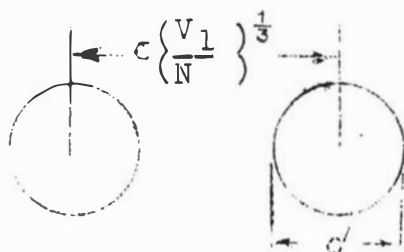
The molal free volume is related to the average volume
of cell v by

$$V_f = Nvf$$

where f is a fluctuation factor taking account of:-

1. Temperature variability of v

2. Encroachment of molecules on each other's free volume

3. Whether or not a molecule is counted as being able
   to occupy the physical volume assigned to another
   without changing places with it.

Suppose the liquid is divided into cells of
average volume $\frac{V_1}{N}$ - one per molecule. Diameter of a
cell is proportional to $\left(\frac{V_1}{N}\right)^{\frac{1}{3}}$

i.e. distance between 2 molecules = $c\left(\frac{V_1}{N}\right)^{\frac{1}{3}}$

c depends on shape assumed for cell, i.e. c = 1 for cubes,

so the molecule can move in a length $c\left(\dfrac{V_1}{N}\right)^{\frac{1}{3}} - d$.

∴ Volume of cell in which molecule is free to move

$$= b^3\left[\left(\frac{V_1}{N}\right)^{\frac{1}{3}} - \frac{d}{c}\right]^3$$

b depends on the geometry of packing. For simple cubic $b = 2$.

$$\therefore \quad V_f = Nfb^3\left[\left(\frac{V_1}{N}\right)^{\frac{1}{3}} - d'\right]^3$$

$$= fb^3\left[V_1^{\frac{1}{3}} - N^{\frac{1}{3}}d'\right]^3$$

$$\therefore \left(\frac{\partial \ln V_f}{\partial V}\right)_T = \left(\frac{\partial \ln[b^3f]}{\partial V}\right)_T + (V_1^{\frac{1}{3}} - N^{\frac{1}{3}}d')^{-1}\left[V_1^{-\frac{2}{3}} - 3N^{\frac{1}{3}}\left(\frac{\partial d'}{\partial V}\right)_T\right]$$

$$= f^{\frac{1}{3}}bg\, V_f^{-\frac{1}{3}}\, V_1^{-\frac{2}{3}} + \left(\frac{\partial \ln (b^3f)}{\partial V}\right)_T \quad \cdots \quad (1)$$

where $g = 1 - 3\left(\frac{N}{V_1}\right)\left(\frac{\partial d'}{\partial \ln V}\right)_T = 1 - \left(\frac{\partial d}{\partial l}\right)_T$

g measures the effect of change in volume on the exclusion diameter.

Now Frank and Evans[5] showed $\triangle S = -R\,\ln\left(\dfrac{V_g}{\delta_3 v_f}\right)$

whence

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] = R\left[\frac{\partial \ln (\delta_3 v_f)}{\partial V}\right]_T$$

so $\left(\dfrac{\partial E}{\partial V}\right)_T = RT\left(\dfrac{\partial \ln V_f}{\partial V}\right)_T + RT\left(\dfrac{\partial \ln \delta_3}{\partial V}\right)_T \quad \cdots \quad (2)$

Because P is very much smaller than the "internal pressure" $\left(\dfrac{\partial E}{\partial V}\right)_T$,

so from (1) and (2) we have

$$V_f = \frac{fb^3g^3}{h^3V_1{}^2} \left[\frac{RT}{(\delta E/\delta V)_T} \right]^3$$

where $h = 1 - RT \dfrac{(\partial \ln [b^3f \delta_3] / \partial V)_T}{(\delta E / \delta V)_T}$

Now Hildebrand[18] has shown $\left(\dfrac{\delta E}{\delta V}\right)_T = \dfrac{n \triangle E_V}{V_1}$

so $V_f = \dfrac{fb^3g^3}{h^3n^3} V_1 \left[\dfrac{RT}{\triangle E_V} \right]^3$ . . . (3)

where $\triangle E_V$ is the energy of vaporisation.

Eyring[19,20,21], obtained a similar equation.

$$V_f = b^3f \ V_1 \left[\frac{RT}{\triangle E_V} \right]^3 \quad \text{. . . (4)}$$

or $\quad V_f = \dfrac{1}{V^2} \left[\dfrac{2 \ RT}{P + (\delta E/\delta V)_T} \right]^3$

He derived this latter equation by considering the molecules as hard spheres. This is not necessary as Kincaid and Eyring[22] have treated liquid mercury assuming that the size of the molecules varies with both temperature and volume.

When attempts are made to calculate free volumes from (3) or (4), two main difficulties are encountered.

(i) The values of the parameters f, b, g, h, and n, are not known and approximations must be used.

(ii) The value obtained is that of V_f while that actually needed is the product $\delta_3 V_f$.

The first of these objections can be eliminated by calculating V_f from sound velocity data while approximate values of δ_3 may be obtained from spectroscopic measurements.

Calculation of V_f from sound velocity data.
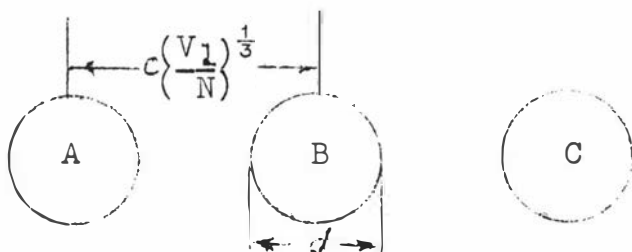
If a sound wave first travels from the inner edge of A to the adjacent edge of B with velocity u_{gas}

$$u_{gas} = \left[\frac{RT\gamma}{M} \right]^{\frac{1}{2}}$$

where γ is the ratio of the specific heats. This equation is obtained from

$$u_{gas} = \sqrt{\frac{\gamma p}{d}}$$

p is the pressure, d the density.

$$pV = RT \qquad \text{or } p\frac{M}{d} = RT$$

$$\therefore \quad u_{gas} = \sqrt{\frac{\gamma p}{\frac{pM}{RT}}} = \left[\frac{RT\gamma}{M} \right]^{\frac{1}{2}}$$

so that u_{gas} is independent of pressure assuming that the gas law holds. As soon as A collides with B the signal is transmitted almost instantaneously to the opposite edge of B.

TABLE I

Liquid Temp. °C.	Acetone A	B	Ether A	B	Chloroform A	B	Carbon Tetrachloride A	B
10			·57	·55	·24	·29	·24	·26
20	·45	·54	·70	·65	·29	·34	·28	·31
30			·90	·79	·34	·40	·33	·37
40	·64	·63			·40	·47	·38	·43

A. V_f from sound velocity measurements.

B. V_f from energy volume coefficients.

$$\text{i.e. from } V_f = \frac{1}{v^2} \left[\frac{2RT}{p + (\partial E/\partial V)_T} \right]^2$$

All figures from Kincaid and Eyring[16].

$$\therefore \quad \frac{u_{gas}}{u_{liq}} = \left(\frac{v_f}{v}\right)^{\frac{1}{3}} \qquad (Eyring\ [19])$$

Because the ratio of the total distance to the free space between two points in a liquid is given by $\left(\frac{v}{v_f}\right)^{\frac{1}{3}}$, or more correctly by $c\left(\frac{v}{v_f}\right)^{\frac{1}{3}}$, c is a proportionality factor $c \lesssim 1$,

$$\therefore \quad u_{liq} = c\left(\frac{v}{v_f}\right)^{\frac{1}{3}} \left(\frac{RT\gamma}{M}\right)^{\frac{1}{2}}.$$

Thus, if the velocity of sound in the liquid and in the gas is known, values of v_f can be calculated.

Quite good agreement is found between values of v_f calculated from sound velocity and from energy volume coefficient data (Table I).

A method of determining free volumes which should become of increasing importance is from spectroscopic measurements.

The frequency of vibration of molecules in liquids is related to the free volume by the approximate relationship[16],

$$\frac{(2\pi mkT)^{\frac{1}{2}}}{h} \frac{V^{\frac{1}{3}}}{u_{liq}} \left(\frac{RT\gamma}{M}\right)^{\frac{1}{2}} = N^{\frac{1}{3}} \frac{kT}{h\vartheta} = \frac{(2\pi mkT)^{\frac{1}{2}}}{h} V_f^{\frac{1}{3}}$$

which connects the velocity of sound in the liquid with the energy $h\vartheta$ for a translational degree of freedom.

Thus one would expect the light scattered from liquids to show the familiar Stokes and anti-Stokes lines of the Raman spectrum. Such lines have been observed[23]

and as Debye[24] noted, they show the same correlation
between frequency and sound velocity as would be expected
from the above equation.

The Free angle ratio.

The value obtained for the free volume of
water at room temperature is about 0·4 cc. but the product
$\delta_3 V_f$ from heats of vaporisation and vapour pressures at
the same temperature is about 0·02 cc.   The discrepancy
of a factor of about 20 may be assigned to a small free
angle ratio, i.e. considerable restricted rotation of the
water molecules.   Cartwright[25] observed frequencies
corresponding to 167 and 500 cm.$^{-1}$ in liquid water at
room temperature and interpreted them as arising from
restricted rotation of the molecules.

Stearn and Eyring[26] using a doubly degenerate
frequency at 167 cm.$^{-1}$ to represent this absorption band
calculated the values of δ_3 shown below (Table II).   Quite
good agreement with vapour pressure figures is obtained.

TABLE II

Free Volumes for Liquid Water

Temp. °C.	V_f (Sound Velocity)	$\delta_3 V_f$ (Vap. Press.)	$1/\delta_3$ (Spectroscopy)	$\delta_3 V_f / \delta_3$
10	·43	·012	25	·36
20	·42	·014	25	·35
30	·42	·017	24	·41
40	·43	·021	24	·50

The free angle ratio, giving a measure of the restricted rotation, may be obtained from dielectric constant values.

If for non-linear molecules $\delta_2 = (\delta_3)^{\frac{2}{3}}$ and θ_1 is the polar angle through which the molecule is free to turn,

$$\text{then } \delta_2 = 1 - \frac{\cos \theta_1}{2} .$$

Kincaid and Eyring list values relating δ_2 to $\mu_1^{2} \mu_g^{-2}$ where μ_1 is the dipole moment in the liquid and μ_g that in the gas where free rotation is assumed.

From the well known equation

$$\frac{\varepsilon - 1}{\varepsilon + 2} V = \frac{4\pi}{3} N \left(\alpha + \frac{\mu^2}{3kT} \right)$$

and

$$\frac{n^2 - 1}{n^2 + 2} V = \frac{4}{3} \pi N \alpha$$

where ε is the dielectric constant

   n the refractive index

   μ the dipole moment

   V the molal volume

   α polarisability

we can calculate values of μ_1^2 / μ_g^{-2} and so obtain values of δ_2 and δ_3.

This method of calculation leads to a value of δ_2 for methanol[27] at $0^\circ C$ of 0·25 while sound velocity and vapour pressure data give 0·13.

There is a tendency for δ_2 from the dielectric constant to be greater than $(\delta_3)^{\frac{2}{3}}$ determined from other sources. This may be due to a restriction on rotation about the axis in which the electric moment of the molecule lies which is probably greater than that about the other two axes.

From these considerations we see that the abnormalities of the so-called associated liquids can be explained from the standpoint of restricted rotation of the molecules. Thus, although water and methanol are ordinarily classed as highly abnormal, their free volumes from sound velocity data are not markedly different from those of other liquids. It is only the product $\delta_3 V_f$ rather than V_f itself which is of a different order of

magnitude for "hydrogen bonded" as compared to normal liquids.

Relationship between Vf and viscosity.

Attempts have been made in the past to link viscosity with free volume by means of an empirical equation.

e.g.   Batschinski[28] $\eta = \dfrac{B}{V_f}$

This equation has been developed by Lederer[30] and by McLeod[29] who obtained an equation

$$\eta = \frac{K \, M_0 \alpha}{v_f}$$

M_0 is the molecular weight and α the degree of association.

The agreement between values calculated from this equation and experimental results is sufficiently good to show that an inverse relationship does exist between free volume and viscosity.

Bosworth[31], using Frenkel's[32] concept of a "phonon gas" derives an expression relating viscosity to free volume or to sound velocity in the liquid

$$\eta = \cdot 2068 \, \frac{1}{N} \sqrt{\frac{MRT}{\gamma}} \, v_f^{-2/3}$$

or $$\eta = \cdot 2068 \, N^{-\frac{1}{3}} \, u^2{}_{liq} \, M^{\frac{5}{6}} \rho^{2/3} \left[RT\gamma^3 \right]^{-\frac{1}{2}}$$

The calculated results agree quite well for "normal"

liquids but wide deviations are found for water and
alcohols.   This may possibly be due to the fact that the
equation

$$u_{liq} = \left(\frac{V}{V_f}\right)^{\frac{1}{3}} \left(\frac{RT\delta}{M}\right)^{\frac{1}{2}}$$

does not apply strictly to "associated" liquids, a
proportionality factor c being required, as was seen
above.

e.g. $$u_{liq} = c \left(\frac{V}{V_f}\right)^{\frac{1}{3}} \left(\frac{RT\delta}{M}\right)^{\frac{1}{2}}$$

where c $\leqslant$ 1.

This would <u>increase</u> the calculated values of η and bring
them nearer to the observed ones.   Alternatively it
may be necessary to use the product $\delta_3 V_f$ in place of V_f ,
which for highly associated liquids is much less than V_f ,
here again an increase in η would result.

Eyring[19,34,35] attempted to obtain an equation
from statistical theory but his final equation of the
form

$$\eta = \frac{N}{V} \; V_f^{\frac{1}{3}} \; (2\pi mkT)^{\frac{1}{2}} \; e^{-\epsilon_o/kT}$$

gives a direct relationship between viscosity and free
volume.

The author, by changing one of Eyring's assump-
tions, obtained an equation which is very similar to that
of Bosworth.   Powell, Roseveare and Eyring[33] derive an
expression,

$$\eta = \frac{Nh}{V} e^{\Delta G*/RT}$$

where $\Delta G*$ is the energy of activation of the molecule to the mobile state.

Let λ be the distance between equilibrium positions in the direction of flow and λ_1 λ_2 λ_3 be distances between neighbouring molecules in the three directions at right angles. Using the theory of absolute reaction rates and postulating a symmetrical potential energy barrier
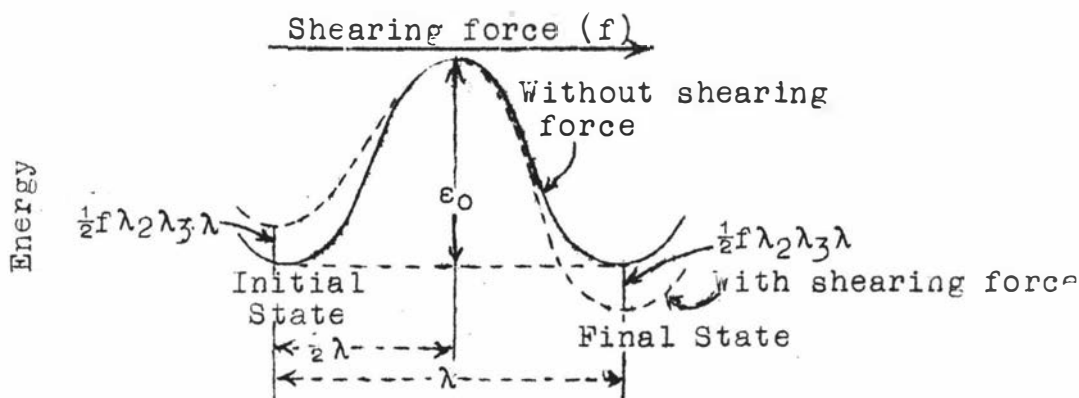
If f is force per square cm. tending to displace one layer with respect to another the applied force on a single molecule in direction of motion is $f \lambda_2 \lambda_3$ as $\lambda_2 \lambda_3$ is effective area per molecule.

Hence the energy acquired by a molecule at the top of the barrier $= f\lambda_2 \lambda_3 \times \frac{1}{2} \lambda$

$$= \frac{1}{2}f \lambda_2 \lambda_3 \lambda$$

If ε_0 is the energy of activation at 0^oK, the number of

times a molecule passes over the barrier per second is:-

$$\varkappa = \frac{kT}{h} \frac{F^*}{F} e^{-\varepsilon_0/kT}$$

F^* and F are the partition functions for unit volume of molecule in activated and initial states.

Specific rate of flow in the forward direction is

$$\varkappa_f = \frac{kT}{h} \frac{F^*}{F} e^{-(\varepsilon_0 - \frac{1}{2}f\lambda_2\lambda_3\lambda)/kT}$$

$$= \varkappa e^{\frac{1}{2}f\lambda_2\lambda_3\lambda/kT}$$

and in the backward direction

$$\varkappa_b = \varkappa e^{-\frac{1}{2}f\lambda_2\lambda_3\lambda/kT}$$

Hence the distance moved by a molecule per second is $\varkappa_f \lambda$ in one direction and $\varkappa_b \lambda$ in the other.

∴ Nett rate of flow in forward direction Δu is given by

$$\Delta u = \lambda(\varkappa_f - \varkappa_b)$$

or

$$\Delta u = 2\lambda \varkappa \sinh \frac{f\lambda_2\lambda_3\lambda}{2 \; kT}$$

(From above equation for $\varkappa_f$ and $\varkappa_b$)

But we know by definition that

$$\eta = \frac{f\lambda_1}{\Delta u}$$

∴

$$\eta = \frac{\lambda_1 f}{2\lambda\varkappa \sinh \; (f\lambda_2\lambda_3\lambda/2kT)}$$

Now $2kT \gg f\lambda_2\lambda_3\lambda$ and on expanding

$$\eta = \frac{\lambda_1 kT}{\lambda_2 \lambda_3 \lambda^2 \varkappa}$$

From above $\qquad \varkappa = \frac{kT}{h} \frac{F^*}{F} e^{-\varepsilon_0/kT}$

$\therefore \qquad \eta = \frac{\lambda_1 h}{\lambda_2 \lambda_3 \lambda^2} \frac{F}{F^*} e^{\varepsilon_0/kT}$

Eyring here assumes that $\lambda = \lambda_1$ and because $\lambda_1 \lambda_2 \lambda_3 = \frac{V}{N}$

he obtains

$$\eta = \frac{Nh}{V} \frac{F}{F^*} e^{\varepsilon_0/kT}$$

or replacing $\frac{F}{F^*}$ by $\left(\frac{2\Pi MkT}{h}\right)^{\frac{1}{2}} v_f^{\frac{1}{3}}$ (which is equal to the ratio of the partition functions).

$$\eta = \frac{N}{V} v_f^{\frac{1}{3}} (2 \Pi MkT)^{\frac{1}{2}} e^{\varepsilon_0/kT}$$

The assumption that $\lambda = \lambda_1 = \left(\frac{V}{N}\right)^{\frac{1}{3}}$ appears to the author to be rather doubtful. This distance would be expected to lie somewhere between $\left(\frac{V}{N}\right)^{\frac{1}{3}}$ and $\left(\frac{V}{N}\right)^{\frac{1}{3}} - b\left(\frac{Vf}{N}\right)^{\frac{1}{3}}$ and probably much closer to the latter.

Assuming that $\lambda = \left(\frac{V}{N}\right)^{\frac{1}{3}} - b\left(\frac{Vf}{N}\right)^{\frac{1}{3}}$

($b \geqslant 1$ depending on cell shape.

The most likely value is $b = 2$)

$\therefore \qquad \eta = \frac{Nh}{V^{\frac{1}{3}}\left[V^{\frac{1}{3}} - bV_f^{\frac{1}{3}}\right]^2} \frac{F}{F^*} e^{\varepsilon_0/kT}$

$\qquad = \frac{Nh}{V^{\frac{1}{3}}\left[V^{2/3} + bV_f^{2/3} - 2bV^{\frac{1}{3}}V_f^{\frac{1}{3}}\right]} \frac{F}{F^*} e^{\varepsilon_0/kT}$

$\qquad = \frac{Nh}{V + b^2 V^{\frac{1}{3}}V_f^{\frac{2}{3}} - 2bV^{\frac{2}{3}} V_f^{\frac{1}{3}}} \frac{F}{F^*} e^{\varepsilon_0/kT}$

$$= \frac{N}{V + b^2 V^{\frac{1}{3}} V_f^{2/3} \; 2bV^{2/3}V_f^{\frac{1}{3}}(2\Pi MkT)^{\frac{1}{2}}V_f^{\frac{1}{3}}e^{\varepsilon_0/kT}}$$

or since $K^* = \dfrac{F}{F^*} \quad e^{\varepsilon_0/kT} = e^{\Delta G^*/RT}$

$$\eta = \frac{Nh}{b^2 V^{\frac{1}{3}}V_f^{2/3} + V - 2bV^{2/3}V_f^{\frac{1}{3}}} \; e^{\Delta G^*/RT}.$$

Here, as in the equations of Bosworth, McLeod and others, the viscosity is inversely proportional to the free volume.

The replacement of $\left(\dfrac{V}{N}\right)^{\frac{1}{3}}$ by $\left(\dfrac{V}{N}\right)^{\frac{1}{3}} - b\left(\dfrac{V_f}{N}\right)^{\frac{1}{3}}$ will increase the values of η by a factor of approximately 1·5 – 3.

This equation reduces to Eyring's for liquids with small free volumes,

i.e. $\displaystyle\operatorname*{Lt}_{V_f \to 0} \left(\dfrac{V}{N}\right)^{\frac{1}{3}} - b\left(\dfrac{V_f}{N}\right)^{\frac{1}{3}} = \left(\dfrac{V}{N}\right)^{\frac{1}{3}}$

and so we are left with

$$\eta = \frac{Nh}{V} \; \frac{F}{F^*} \; e^{\varepsilon_0/kT}$$

Powell, Roseveare and Eyring[33] using their equation $\eta = \dfrac{Nh}{V} e^{\Delta G^*/RT}$ found that ΔG^* was a function of the energy of vaporisation of the liquid,

i.e. $\Delta G^* = \dfrac{\Delta E_{vap}}{2\cdot 45}$

Since the energy of activation for viscous flow is related to the work required to form a hole in the liquid the

experimentally observed activation energy ΔE_{vis} may be expected to be some fraction of ΔE_{vap},

$$\text{i.e.} \quad \Delta E_{vis} = \frac{\Delta E_{vap}}{n}$$

Eyring finds the following values for n at $25^{\circ}C$.

n = 3 for CCl_4, C_6H_6

n = 4 for CS_2, $CHCl_3$, Ether, Acetone

n = 2·4 for water.

i.e. liquids with smaller free volumes ($\delta_3 V_f$) have smaller values of n.

The activation energy for viscosity ΔE_{vis} differs from the free energy of activation ΔG_{vis}^{*} on account of the entropy change accompanying activation for viscous flow.

For gases (where $V \gg V_f$) the author's equation for viscosity reduces to that obtained by Eyring[21,34].

$$\text{e.g.} \quad \eta = \frac{(2\,\Pi\,mkT)^{\frac{1}{2}}}{V_f^{2/3}}$$

i.e. ϵ_0 is zero and writing $\frac{(2\Pi mkT)^{\frac{1}{2}}}{h} V_f^{\frac{1}{3}}$ for the ratio $\frac{F}{F^*}$.

From the above equation for viscosity it should be possible to calculate values of V_f when η and ΔE_{vap} are known. This equation will be referred to later in connection with rates of solution of gases where it is found to give much better agreement with experiment than

that of Eyring et al. Prigogine[40] found that values of η calculated from Eyring's equation were closer to the experimental values when values of V_f calculated from the Lennard-Jones model were used. Summarising these relationships between free volume and quantities capable of experimental measurement we have:-

$$\delta_3 V_f = \frac{RT}{p} \, e^{\frac{-\Delta H_{vap}}{RT}}$$

$$V_f = \frac{f b^3 g^3}{h^3 n^3} \, V_l \left[\frac{RT}{\Delta E_{vap}}\right]^3$$

$$u_{liq} = c \left(\frac{V}{V_f}\right)^{\frac{1}{3}} \left(\frac{RT\gamma}{M}\right)^{\frac{1}{2}}$$

$$u_{liq} = \frac{1}{\sqrt{\beta_\varphi \rho}} \quad (\beta_\varphi \text{ adiabatic compressi-} \atop \text{bility})$$

$$\eta = \frac{Nh}{V - 2bV^{2/3}V_f^{\frac{1}{3}} + b^2 V^{\frac{1}{3}}V_f^{2/3}} \, e^{\frac{\Delta E_{vap}}{nRT}}$$

CORRELATION OF GAS SOLUBILITY WITH PHYSICAL
PROPERTIES OF THE SOLVENT

Many attempts have been made to discover regularities in the solubility of gases. G. Just[36] found that the solubility of one gas in a solvent may be found approximately by multiplying its solubility in another solvent by a factor which depends only on the solvents and not on the gases. He also observed a negative correlation between the refractive index and the dissolving power of solvents. Skirrow[37] and Christoff[38] found that surface tension and dissolving capacity are negatively correlated. This was also noted by Uhlig[11] who found

$$\ln \gamma = \frac{-4 \pi r^2 \sigma}{kT} + E$$

where γ is the Ostwald coefficient.

i.e. a plot of $\ln \gamma$ against σ for one gas in a number of solvents is linear.

Sisskind and Kassarnowsky[7] examined the relation between electric polarisability, dipole moment, and solvent power. An increase in either of these two appears to increase the solvent power but certain deviations are found. Hildebrand[39] discussed the influence of cohesive forces on solubility and expressed these in terms of internal pressure. He found that the solubility decreased

more or less regularly as the function $(\frac{a}{V2})^{\frac{1}{2}}$ increased.
He ascribed the discrepencies as did Tammann[41] to the
disconcerting lack of agreement of the published data.

When it is remembered that the internal
pressure $\left(\frac{\partial E}{\partial V}\right)_T$ appears in the equation for free volume

$$V_f = \frac{fb^3g^3}{h^3V_1^2}\left[\frac{RT}{(\partial E/\partial V)_T}\right]^3$$

it seems very likely that the solubility of any one gas
in a number of solvents should be proportional to the
free volumes of the solvents or to the product δ_3V_f.

On plotting values of γV_1 [i.e. solubility
converted to a mole fraction basis] against δ_3V_f the
author found that for a number of gases the points
scattered about straight lines with remarkably small
deviations when the accuracy of the data used was con-
sidered. (Table III. Graph I).

Values of δ_3V_f are only available for a few
solvents so that from the remaining solubility figures
values of δ_3 for the solvent may be calculated and compared
with known δ_3 values. Values calculated in this way are
compared in Table IV with values from the work of Eyring
and Frank and Evans.

Frank and Evans calculate values of β from

$$p_{vap} = \frac{RT}{\beta V_1}\left[\frac{\Delta E_{vap}}{RT}\right]^3 e^{-\Delta H/RT}$$

where $\beta = \delta_3 f b^3 g^3 / h^3 n^3$

They then assume as a first approximation that

$$\delta_3 = \frac{\beta}{16} \text{ for most liquids.}$$

The straight lines were found to have slopes proportional to the volume of the gas molecule and calculated values of r_{gas} are compared below with those obtained from electron diffraction work by Lenard[42], Ramsauer[43] and Mayer[44].

	He	Ne	H_2	**A**	N_2	O_2
r_{calc}	1·28	1·50	1·85	2·8	2·29	2·69
r_{exp}	1·41	1·48	2·0	2·8		

Thus it is found that

$$\gamma V_1 = \delta_3 V_f \text{ x } v$$

$$\text{or} \quad \delta_3 V_f = \frac{\gamma V_1}{v}$$

where v is the volume of the gas molecule or effectively Van de Waal's b. From this it is seen that a plot of γV_1 against b for a number of gases in any one solvent should also be linear and this is found to be the case as is shown by Graph II.

An empirical relationship between the velocity of sound in the liquid and its molecular weight and density

TABLE III

Υ (Ostwald Coefficient)

All Figures at 25°C.

	Et$_2$O	CH$_3$COCH$_3$	C$_6$H$_6$	CHCl$_3$	C$_2$H$_5$OH	H$_2$O	CH$_3$OH	CCl$_4$
He	–	·036	·021	–	·032	·0086	·036	–
Ne	–	·052	·031	–	·045	·013	·048	–
H$_2$	·145	·100	·072	·067	·085	·018	·099	·085
N$_2$	·293	·179	·120	–	–	–	·141	·162
O$_2$	·455	·280	·223	–	–	·031	·24	·302
A	–	·299	(·242)	(·18)	·258	·034	·267	–
Kr	–	(1·2)	(1·0)	–	–	·061	–	(1·36)
Xe	–	–	–	–	–	·109	–	–
Rn	14·0	5·8	11·0	13·8	5·7	·21	–	–

$V_1 =$ solubility corrected to molal volume basis.

	Et$_2$O	CH$_3$COCH$_3$	C$_6$H$_6$	CHCl$_3$	C$_2$H$_5$OH	H$_2$O	CH$_3$OH	CCl$_4$
He	–	2·7	1·9	–	1·7	·055	1·5	–
Ne	–	3·8	2·8	–	2·5	·24	1·7	–
H$_2$	15·2	7·4	6·4	5·41	5·2	·34	3·8	8·2
N$_2$	30·6	13·2	10·7	–	–	–	5·7	15·7
O$_2$	47·6	20·7	19·9	–	–	·56	9·8	29·3
A	–	22·1	(21·7)	(14·5)	13·9	·65	10·9	–
Kr	–	(88·8)	(88)	–	–	1·10	–	132·1
Xe	–	–	–	–	–	1·96	–	–
Rn	1464·4	429	982·3	1113	334	3·8	–	–

GRAPH I
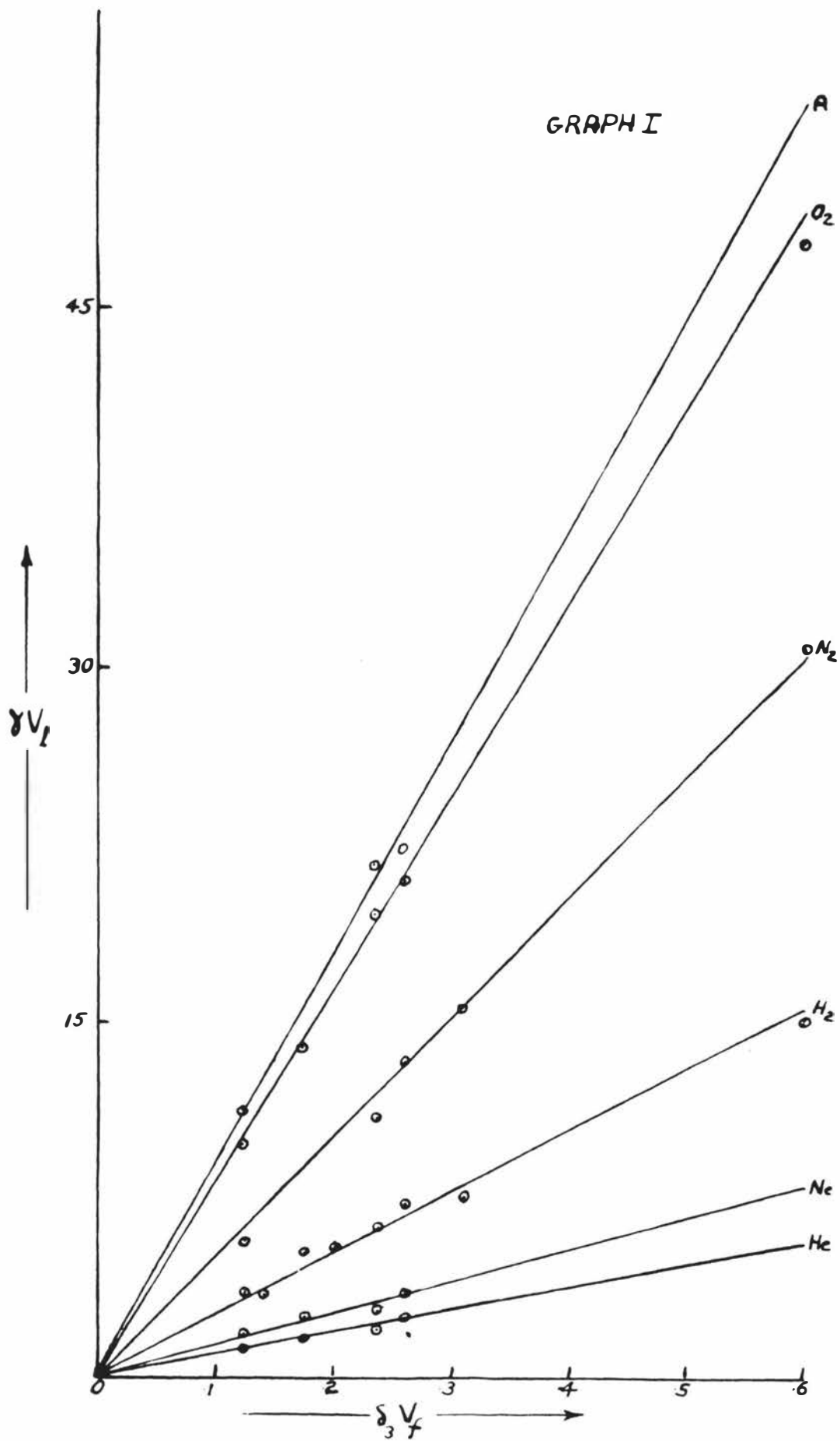
TABLE IV

(at 25°C.)

Liquid	Molal Vol.	V_f Sound Velocity	V_f Energy Vol. Coeff.	$\delta_3 V_f$ (Frank and Evans)	$\delta_3 V_f$ (Law)	From Solubility Data δ_3(S.V)	δ_3(E.V.C.)	δ_2(S.V.)	δ_2(E.V.C.)	δ_2(Calc) (E & n)
Et_2O	104·6	·68	·67	·59	·60	·88	·89	·92	·93	—
CH_3COCH_3	74·0	·47	·55	·20	·26	·55	·47	·67	·60	—
$CHCl_3$	80·7	·29	·35	—	—	—	—	—	—	—
C_6H_6	89·3	·27	·29	·21	·238	·87	·82	·91	·88	·89
CCl_4	97·1	·32	·33	·31	·31	·97	·94	·98	·96	—
C_2H_5OH	58·6	·52	—	—	·175	·34	—	·48	—	—
CH_3OH	40·7	·92	—	—	·125	·13	—	·25	—	·13 – ·25
H_2O	18·0	·49	·42	·015	·015	·030	·036	·12	·19	·12
CH_3COOH	57·5	·22	—	—	·14	·64	—	·74	—	—
CS_2	60·6	·28	·62	—	·19	·70	·31	·79	·46	—
nC_6H_{14}	110·0	·46	—	—	·46	1·0	1·0	1·0	1·0	—

GRAPH II
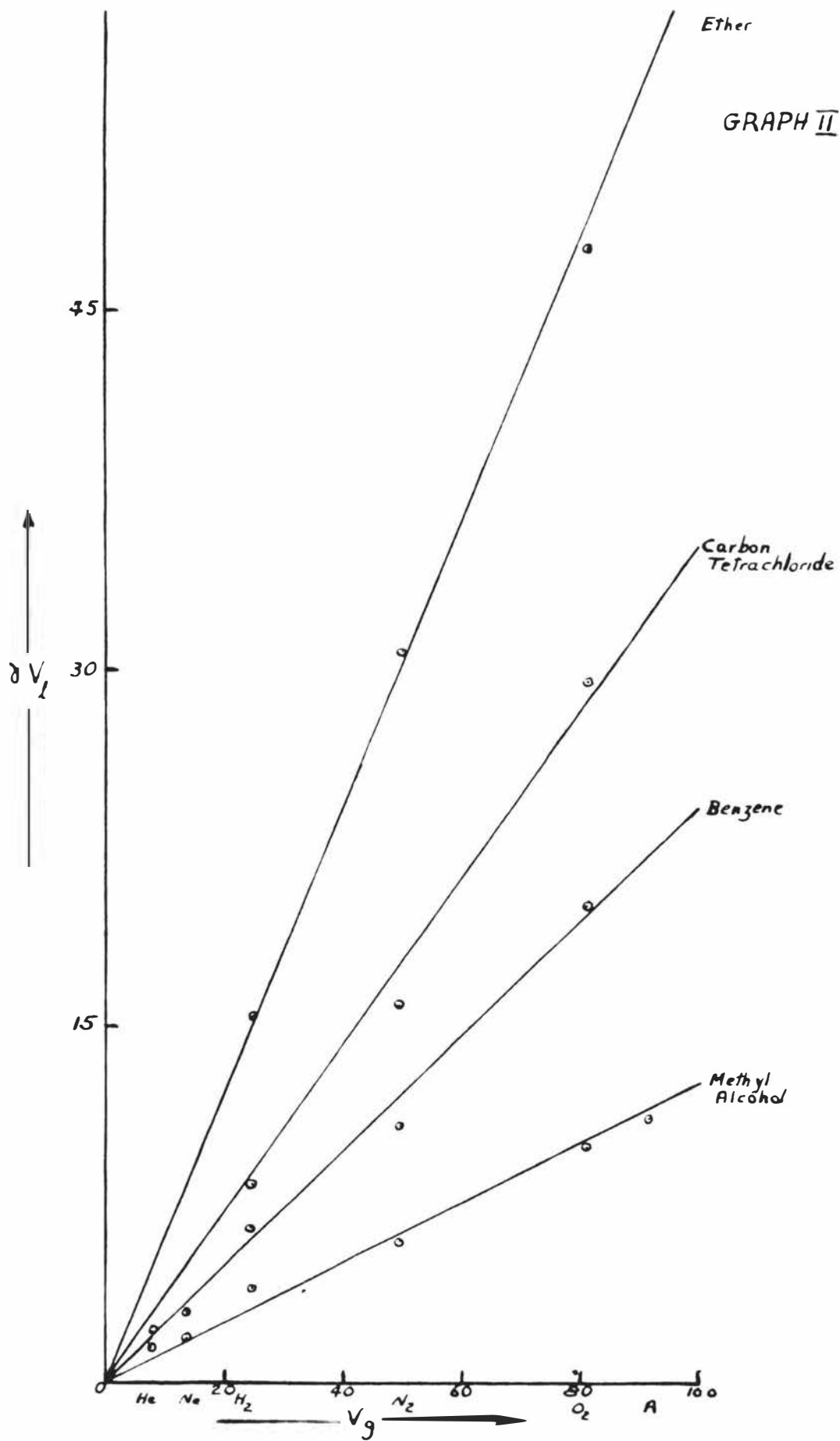
was put forward by Rao[46]

$$R = u_{liq}^{\frac{1}{3}} \frac{M}{\rho}$$

i.e. relates u_{liq} with molal volumes.

This work led Lagemann[48] to note that the ratio $\frac{u_{liq}}{u_{gas}}$ appeared to give an indication of the amount of association occurring in the liquid. Table V gives the values of this ratio for a number of liquids. It may be seen that for those compounds commonly accepted as being associated the ratio is smaller than for normal liquids.

<div align="center">TABLE V</div>

Liquid	Metres/sec. u_{liq}	Ref.	$\frac{u_{liq}}{u_{gas}}$
CH_3COCH_3	1173	(47)	6·16
$CHCl_3$	984	(47)	6·52
C_6H_6	1310 1300	(46) (47)	6·86
CCl_4	919	(47)	6·71
CH_3COOH	1140	(45)	6·39
C_2H_5OH	1207	(46)	4·84
CH_3OH	1130	(46)	3·54
H_2O	1494	(47)	2·88

The relatively high value for acetic acid may be due to the fact that it is associated to about the same extent in the liquid and in the vapour.

This empirical relation of Lagemann is seen to have some theoretical basis when it is remembered that

$$\frac{u_{liq}}{u_{gas}} = c \left(\frac{V}{V_f}\right)^{\frac{1}{3}} \quad \text{where } c \lesssim 1$$

It was seen above that values of V_f for both associated and normal liquids are of the same order, but that c is much less than unity for associated liquids so that the ratio $\frac{u_{liq}}{u_{gas}}$ would be expected to give a measure of the amount of association. This method has the advantage that it is independent of measurements connected with the liquid surface where conditions must differ from those in the bulk liquid.

———————

THE NATURE OF ALCOHOL-WATER MIXTURES

The present investigation of gas solubilities in alcohol-water mixtures was carried out in the hope of elucidating the structure of these mixtures. Measurements of their physical properties show that important changes in the structure of water and of the alcohol occur when they are mixed.

These changes, for which an explanation will later be attempted on the basis of the concept of free volume, are best discussed under the following headings:-

    (i)   Partial Molal Volumes

   (ii)   Heat, Entropy and Free Energy of Mixing

 (iii)   Viscosity

  (iv)   Sound Velocity

   (v)   Gas Solubility and Entropy of Solution.

(i) PARTIAL MOLAL VOLUMES.

The partial molal volume

$$\bar{V}_1 = \frac{dV}{dn_1}$$

$$\bar{V}_2 = \frac{dV}{dn_2}$$

gives a measure of the variation of the volume of the
solution V when a small quantity dn_1 of one component or
dn_2 of the other is added.

Thus $dV = \bar{V}_1\, dn_1 + \bar{V}_2\, dn_2$

or for finite amounts of the two components

$$V = \bar{V}_1\, n_1 + \bar{V}_2\, n_2$$

Lewis and Randall[49] give values of $\bar{V}_1$ and $\bar{V}_2$
for ethanol-water mixtures and the author using their metho⌐
of intercepts calculated the corresponding values for water
methanol.   These are shown in Table VI and Graph III,
where, for the sake of convenience, the partial molal vol-
ume less the molal volume of the pure liquid is used as
the ordinate.   All the figures listed are at $25\,^{\circ}C$.

It is seen that for ethanol-water mixtures at
10 Mole % a considerable contraction occurs on mixing while
for methanol-water mixtures a similar phenomenon occurs at
20 Mole % though to a lesser extent.   The fact that more
water has to be added to ethanol than to methanol to
produce this minimum is not unexpected when it is remembered
that $\delta_3 V_f \text{ (EtOH)} > \delta_3 V_f \text{ (MeOH)}$.

TABLE VI

Methanol – Water

Mole % MeOH	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1 - V_o$	$\bar{V}_2 - V_c$
0	18·054	37·44	0	−3·23
10	18·05	37·43	0	−3·24
20	18·10	37·31	+ ·05	−3·36
30	18·00	37·86	− ·05	−2·81
60	17·10	39·49	− ·95	−1·18
80	16·05	40·22	−2·00	− ·45
100	14·15	40·672	−3·90	0

Ethanol – Water

Mole % EtOH	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1 - V_o$	$\bar{V}_2 - V_o$
0	18·05	54·65	0	−4·00
10	18·05	53·25	0	−5·40
20	17·70	55·87	− ·35	−2·78
30	17·42	56·65	− ·63	−2·00
60	16·07	57·43	−1·98	− ·80
80	15·20	58·21	−2·85	− ·30
100	13·65	58·655	−4·40	0
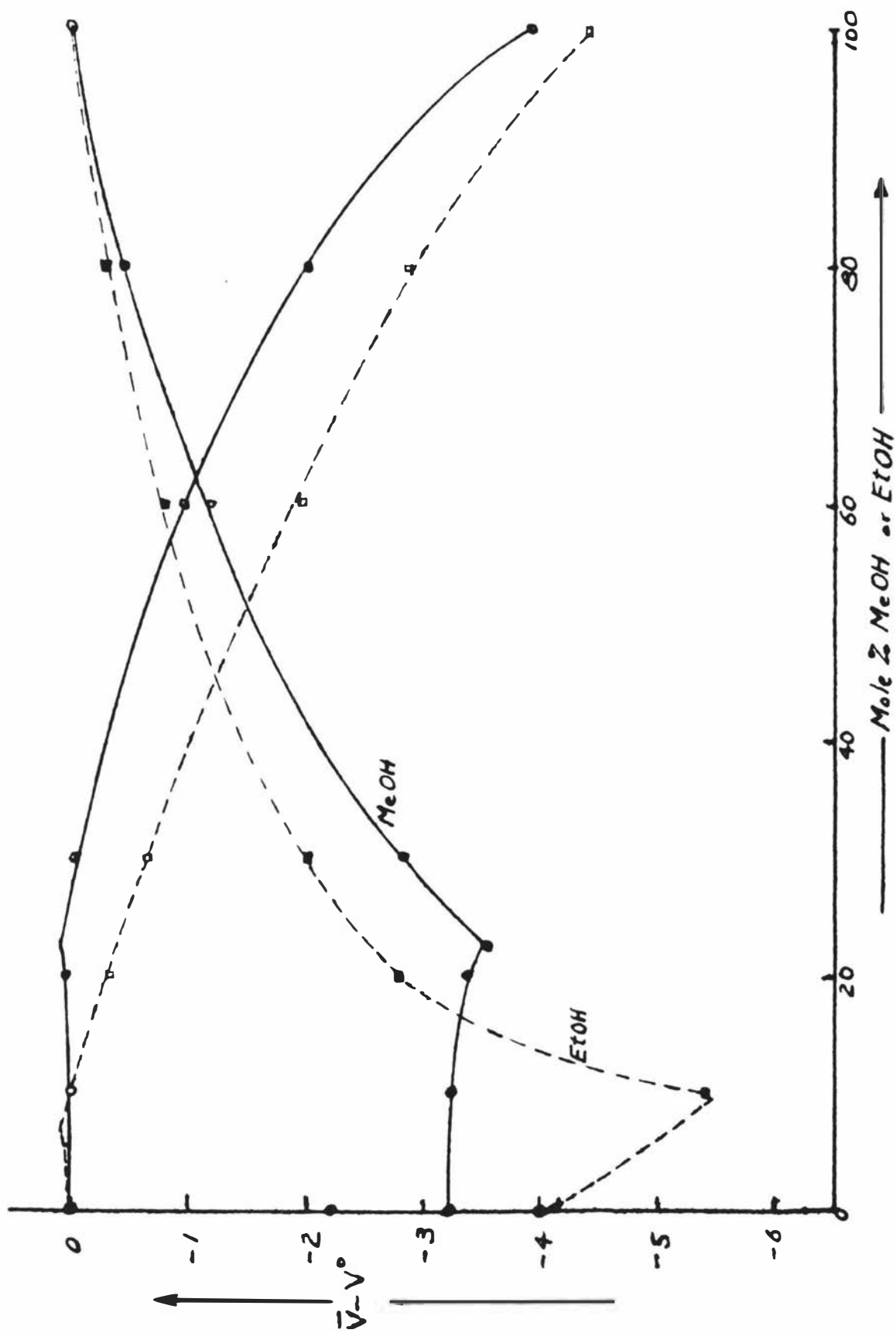
(ii) HEAT, ENTROPY AND FREE ENERGY OF MIXING.

These thermodynamic functions were calculated from vapour pressure measurements by the method of Scatchard and Raymond[50]. The standard states were taken as the pure components at the same temperature and pressure as the mixture.

The difference in any of these functions in the state under discussion and in the standard state will be designated by a superscript M. (mixing) and the difference between that function and one for an ideal solution of the same composition by a superscript E. (excess).

Thus for the chemical potential,

$$\mu_1{}^M = RT \ln a_1$$
$$\mu_1{}^E = RT \ln \gamma_1$$

where a_1 and γ_1 are the activity and the activity coefficient of the first component.

Scatchard and Raymond show that the chemical potentials of the components in a solution at pressure P_O are given by

$$\mu_1 = F_{10} + RT \ln Py + \beta_1 P + \delta P(1-y)^2 + V_1 (P_O - P) \qquad (1)$$
$$\mu_2 = F_{20} + RT \ln P(1-y) + \beta_2 P + \delta Py^2 + V_2 (P_O - P) \qquad (2)$$

where:

F_{10} and F_{20} are functions of the temperature only.

P the vapour pressure of the mixture.

Py and P(1-y) are the partial pressures of the two components.

y the mole fraction of component 1 in the vapour.

V_1 and V_2 molal volumes of the components.

$$\delta = 2\beta_{1.2.} - \beta_1 - \beta_2$$

where β is a function of the reduced temperature and pressure of the gases.

From equations (1) and (2)

$$\mu_1^M = F_{10} + RT \ln Py + \beta_1 P + \delta P(1-y)^2 + V_1(P_0-P) -$$
$$\left[F_{10} + RT \ln P_1 + \beta_1 P_1 + V_1(P_0-P_1) \right]$$

$$= RT \ln \frac{Py}{P_1} + (\beta_1 - V_1)(P-P_1) + \delta P(1-y)^2 \quad \ldots \quad (3)$$

$$\mu_2^M = RT \ln \frac{P(1-y)}{P_2} + (\beta_2 - V_2)(P-P_2) + \delta Py^2 \quad \ldots \quad (4)$$

where P_1 and P_2 are the vapour pressures of the pure components.

$$\mu_1^E = \mu_1^M - RT \ln x = RT \ln \frac{Py}{P_1 x} + (\beta_1 - V_1)(P-P_1) + \delta P(1-y)^2$$
$$(5)$$

$$\mu_2^E = RT \ln \frac{P(1-y)}{P_2(1-x)} + (\beta_2 - V_2)(P-P_2) + \delta Py^2 \quad \ldots \quad (6)$$

where x is the mole fraction in the liquid.

$$\Delta G_x^E = \Delta G^E(N_1 + N_2) = x \mu_1^E + (1-x) \mu_2^E$$

$$\Delta S_x^E = - (\partial \Delta G_x^E / \partial T)_{p.N.}$$

$$\Delta H_x^M = \Delta H_x^E = \Delta G_x^E + T \Delta S_x^E$$

These are all per mole of liquid.

According to this theory of corresponding states the limit at zero pressure of $\beta P_c / T_c$ should be the same

function of T_r for all gases, where T_r is the reduced

temperature $\dfrac{T}{T_c}$.   In terms of critical and reduced

quantities the equation of Keyes, Smith and Gerry[51]

becomes

$$\beta P_c / T_c = 11 \cdot 5 - (24 \cdot 78 / T_r) \times 10^{0 \cdot 1930 / T_r^2}$$

where β is in cc./mole, P_c in atmospheres and T_c in degrees

absolute.   Values of β and V used are shown in Table VIII

while the results for alcohol-water mixtures calculated

on the assumptions that $\delta = 0$ and that the ratio β_1 / β_2

was given by the theory of corresponding states are shown

in Table X and Graph IV.

The listed vapour pressure figures are taken

from the work of Bredig and Bayer[52], Vrewski[55], Dobson[56],

and Butler[53].   These figures however do not give

sufficiently reliable values of ΔG_X^E to enable ΔS_X^E to be

calculated from their temperature coefficients.   This is

shown by Table IX where values of ΔG_X^E at three tempera-

tures calculated by the above theory are given.   To obtain

values of ΔS_X^E which were even qualitatively correct the

author calculated ΔG_X^E from Butler and Dobson's vapour

pressure figures and used values of ΔH_X^E interpolated from

the work of Bose[54] whose results are shown in Table XI.

Graph IV shows that ethanol-water mixtures depart

from ideal behaviour to a greater extent than do methanol-

water mixtures.   This divergence is greatest at 20 Mole %

<div align="center">

TABLE VIII

</div>

	T_c	P_c	$-\beta_j$(cc./mole)
Temp.			25	39·80	49·76	54·81
Methanol	513·1	78·7	− 963	−800·4	−713·3	−676
Water	647·1	217·7	−1266	−985	−845·1	−787
Ethanol	516·3	63·1	−1239	−1028	−	−867·3

<div align="center">

$\underline{V_j}$

</div>

Temp.	25	39·76	49·76	54·81
Methanol	40·7	41·4	41·9	−
Water	18·05	18·1	18·2	−
Ethanol	58·7	59·6	−	60·6

TABLE VIII (cont.)

METHANOL-WATER

	25°C.[53]			39.76°C.[52]			39.90°C.[55]			49.76°C.[52]	
x_{CH_3OH}	y_{CH_3OH}	P(mm.)	x_{CH_3OH}	y_{CH_3OH}	P	x_{CH_3OH}	y_{CH_3OH}	P	x_{CH_3OH}	y_{CH_3OH}	P
·0000	·0000	23·8	·0000	·0000	54·6	·0000	·0000	54·7	·0000	·0000	92·0
·0202	·1438	26·7	·0478	·2559	68·1	·1499	·6279	105·3	·0486	·2741	119·5
·0403	·2564	30·0	·0925	·4595	86·0	·1785	·6624	114·0	·1218	·4741	157·0
·0620	·3426	33·9	·1523	·6164	103·4	·2107	·6960	122·4	·1478	·5220	169·7
·0791	·4152	36·3	·2027	·6796	119·1	·2385	·7125	129·6	·2131	·6294	196·0
·1145	·5043	42·6	·3065	·7612	142·7	·2731	·7378	136·4	·3252	·7580	236·6
·2017	·6480	55·3	·4172	·8048	161·5	·3106	·7573	143·7	·5143	·8203	283·0
·3973	·7940	75·4	·5033	·8457	175·4	·4014	·7956	160·5	·6279	·8654	306·4
·6579	·8900	96·2	·5933	·8619	188·2	·4704	·8181	173·1	·7083	·9007	324·1
·8137	·9518	109·9	·6949	·8974	206·4	·5580	·8532	185·7	·8037	·9406	348·4
1·0000	1·0000	126·6	·8002	·9536	223·1	·6899	·9004	207·5	·9007	·9627	373·5
			·9270	·9761	244·5	·8607	·9572	235·3	·9461	·9736	391·1
			1·0000	1·0000	259·8	1·0000	1·0000	260·7	1·0000	1·0000	404·6

TABLE VIII (contd.)

ETHANOL-WATER

25°C.[56]			39.76°C.[55]			54.81°C.[55]		
$x_{C_2H_5OH}$	$y_{C_2H_5OH}$	P(mm.)	$x_{C_2H_5OH}$	$y_{C_2H_5OH}$	P	$x_{C_2H_5OH}$	$y_{C_2H_5OH}$	P
·0000	·0000	23·8	·0000	·0000	54·6	·0000	·0000	116·6
·0523	·3165	33·17	·0689	·4560	81·4	·0916	·4753	192·9
·0917	·4336	38·44	·1452	·5431	99·4	·1157	·5036	204·2
·1343	·5130	43·42	·2208	·5874	107·3	·2120	·5727	228·1
·2023	·5685	47·21	·3677	·6341	115·7	·3698	·6151	247·5
·2849	·6102	50·33	·4808	·6726	121·9	·4788	·6554	256·6
·4904	·6792	53·95	·6089	·7189	125·3	·6102	·7102	264·6
·7811	·8161	58·08	·7796	·8129	129·2	·9145	·9145	275·9
1·0000	1·0000	59·01	·9390	·9397	131·5	1·0000	1·0000	275·2
			·9552	·9552	131·4			
			1·0000	1·0000	129·8			

TABLE IX

METHANOL-WATER.

Values of ΔG_x^E (cals)

Mole % MeOH	$25^{\circ}C.$ [53]	$39 \cdot 9^{\circ}C.$ [55]	$49 \cdot 76^{\circ}C.$ [52]
0	0	0	0
10	20·0	−9·0	32·0
20	51·2	−12·6	61·8
30	63·8	+22·1	71·6
40	68·9	+55·0	76·0
50	69·0	+70·2	76·0
60	66·8	+72·1	70·0
70	59·0	+65·0	58·6
80	39·7	+44·7	36·3
90	19·0	+19·0	12·4
100	0	0	0

TABLE X

At 25°C

Mole % Alcohol.	METHANOL-WATER			ETHANOL-WATER		
	ΔG_x^E	$T \Delta S_x^E$	ΔH_x^E	ΔG_x^E	ΔS_x^E	ΔH_x^E
0	0	0	0	0	0	0
10	22	113	135	70	96	166
20	50	150	200	141	53	194
30	63	147	210	176	- 8	168
40	69	136	205	182	-46	136
50	70	117	187	175	-70	106
60	68	97	165	156	-71	85
70	59	79	138	136	-70	65
80	40	60	107	113	-66	47
90	20	40	60	74	-48	26
100	0	0	0	0	0	0

All values in calories.
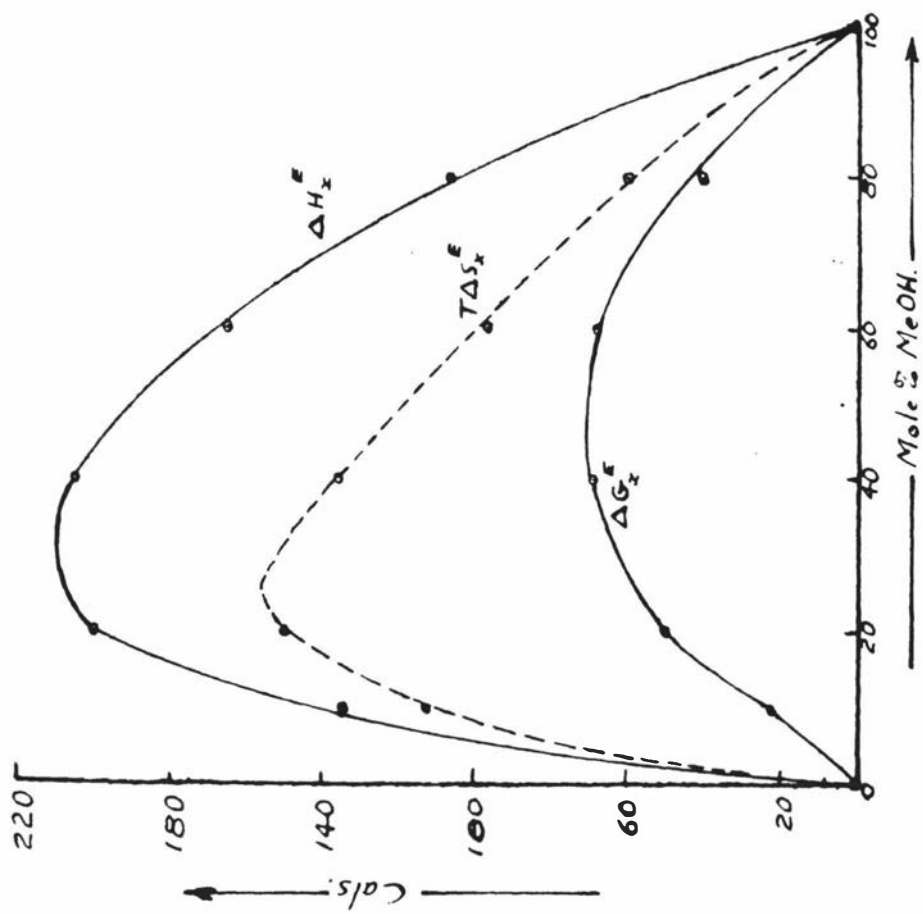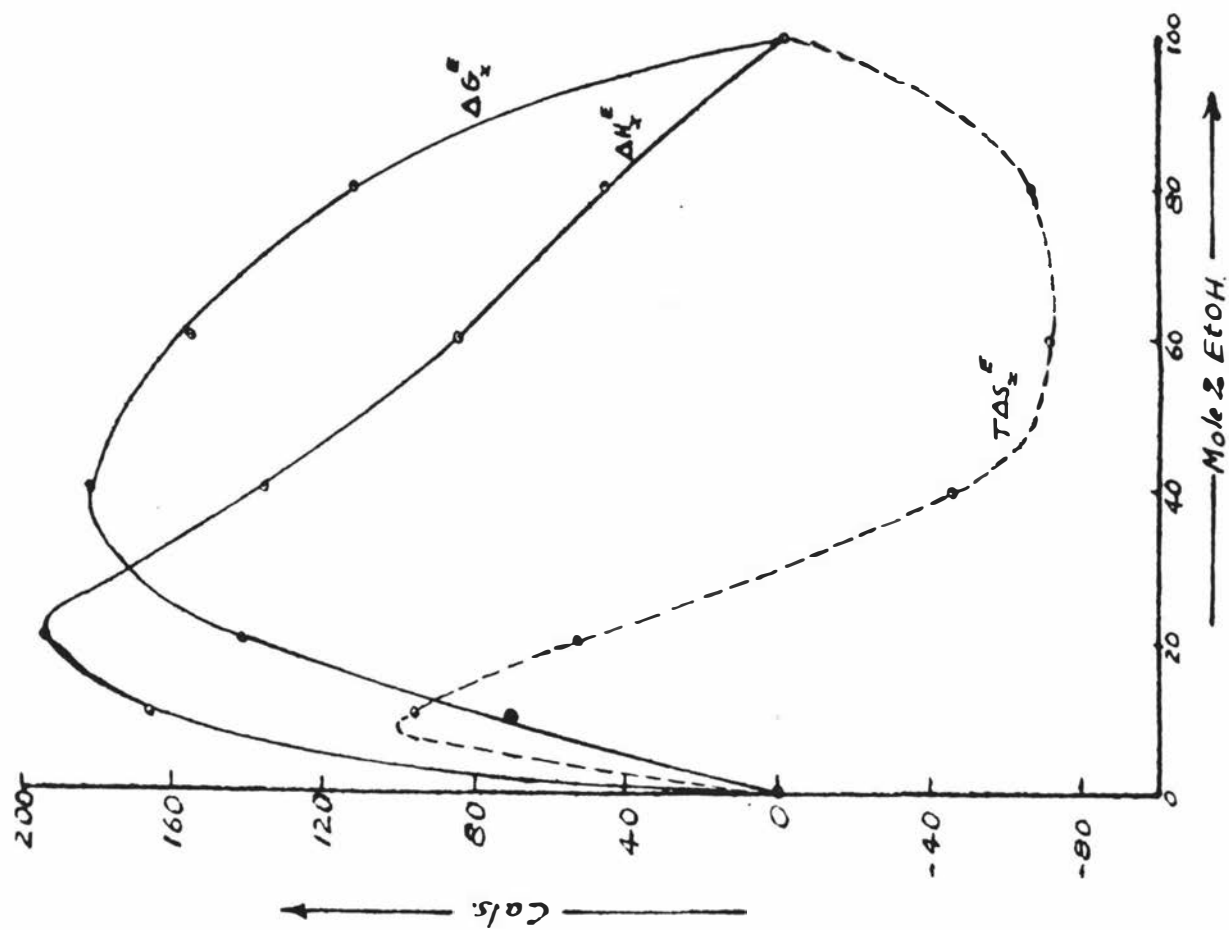
TABLE XI

Calorimetrically measured heats of mixing.[54]

Mole % Alcohol.	METHANOL-WATER			ETHANOL-WATER		
	0°C.	$19 \cdot 69^{\circ}$C.	$42 \cdot 37^{\circ}$C.	0°C.	$17 \cdot 33^{\circ}$C.	$42 \cdot 05^{\circ}$C.
0	·00	·00	·00	·00	·00	·00
5	100·0	81·6	60·0	148·6	116·7	74·0
10	168·0	143·5	104·1	237·5	186·8	109·8
15	205·8	182·3	133·8	265·9	208·3	117·6
20	229·1	209·3	152·5	258·0	204·2	112·7
25	237·3	218·7	160·6	238·0	192·0	101·4
30	237·3	219·8	162·9	219·5	178·2	86·5
40	227·5	212·1	155·7	181·0	144·1	60·8
50	209·3	194·5	141·7	147·1	113·7	40·4
60	185·3	171·8	124·0	119·2	89·9	23·7
70	154·7	143·9	100·2	98·3	70·4	12·4
80	116·3	109·0	68·7	75·2	51·0	5·3
90	66·8	60·0	32·2	45·4	28·1	1·3
100	·00	·00	·00	·00	·00	·00

for methanol and at 9 Mole % for ethanol.   This is shown more clearly when the total entropy of mixing is used in place of ΔS_x^E.

The entropy of mixing of an ideal system is given by the well known equation

$$\Delta S_{Ideal} = -RN_1 \ln N_1 - RN_2 \ln N_2.$$
$$\therefore \quad \Delta S_{Mixing} = \Delta S_x^E + \Delta S_{Ideal}$$

The values for water-methanol and water-ethanol systems are shown in Table XII.

<div align="center">

TABLE XII

$T \Delta S_{Mixing}$ at $25^{\circ}C$.

</div>

Mole %	Methanol-water	Ethanol-water
0	0	0
10	290	273
20	448	348
30	504	348
40	523	347
50	533	347
60	485	317
70	438	288
80	358	233
90	219	129
100	0	0

These show that as we pass from methanol to ethanol there is a decrease in the amount of random orientation in the solution which is at a maximum for methanol at 45 Mole % and for ethanol at 30 Mole %.

The type of $T \Delta S_x^E$ plot given by ethanol–water is very similar to that reported by Scatchard and Raymond[50] for ethanol–chloroform mixtures. They state that the positive excess entropy of mixing is due to the reduction in the amount of association of the alcohol and the negative excess entropy to an association of chloroform and alcohol. If we apply their explanation to ethanol–water mixtures it would indicate that the number of alcohol molecules in a cluster is greater if the cluster also contains a water molecule since the negative excess entropy occurs in alcohol rich solutions, but that each molecule is then less tightly held.

Until more accurate vapour pressure data is available however it seems unwise to attempt to draw any detailed conclusions from these entropy figures.

(iii) <u>VISCOSITY</u>.

Knowledge of the viscosity of water-alcohol mixtures should lead to information about their free volume and general structure when it is remembered that

$$\eta = \frac{Nh}{V - 2bV^{2/3} V_f^{\frac{1}{3}} + b^2 V^{\frac{1}{3}}V_f^{2/3}} \; e^{\frac{\Delta E_{vap}}{nRT}}$$

Gugel[57], on the basis of kinetic theory obtained an equation similar to that of Batchinski,

$$\eta = \frac{c}{V_f}$$

where $V_f^{\frac{1}{3}} = V_e^{\frac{1}{3}} - D$

D being connected to the molecular diameter d by:

$$d = D \sqrt[3]{M/N}$$

where M is the molecular weight and $N = 6.06 \times 10^{23}$

He calculated that d for MeOH = .9890

and for   EtOH = 1.0182.

An early theoretical approach to the viscosity of binary liquid mixtures was attempted by McLeod[58] who proposed that it was a simple function of the "free space" within the liquid. Previous to this the change in volume on mixing liquids had been effectively neglected as shown by the work of Kendall et al.[59].

McLeod obtained an equation,

$$\eta = \eta_1 N_1 \frac{x_1}{x} + \eta_2 N_2 \frac{x_2}{x}$$

N_1 and N_2 Mole percentages of the components.

x_1 and x_2 their "free space".

$x = x_1 v_1 + x_2 v_2 \pm c.$

v_1 and v_2 volume percentages.

c change of volume for 1 cc. on mixing.

The free space (x) at any temperature was obtained from a knowledge of the viscosity and density at two temperatures but this was unsatisfactory for associated liquids where the degree of association changed with temperature. For normal liquids, however, quite good agreement was obtained.

Recent work by Panchenkov[60] who proposed the equation,

$$\eta = 3\sqrt{6R}\ \sqrt[3]{w^2/N}\ (\rho^{4/3}M^{5/6})\ T\ e^{\varepsilon/RT}\ (1-e^{-\varepsilon/RT})^2$$

where ε is the bond energy of the molecules.

For mixtures use $\varepsilon_M = \varepsilon_{11}c_1^2 + 2\varepsilon_{12}c_1 c_2 + \varepsilon_{22}c_2^2$

c_1 and ε_{11} Mole fraction and bond energy of component 1.

ε_{12} mutual bond energy.

and Srinivasan[61]

$$\eta^{\frac{1}{3}} = (\rho_0/100)\ (\eta_1^{\frac{1}{3}} v_1 + \eta_2^{\frac{1}{3}} v_2)\ (\rho_0/\rho_c)^{m}$$

m is a constant.

v_1 and v_2 volume of component in 100g. of mixture.

ρ_0 observed density and ρ_c calculated density from $\dfrac{100}{v_1 + v_2}$

has made possible fairly accurate calculation of the
viscosities of associated liquids.   These equations
give good agreement for water-ethanol and water-methanol
mixtures.

The viscosities of water-methanol and water-
ethanol mixtures as measured by Tammann and Pillsbury[62]
and by Bingham and Jackson (Graph V) are seen to pass
through a maximum.   It appears likely that the
occurrence of a maximum in the viscosity curve is
associated with a minimum in the free volume.   This is
not altogether unexpected as we would expect a considerable
tightening up of the water structure when even small
amounts of alcohol are added and here as before the effect
is produced by less ethanol than methanol.

GRAPH V
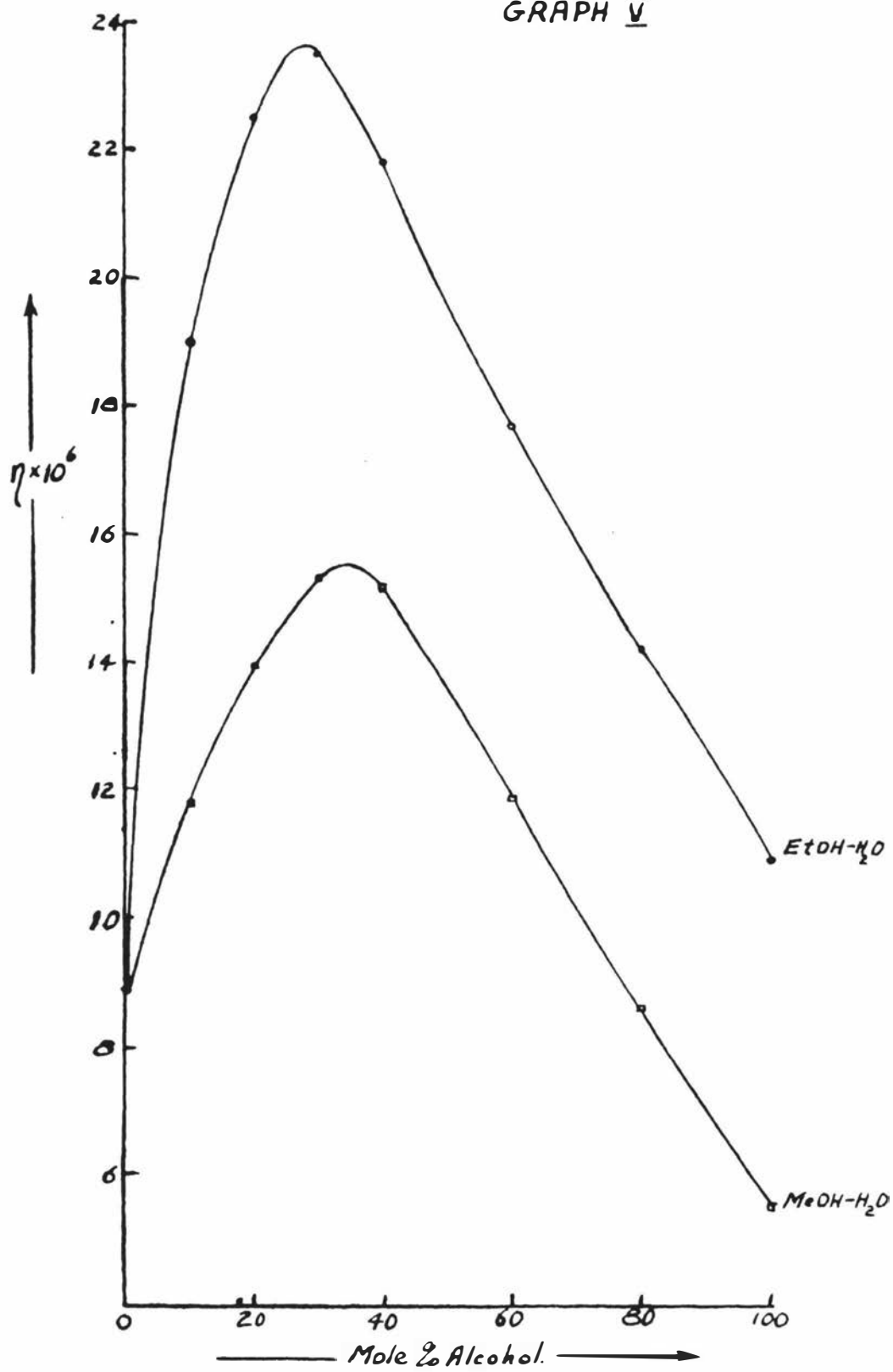
(iv) SOUND VELOCITY AND COMPRESSIBILITY.

Mikhailov[64] noted that many mixed solvents showing a maximum viscosity also gave a maximum sound velocity at or about the same composition when one of the components was water. He explained this as being due to increased association in this region, i.e. a reduction in the free angle ratio, but it appears more likely that the real reason is a decrease in free volume V_f rather than δ_3. This point of view is supported by the work of Parshad[65] who claimed that the association of water is decreased by the addition of alcohols, i.e. an actual increase in δ_3. It will be seen later that the increase in δ_3 is sufficient to overcome the decrease in V_f and so make $\delta_3 V_f$ increase steadily from water to alcohol.

The velocity of sound in the liquid (u_{liq}) is related to the adiabatic compressibility β_φ by

$$u_{liq.} = \sqrt{\frac{1}{\beta_\varphi \rho}} \quad \text{where } \rho \text{ is the density}$$

and to the free volume V_f by

$$u_{liq.} = c \left(\frac{V}{V_f}\right)^{\frac{1}{3}} \left(\frac{RT\gamma}{M}\right)^{\frac{1}{2}} \quad \gamma \text{ is the ratio } \frac{c_p}{c_v.}$$

Table XIII shows the variation of u_{liq} and β_φ in alcohol-water mixtures for the latter of which the minimum is seen to lie at about 18 Mole % alcohol.

TABLE XIII

	METHANOL-WATER[64]			ETHANOL-WATER[66]	
Mole %	u_{liq}	β_ϕ		u_{liq}	β_ϕ
0	1494	45·2		1494	45·2
20	1562	42·7		1647	39·5
40	1450	52·4		1545	47·5
60	1338	67·9		1409	60·0
80	1223	86·0		1281	75·2
100	1113	105·8		1151	98·0

Velocity of Sound in Gas at 25°C.

Water	Methanol	Ethanol
401	319·4	249·1

(v)   GAS SOLUBILITY AND ENTROPY OF SOLUTION

Previous to the present work, the only gas solubilities measured in water-alcohol mixtures were hydrogen[67], oxygen[67] and nitrogen[36] in ethanol-water mixtures. The results obtained (Table XIV) all show a minimum at about 10 Mole % . (Graph VI). In methanol solutions hydrogen shows no minimum but the rare gases, helium and neon, do (see below). For all these three, however, γV_1 shows no minimum. This appears to indicate that $\delta_3 V_f$ passes through a minimum for ethanol-water mixtures but not for methanol-water mixtures.

Calculated values of ΔG_{soln} show a maximum for the rare gases at 15 - 20 Mole % methanol while ΔS_{soln} at high temperatures shows a minimum in the same region. This would indicate more freedom of the solute molecules at this concentration and probably explains why King[68] found that the absolute partial molal ionic entropies of Na^+ and K^+ pass through a maximum at about 20 Mole % methanol.

TABLE XIV

HYDROGEN		OXYGEN	NITROGEN	
Mole % EtOH	β_{20}	β_{20}	Mole % EtOH	β_{25}
0	·0180	·0273	0	·0149
3·7	·0133	·0259	6·1	·0141
7·3	·0120	·0241	12·1	·0158
10·5	·0109	·0235	100	·1311
13·6	·0097	·0232		
16·3	·0109	·0249		
28·1	·0188	·0326		
43·9	·0238	·0461		
100·0	·0862	·2201		

GRAPH VI.
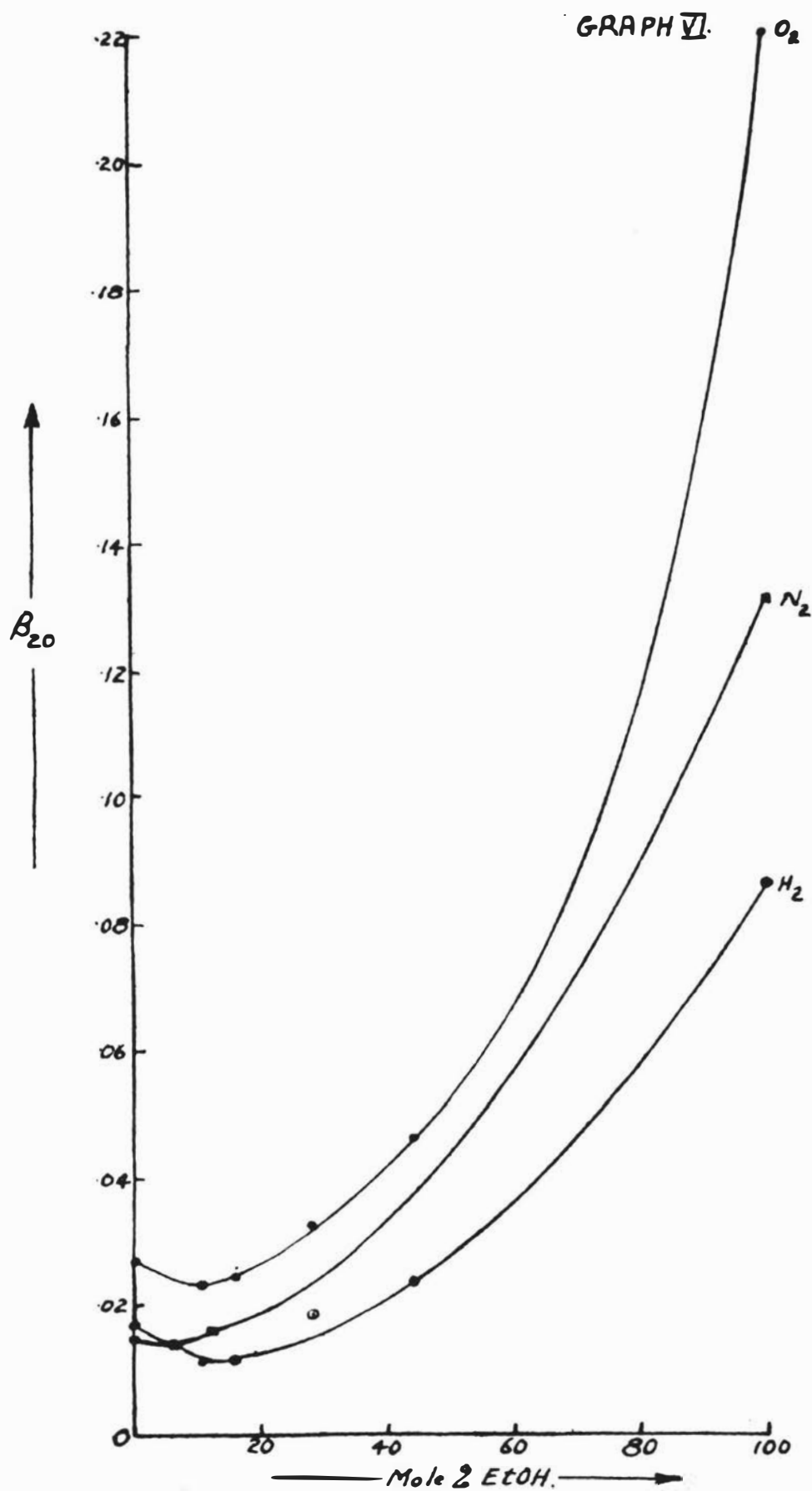
SUMMARY AND CALCULATION OF FREE VOLUME

OF WATER-ALCOHOL MIXTURES

Summarising the above lines of evidence we have:-

WATER-METHANOL.

The free volume V_f appears to pass through a minimum at or below 20 Mole % methanol while the product $\delta_3 V_f$ should show no such decrease. A maximum in the free angle ratio δ_3 is indicated particularly at higher temperatures, e.g. 40^oC. at a low methanol concentration. At room temperatures no maximum should exist.

WATER-ETHANOL.

Both the free volume V_f and the product $\delta_3 V_f$ should pass through a minimum at an alcohol concentration less than that required for methanol. The free angle ratio δ_3 does not appear to pass through a minimum and should be greater than the corresponding values for methanol-water mixtures, i.e. less restriction on the rotation of the molecules especially in alcohol rich solutions.

We will now attempt to calculate values of V_f and $\delta_3 V_f$. The free volume may be obtained from listed data on sound velocity since,

$$\frac{u_{gas}}{u_{liq}} = \left(\frac{V_f}{V}\right)^{\frac{1}{3}}$$

while $\delta_3 V_f$ may be calculated from gas solubility data.

$$\delta_3 V_f = \gamma \frac{V_1}{v}$$

or from heats of vaporisation

$$\delta_3 V_f = \frac{RT}{p} \; e^{-\Delta H_{vap}/RT}$$

where p is the vapour pressure in atmospheres.

Table XV shows values of V_f calculated from sound velocity and also δ_3 and $\delta_3 V_f$ obtained as above. These values are plotted against alcohol concentration in Graph VII.

Studies of nitration and picration in ethanol-water mixtures by Kortum[90] showed that a maximum occurred in the absorption band at about 20 Mole % ethanol. He accounted for this on the basis of a varying structure of the solvent which seems to confirm the fact noted above that the solvent is most closely packed at about this concentration.

The values of the free volume of water-ethanol mixtures listed above may be compared with those calculated by Matsuyama[131] which, while not referring to quite the same thing, may be taken as a measure of the volume in which the molecules are free to move. He calculated the

GRAPH VII
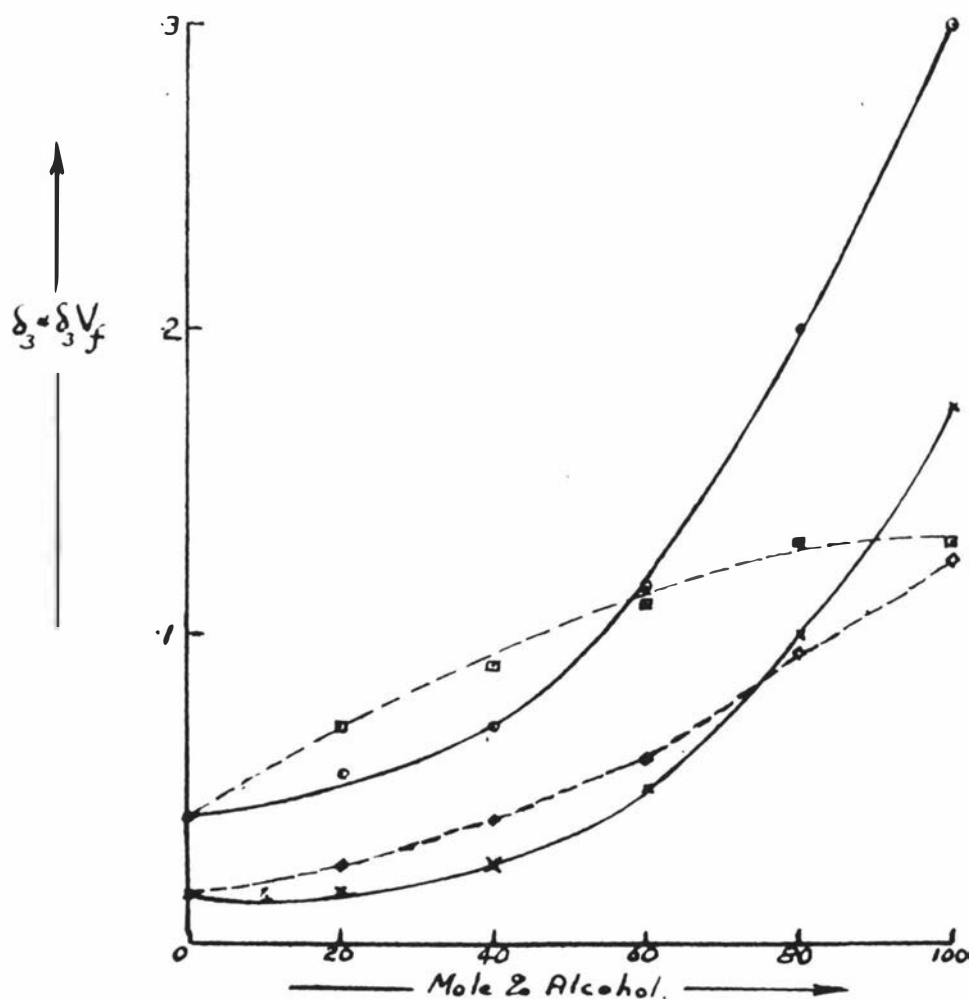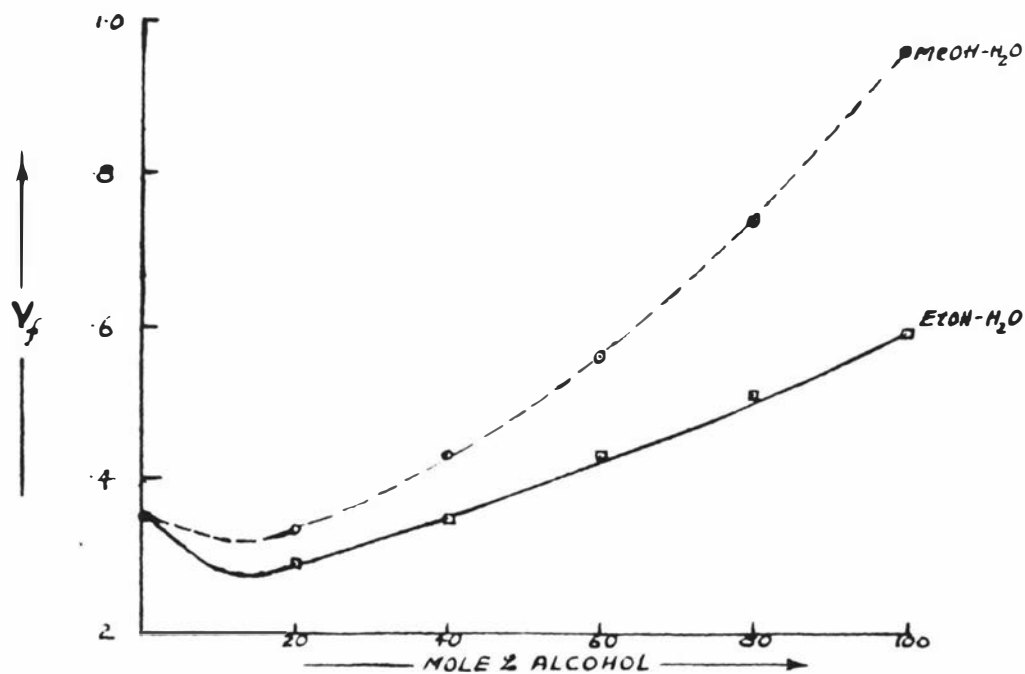
volume occupied by 1 mole of water and 1 mole of ethanol from known dimensions of the molecules and obtained figures of V_{H_2O} 10·6 c.c. and $V_{C_2H_5OH}$ 31·9 c.c.

Then for a given solution the "free volume" was defined from

$$\text{"Free volume"} = V - (10·6\ N_{H_2O} + 31·9\ N_{C_2H_5OH})$$

where V is the molal volume of the solution.

The relative free volume is then defined by $\dfrac{\text{"Free volume"}}{V}$ and the following results obtained:

Mole % EtOH	V	"Free Volume"	"Relative Free Volume"
0	18·069	7·47	0·415
20	21·230	8·72	0·411
40	25·572	10·6	0·415
50	28·467	11·9	0·418
60	32·001	13·5	0·422
80	41·861	18·2	0·436
100	58·680	26·8	0·457

These values are seen to show the same trend as those calculated from solubility and sound velocity data in that a minimum is found in the region of 20 Mole % ethanol.

TABLE XV

METHANOL-WATER

Mole % MeOH	u_{liq}	V_f	Gas Solubility $\delta_3 V_f$	δ_3
0	1494	·35	·015	·04
20	1562	·33	·025	·07
40	1450	·43	·040	·09
60	1338	·56	·060	·11
80	1223	·74	·095	·13
100	1113	·96	·125	·13

ETHANOL-WATER

Mole % EtOH	u_{liq}	V_f	Gas Solubility $\delta_3 V_f$	δ_3
0	1494	·35	·015	·04
20	1647	·29	·016	·055
40	1545	·35	·025	·07
60	1409	·43	·050	·115
80	1281	·51	·100	·20
100	1151	·59	·175	·30

GAS SOLUBILITY MEASUREMENTS

Many methods of procedure and kinds of apparatus have been used in the measurement of gas solubility. Most of these can be classed definitely as either physical or chemical. The latter methods depend on specific chemical properties of the gas and thus can be used with only a limited number of gases. The main physical methods depend on the measurement of the quantity of gas necessary to saturate a known volume of initially gas-free solvent. This may appear to be a simple matter but the following difficulties are encountered:-

1. Complete degassing of solvent.
2. Attaining equilibrium without the danger of supersaturation.
3. Measurement of solvent volume and gas space above it.
4. Use of dry gas or gas saturated with solvent vapour.

1. The production of gas-free solvent is not an easy matter as was shown by Leduc[69] who found that even after boiling distilled water a long time it gave up gas bubbles on freezing. The usual method of preparing gas-free liquid for solubility measurements has been boiling

followed by cooling in a vacuum.   After degassing care
must be taken that the solvent does not come in contact
with air or low solubility results are obtained.   For
organic solvents, 30 minutes degassing is sufficient but
for water prolonged boiling over several hours is required.

2.   In the earliest gas solubility work, by Bunsen[70],
equilibrium was attained by vigorously shaking the gas and
solvent in the absorption vessel where both the gas and
solvent volumes were measured.   Ostwald[71] introduced a
method which proved to be much better than Bunsen's, the
fundamental difference being that the gas volumes were
measured in a burette connected to the absorption vessel
rather than in the vessel itself.   Equilibrium was still
attained by shaking the absorption vessel which was
connected to the burette by a flexible capillary tube.

Stern[72] used a glass capillary spiral as did
Maxted and Moon[73] (Fig. 3) while metal spirals were used
by Steiner[74] (Platinum), Timofejew[75] (Platinum), Estreicher[76]
and Curry and Hazelton[77] (Copper).

The whole apparatus was shaken by McDaniel[78]
and by Lannung[79] (Fig. 1), but wherever vigorous shaking
is used to secure equilibrium there appears to be a danger
of supersaturating the solution.   This aspect was discussed
by Cady, Elsey and Berger[80] who considered that supersat-
uration was easily attained.   Morgan and Pyne[81] attempted

to test this by using an apparatus in which the gas was repeatedly bubbled through the solvent. They obtained similar results for the system carbon dioxide-water as other workers who had used violent agitation, but their method seems just as likely to cause supersaturation as the ones used by the workers whom they were trying to check.

Rakestraw and Emmel[82] found that when sea water was shaken with air and the solution allowed to stand until bubbles were no longer visible the nitrogen content was two per cent higher than the equilibrium value.

A method of stirring which ensures that the correct equilibrium is obtained is by means of an iron bob enclosed in glass, and a magnet. This was used by Akerlof[27], Antropoff[83], Cady, Elsey and Berger[80] (Fig. 2), Cassuto[84], Wright and Maas[85] and Horiuti[86]. Although there appears to be no danger of supersaturation when this method is used it has the disadvantage of requiring a large dead gas space above the solvent thus reducing the accuracy of the results.

3.   The usual method of determining the solvent volume is by mercury displacement (Lannung), or by weighing the absorption vessel (Maxted and Moon). Both of these result in the absorption vessel being completely filled

with degassed solvent and McDaniel[78] produced a suitable
gas-liquid interface by running out solvent and weighing
it to find the volume of gas which replaced it.   When
this procedure is followed there is some danger that a
part of the solute will be lost especially when the
density of the solvent increases after gas solution.
Horiuti showed that a considerable error was introduced
by this method for the systems sulphur dioxide and nitrous
oxide in acetone.   A better alternative method is to
leave mercury in the absorption vessel and run it out in
the same manner.   This was done by Lannung, Horiuti and
Cady, Elsey and Berger.

Lunge connected the bottom of the absorption
vessel to a levelling bulb of mercury which could be
lowered to let mercury out of the vessel.   After equi-
librium was attained the solvent level was raised to the
original mark and the gas volume measured.   A similar
method was used by Cady, Elsey and Berger.

Christoff[38] brought the liquid and gas into
contact before measuring the gas volume.   He found that
the rate of solution was such that no appreciable volume
of gas dissolved during the measurement.   It will be
seen later that while this may be true for water as a
solvent, it is certainly not true for organic solvents
such as ether.   Estreicher[76] and Drucker and Moles[88] left

a vacuum over the liquid when the vessel was filled, which
was later filled with gas from the burette after the
volume had been measured.

The change in volume of the solution as a gas
dissolves introduces a certain error.   Markham and Kobe[89]
showed that the solubility of carbon dioxide in aqueous
solutions might be in error up to 0·1% for this reason,
while Cady, Elsey and Berger[80] consider that it constitutes
one of the main errors in Antropoff's[83]solubility work on
helium.   Another source of inaccuracy is the variation
in solvent volume with temperature.   This is very
important in an apparatus such as Lannung's where the
solvent level is not returned to the same mark before a
reading is taken.   For this reason the author considers
that Lunge's method probably leads to the most accurate
results under ordinary conditions.

4.   Some workers have used dry gas in the burette
while others have used gas saturated with solvent vapour.
If the gas in the burette is saturated, the vapour pressure
of the solvent is of little importance, but if it is dry
the vapour pressure must be known accurately since all gas
coming into the free space above the liquid in the
absorption vessel picks up vapour increasing its volume
to an extent determined by the vapour pressure.

When wet gas is used the whole apparatus must
be kept in the thermostat or solvent vapour will condense
out and cause errors.   Horiuti claims that wet gas gives
anomalous results near the boiling point of the solvent
but this appears rather unlikely as in all gas solubility
work the gas over the solvent in the absorption .vessel
is saturated with solvent vapour.

When a mixed solvent such as alcohol—water is
used, the gas taken into the burette must be dry, as it
is practically impossible to have degassed solvent of the
same composition as the solvent in the gas saturator since
the alcohol content of the solvent is considerably reduced
during degassing.
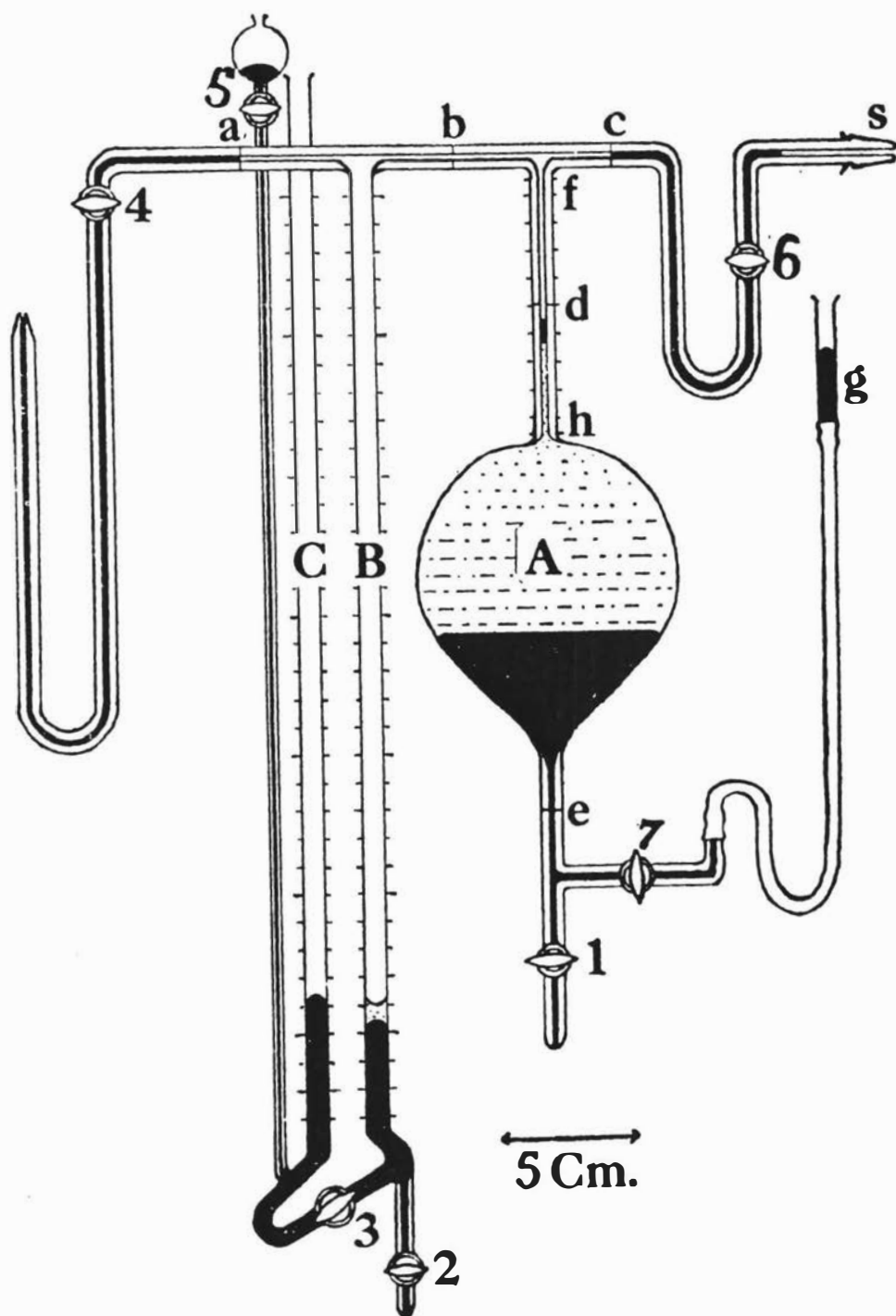
FIGURE 1

TYPES OF GAS SOLUBILITY APPARATUS

The general principles which have been discussed
are best illustrated by considering representative types
of apparatus:-

A diagram of the essential features of Lannung's
apparatus is shown in Figure 1.   Solvent was brought in
through S by allowing mercury to run out through 1 until
A was about half full of solvent.   The joint S was then
connected through drying towers to a pump and the solvent
degassed at room temperature.   Mercury was then let in
through 7 until the solvent surface was at d.   The tap
3 was opened and the remainder of the apparatus filled
with mercury.   The whole apparatus was then placed in
an air thermostat and brought to $20^{o}C$. the solvent level
being kept at d by raising or lowering g.   The gas burette
was then filled and mercury brought through the syphon
tube to a.   Tap 4 was then closed.   By opening 7 and
raising g a few drops of solvent were passed over into the
gas burette to saturate the gas with solvent vapour.   After
bringing the solvent surface to f a small quantity of
mercury was blown from the horizontal capillary to the
surface of the solvent.   The rest of the mercury was
then sucked back to C.   As the bulb A and vertical
capillary hf constituted a sensitive thermometer it was
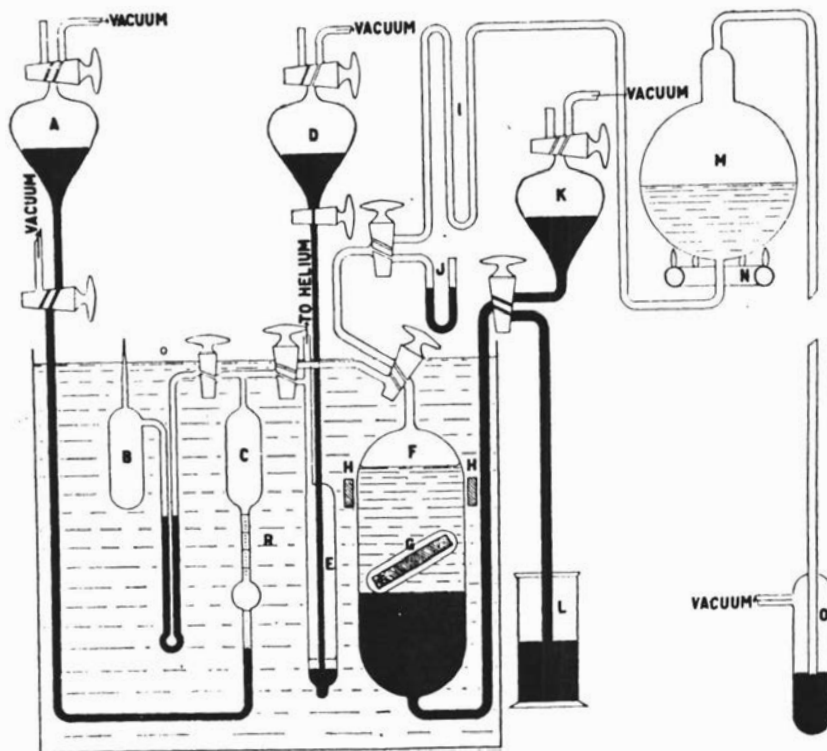
FIGURE 2

easy to tell when temperature equilibrium was attained.

Saturation of the solvent was brought about
by running out through 1 about 1 cc. of mercury which was
weighed, and then putting the apparatus into an air
thermostat where it was mechanically shaken.   The change
in gas volume was read from the levels in B and C and
the solubility calculated directly.

With the vigorous shaking employed by Lannung
there is some danger of supersaturation, which was
eliminated by Cady, Elsey and Berger[80] who used a magnetic
stirrer (Figure 2).   To start a measurement the bulb B
was filled with dry air at atmospheric pressure and
sealed.   C and F were pumped out through the three-way
stopcock below A.   During the process, the stopcock
between B and C was carefully opened until expansion of
air in B had driven the mercury in the manometer up to
the stopcock and through its bore.   The cock was then
closed and the evacuation of C and F completed.   The
bulb F was then filled with mercury from K.   The solvent
in M was degassed for about $\frac{1}{2}$ hour and then brought to
atmospheric pressure.   The gas was introduced into the
system as follows.   The bulb E was evacuated and filled
with mercury from D.   A small amount of solvent was
introduced and boiled under reduced pressure to remove the
air.   Helium was then introduced and the water boiled

again by reducing the pressure ensuring the removal of air from the water.

Finally E was left filled with pure helium under atmospheric pressure and in contact with water. The gas-measuring system C was then filled with helium from E and brought to the pressure of the air in B. Degassed solvent was brought over from M into F by running out mercury into L which was weighed to determine the volume of solvent. The levels of the manometer between B and C and the level of the mercury in the gas burette C were read, then the greater part of the gas was transferred to F and its solution started. The rate of solution was increased by using a magnetic stirrer but equilibrium was only obtained after about 24 hours. The solvent level was then returned to its original mark, the pressure adjusted and the volume of the remaining gas read.

The main disadvantage of using a magnetic stirrer is the long time required to attain equilibrium. This is considerably shortened by using a gentle shaking method developed by Maxted and Moon[75] (Figure 3).

In this apparatus the gas space above the solvent was reduced to a minimum by employing an absorption vessel of the form shown at A. This vessel which was immersed in a thermostat contained in addition to the solvent, a small quantity of mercury B, and was rocked so that the
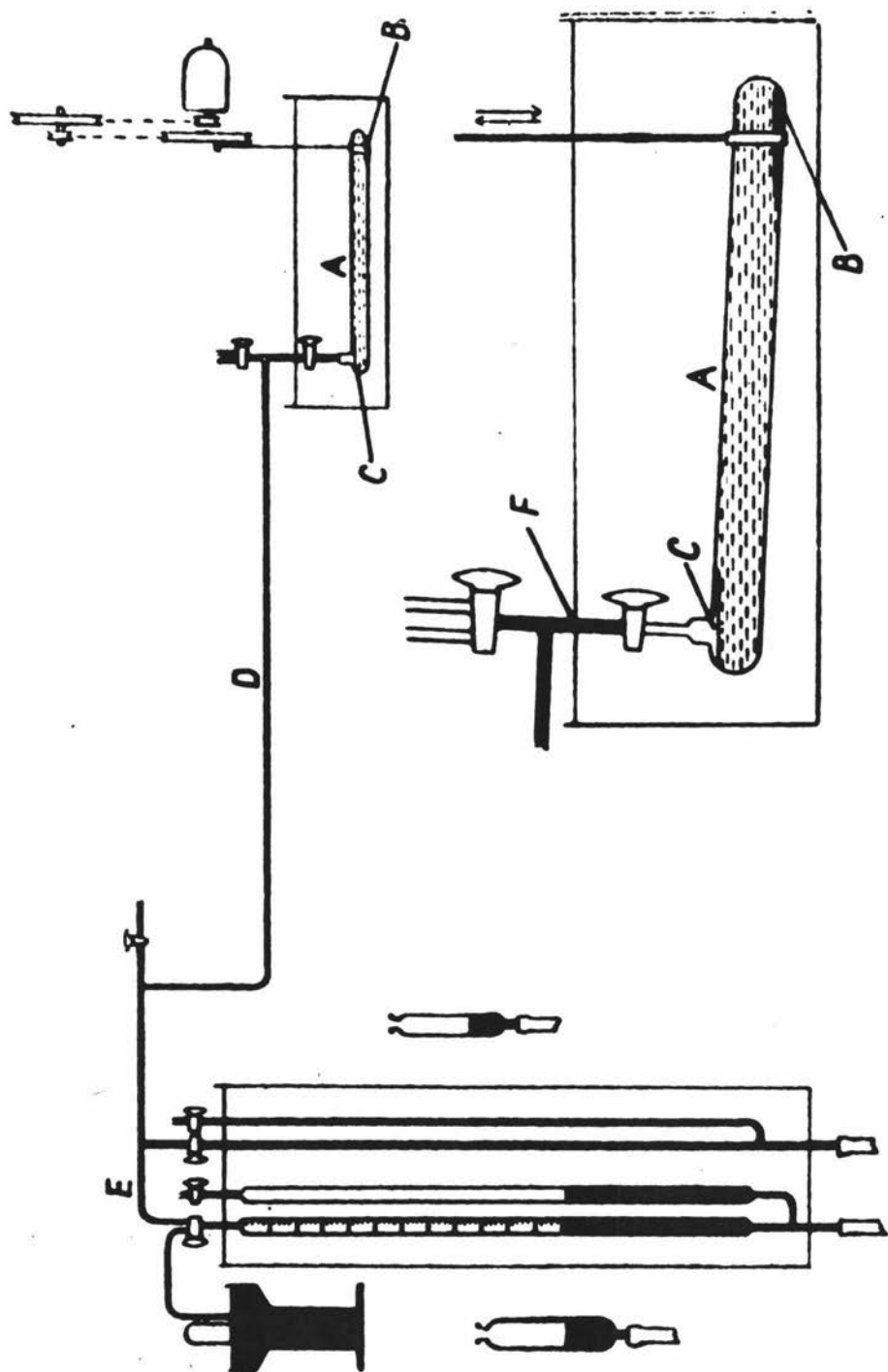
FIGURE 3

mercury and the gas bubble C moved along the tube in opposite directions.   This caused the gas-liquid interface to be constantly renewed while the mercury stirred the liquid.   The 1 metre long capillary D was used to obtain sufficient flexibility to enable the absorption vessel to be rocked.

To carry out a measurement the absorption vessel was detached by cutting at F.   A small quantity of mercury was introduced and the vessel filled with solvent except for the space C.   The degassing of the solvent which was carried out in situ was aided by periodically shaking the absorption vessel.

It was then reconnected to the remainder of the apparatus and the capillary link D evacuated with a Hyvac pump.   This was then filled with gas from the burette E and the zero point observed.   This assumed that in the absence of rocking the rate of solution was sufficiently low to be neglected while the initial reading was taken.

The above considerations have lead to the development of a new apparatus using Maxted and Moon's method of securing equilibrium but improving the method of determining gas and solvent volumes.

CRITICISMS OF PREVIOUS GAS SOLUBILITY WORK.

Gas solubility work before 1910 was considered by Markham and Kobe[92] to be all rather inaccurate. This was due to the methods used to attain equilibrium, which consisted in the main of violent shaking which led to supersaturation and high results. Other possible errors were incomplete degassing of solvent and impure gases, the latter factor being important in the case of the inert gases (He, Ne, A, etc.).

Cady, Elsey and Berger eliminated the error due to change in volume of the solvent during a run by pushing the solution back to a known mark after absorption. They only degassed their solvent (water) for about 30 minutes, but in the present work it was found that up to 2 hours were required for the complete degassing of this particular solvent.

The work of Lannung was criticised by Akerlof on the basis that the contact surface was small but a more important error appears to be the failure to correct for the expansion of the solvent when the gas dissolves. Because the volume of the solution is greater than that of the pure solvent the gas space must decrease, so that the solubility figures listed by Lannung will be too low. This difficulty was overcome both in the present work and

by Cady, Elsey and Berger by returning the solvent to a definite mark after saturation.   Degassing the solvent at room temperature also seems rather unsatisfactory, especially for water.

Akerlof used a method which measured the difference in pressure after solution.   This eliminated the error in Lannung's work and higher results were obtained.

$$\beta_{25}$$

	Lannung	Akerlof
He	·0086	·0087
A	·0310	·0332

Maxted and Moon give but few details of their apparatus, but it seems that there was at least no danger of supersaturation while equilibrium was attained in a reasonably short time.   The capillary connecting the burette to the absorption vessel, however, was at a temperature differing from that of the solvent and the gas in the burette and this would introduce errors which were probably not unappreciable.
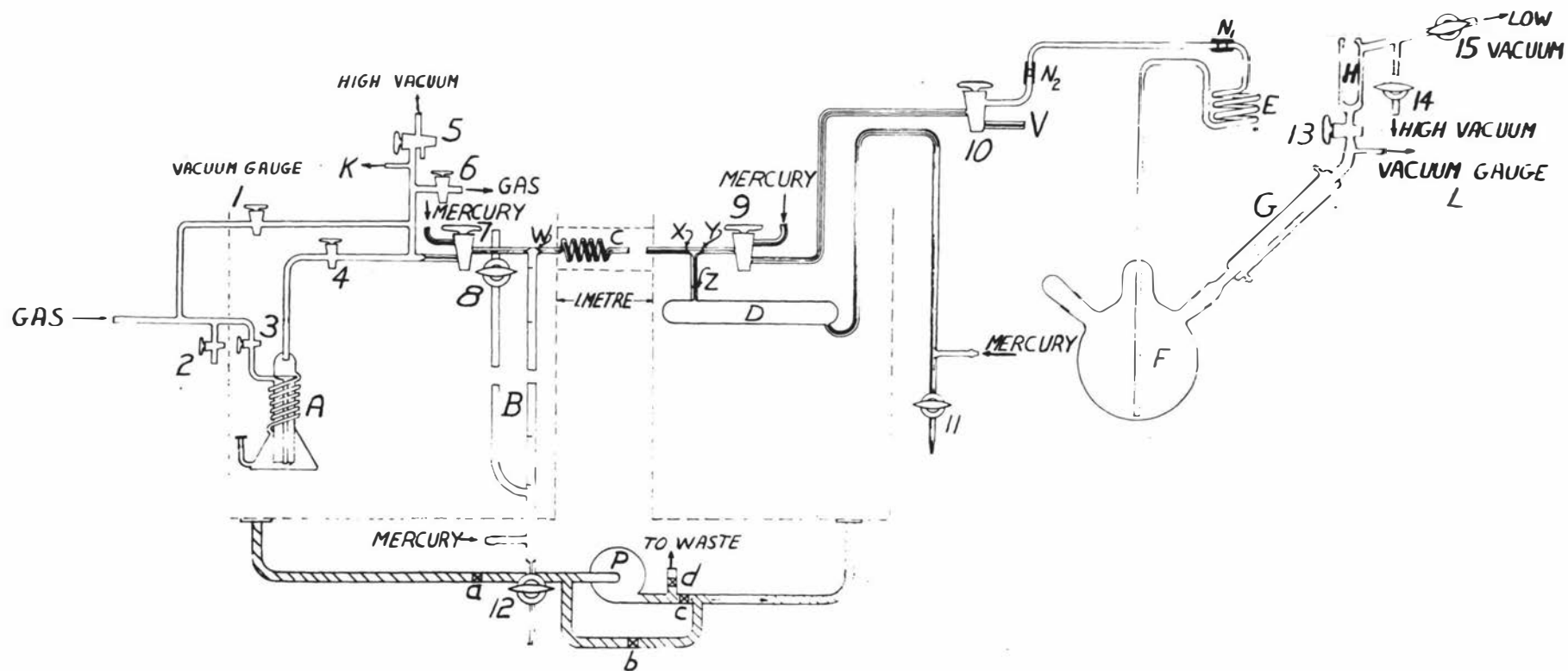
FIGURE 4.

THE   APPARATUS

In Maxted and Moon's apparatus the solvent volume was determined by weighing the pipette before and after filling with solvent.   One must then assume no solvent loss on degassing which appears rather unlikely, especially for organic solvents of low boiling points. However, the method of securing equilibrium was very efficient and this principle was employed in the present apparatus (Figure 4).   The solvent volume is determined by mercury displacement and the apparatus is so designed that during a run neither the gas nor the solvent is in contact with any stopcocks.

The apparatus consists essentially of

(i) A gas measuring system.

(ii) A pipette in which equilibrium is attained.

These two parts are each immersed in thermostats containing about 30 gallons of water, the two being 1 metre apart to obtain sufficient flexibility to allow the pipette to be shaken.   The coil (C) was put in to increase this flexibility and together with the connecting capillary is jacketed and water circulated round it from the thermostats by means of the pump (P).   By means of the valves (a, b, c, d) it is possible to pump out either of the thermostats
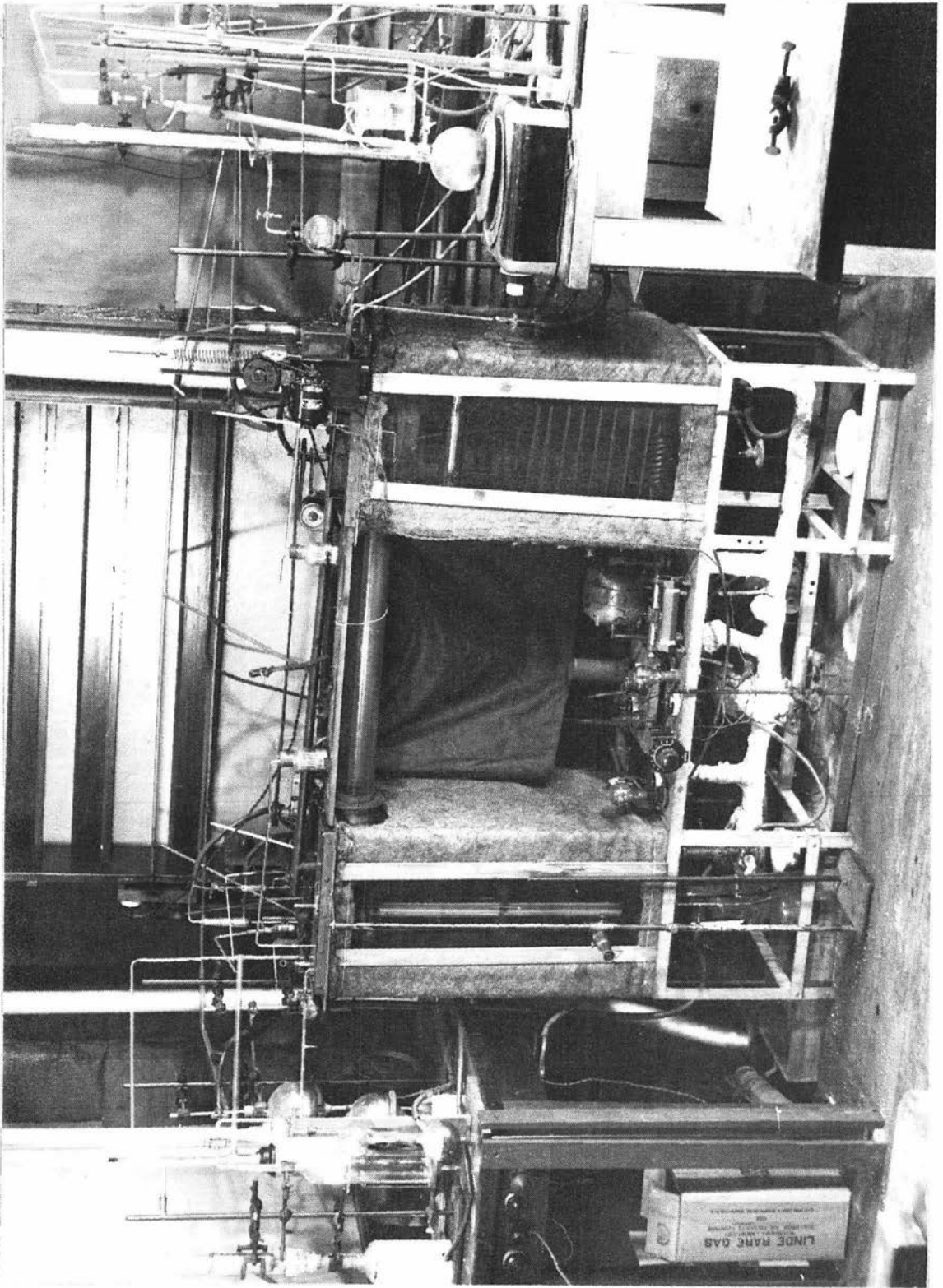
FIGURE 5

to waste or to circulate water from left to right.

The pipette D is fastened to a copper cradle by means of two saddles, the lower half of each being copper and the upper half perspex. The cradle is pivoted from a point opposite W and moves, with bakelite bearings which are water lubricated, against a sheet of copper fastened to the right hand thermostat.

The actual movement is obtained from a $\frac{1}{50}$ h.p. motor through a gear box and flexible coupling on to an eccentric. The cradle is fixed to a spring (Figure 5) which takes up half of the load and gives a smooth even rocking motion.

The solvent is degassed in the flask (F) and brought into the pipette (D), the volume being determined by mercury displacement. The gas which may be wet or dry, depending on whether a pure or mixed solvent is being used is measured in the burette (B) and about 3 cc. pushed over into the pipette (D). This is then rocked to speed up the rate of saturation. The small amount of mercury which remains in the pipette after bringing the solvent over stirs the liquid while the movement of the gas bubble causes the gas-liquid interface to be constantly renewed. N_1 and N_2 are two pieces of neoprene to provide sufficient flexibility between the flask (F) and the rocking pipette (D).

The baths are heated electrically at 35°C. and

40°C. and with gas at lower temperatures while, when necessary, cooled water-glycol mixture from a refrigerator is pumped through the cooling coil.

A description of the procedure for a typical run will make the above points clear:-

(A) If a pure solvent is being used. e.g. water.

About 600 cc. of solvent are placed in the flask (F) and with taps (10) and (14) closed a low vacuum (from a water pump) is applied through (13) and (15). The flask is heated by means of a hot-plate whose output is controlled with a Sunvic energy regulator. For water the degassing process requires several hours, but for organic solvents is much more rapid. The trap (H) which is filled with solid CO_2 and acetone is used to reduce the loss of more volatile solvents. When the solvent is completely degassed the tap (13) is shut, the condenser (G) drained, and the heating continued until the pressure above the solvent is at atmospheric pressure as shown by the gauge (L). This causes the solvent to rise through the coil (E) until it has completely filled the tube up to the tap (10), no air bubble being visible.

The apparatus is then evacuated through (5) by means of a two stage mercury pump, and filled completely with mercury between taps (7) and (10).

The three-way taps (9) and (10) are turned
to the appropriate positions and mercury run out through
(11) until the solvent level is between (9) and (10).
More mercury is then admitted into the apparatus and this
solvent pushed out at V.   This is repeated several times
to ensure that only air free solvent will finally be
admitted into the pipette as initially the bore of tap
(10) was filled with air.

A beaker of ice water is placed round the coil
(E) and the mercury run out through tap (11) into a weighed
beaker until the required amount of solvent has been
admitted.   This is then allowed to come to thermal
equilibrium after which tap (10) is shut and tap (9) opened
so as to allow mercury to fill the capillary up to the
mark (Y), mercury being run out of tap (11).   The tap (9)
is then shut and the solvent is nowhere in contact with
tap grease.   The weight of the mercury run out through
tap (11) gives the total weight of solvent from tap (10)
to the mercury surface.   From this must be subtracted the
previously determined volume between taps (9) and (10),
including the amount in the bore of (9), as this amount
of solvent is trapped when tap (9) is shut.

With taps (1), (2), (5), and (7) shut and (3),
(4), and (6) open gas is passed through the saturator (A)
and out through (6).   The saturator, which was designed by

Markham[91], contains about 200 cc. of pure solvent and ensures that the gas is saturated with solvent vapour. The use of this is only possible with pure solvent as it will be seen later that the composition of a mixed solvent changes during degassing.

After the gas has been passing through the saturator for some time, tap (2) is opened and (3) and (6) shut. The gas in the system is pumped out through tap (5) after which more is admitted. Initially this was done through tap (3) but it was found that solvent from the saturator splashed over into the gas line even after a trap had been placed in the head of the saturator. To eliminate this the pressure is raised to $\frac{1}{2}$ atmospheric pressure by allowing gas in through (1) after which this is shut and (3) opened until normal pressure is shown by the gauge (K). Tap (6) is then opened. By this method some dry gas is introduced but by continuing to pass gas for some time this is removed and quite reproducible solubility figures are obtained.

The three-way tap (7) is opened to the gas line after tap (6) is shut, while tap (8) is opened. Mercury is run out of the burette (B) until about 9·8 ccs. of gas have been admitted. Mercury is then run in through tap (7) to prevent the gas from coming in contact with tap grease during a run which may take up to three days. The two

columns of the gas burette (B) are levelled, and, with
the aid of a telescope containing a scale, the volume
read to ·002 cc. The burette had previously been
calibrated by running mercury out through tap (12) and
weighing each ·1 cc.

At this stage the gas is separated from the
solvent by a mercury thread between (W) and (X). Mercury
is run out through tap (11) into a weighed beaker until the
gas reaches the mark (Z) etched on the vertical capillary,
the columns of mercury in (B) being kept level. The
weight of mercury run out gives the volume between (Z)
and (W). It is necessary to determine this for each run
as the position where the mercury thread breaks at (W)
varies somewhat.

More mercury is run out through tap (11) until a
bubble containing about 3 cc. of gas is formed in the
pipette (D). Rocking is then commenced and continued for
1 to 2 hours. At the end of this period mercury is admitted
to the pipette until the solvent level is at (Z) and the
volume of gas in the burette read. The difference between
this reading and the initial one minus the volume (W-Z)
gives the volume of gas dissolved.

Gas is then pushed over to form another bubble
and the process repeated until no further absorption of gas
is detectable after shaking for some time.

(B)   Mixed solvents. e.g. water-methanol.

The procedure is the same as for pure solvents
except that dry gas must be used.   When the water-methanol
mixture is degassed a considerable loss of methanol occurs
so that the composition of the solvent in the pipette (D)
cannot be determined until after the run when a density
measurement is carried out.

Dry gas is brought into the burette through
tap (1).   This is then saturated by means of the solvent
in the pipette at the same time as the solution process
is continuing.   The amount of solvent used for this is
negligible and is neglected.   The solution process is
always complete before saturation of the gas, and gas must
be passed from burette to pipette and back until no further
increase in volume is noted.
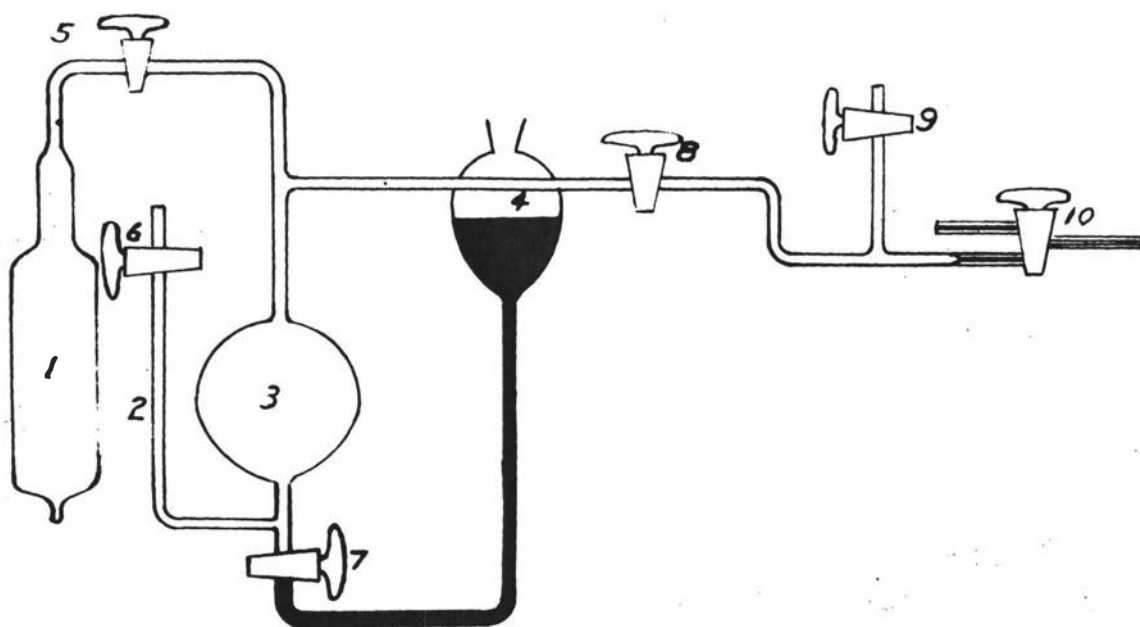
FIGURE 6

MANIPULATION OF RARE GASES

The method employed to get rare gas from a sealed bulb into the burette is shown in Figure 6. The bulb of rare gas (1) is sealed through tap (5) to a bulb (3) of 1 litre capacity, the two being connected through taps (8) and (9) to a high vacuum system. The tap (10) shown here is identical with tap (7) of Figure 4 and connects with the gas burette.

Taps (10), (6) and (7) are shut and the system pumped out through (9). By using a two-stage mercury diffusion pump backed by a two-stage rotary oil pump, vacua better than 10^{-6} mm. of mercury are obtained. At this stage sufficient mercury is admitted through tap (7) to fill the tube (2) when the vacuum is lowered. Tap (9) is then shut and the pip of the rare gas bulb broken by means of a magnetically operated steel ball. Tap (5) is then closed and the gas in the rest of the system brought to atmospheric pressure by admitting mercury through tap (7). When this is attained the level of mercury in (2) (with tap (6) open) is the same as the level of the mercury in bulb (3).

When rare gas has to be admitted to the burette, the latter is evacuated through taps (9) and (10) and filled

with mercury.   Taps (8) and (10) are then closed and the T-tube pumped out through (9).   This is then closed and gas allowed in through (8). When gas is required it may then be drawn directly into the burette through tap (10).

When working with He, Ne, and A only dry gas was used as insufficient was available to use a saturator in the line, but it was found with hydrogen that the same result was obtained with either wet or dry gas.

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PURIFICATION OF MATERIALS

Methanol.

The methanol was refluxed for six hours over quicklime and distilled. It was then dehydrated by the method of Lund and Bjerrum, described by Weissberger and Proskauer[95], using magnesium activated by iodine, finally being distilled and the middle fraction collected. This distillation was in an all glass apparatus with a 50 cm. fractionating column filled with glass beads.

Physical Constants.

(a) Boiling Point   63·75°C.

(b) Refractive Index   1·3284 / 20°C.

Helium and Argon.

Spectroscopically pure samples from the British Oxygen Company were used.

Neon.

Spectroscopically pure neon from the Linde Air Company was used.

Hydrogen.

Electrolytic hydrogen from a cylinder was passed through potassium hydroxide solution to remove carbon dioxide, through concentrated sulphuric acid and over heated

copper and platinised asbestos to remove oxygen.   The gas was then dried over phosphorus pentoxide and passed through a liquid air trap to remove easily condensable impurities.

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METHODS OF EXPRESSING GAS SOLUBILITY

Two coefficients have been employed to express the results of solubility measurements with gases.

The first, proposed by Bunsen (1857) is defined as the volume of gas reduced to N.T.P. dissolved by unit volume of solvent at the temperature of the experiment under a partial pressure of the gas of 1 atmosphere.

If v_0 is the volume of gas dissolved, at N.T.P.

V is the volume of the solvent,

p is the partial pressure of the gas in atmospheres.

Then the Bunsen Coefficient β is given by

$$\beta = \frac{v_0}{Vp} \quad .$$

This assumes that the ideal gas laws hold, but Markham and Kobe[92] showed that an error of 0.7% was introduced for the solubility of carbon dioxide in water at $0^{\circ}C$.

If the solubility is expressed per gramme of solvent we have what is known as the Kuenen Coefficient.

A more useful coefficient is that suggested by Ostwald (1888) ,γ, which is defined as the volume of gas measured at the temperature and pressure of the experiment

dissolved by unit volume of the solvent. If v is the
volume of gas dissolved at a temperature T and a partial
pressure of the gas p, then assuming the gas laws are
obeyed,

$$v = v_0 \frac{T}{273} \cdot \frac{1}{p}$$

$$\therefore \gamma = \beta \frac{T}{273}.$$

STANDARD STATES

The particular states used for both the gas and the solution in calculating thermodynamic functions for the process

$$X_{(gas)} \longrightarrow X_{(solution)}$$

have varied from author to author, no two apparently using the same states for both.

Butler[94] employed as standard states $N_2 = 1$ for the solution and a pressure of 1 mm. for the gas.

Bell[93] used a pressure of 1 atmosphere for the gas but for the solution he chose the state at which the concentration of the solution is equal to the concentration of the gaseous phase.

Eley's[4] standard states are a pressure of 1 atmosphere for the gas and a concentration of 1 mole per litre for the solution.

Frank and Evans[5] used a pressure of 1 atmosphere for the gas and $N_2 = 1$ for the solution.

The problem of whether to use $N_2 = 1$ or 1 mole litre^{-1} as the standard state for the solution is a complex one but when comparing the thermodynamic functions for any one gas in a number of solvents the former is the more satisfactory. In the present work results are quoted on

the basis of both Eley's and Frank and Evans' standard states.

The above variations in standard states give rise to different equations for ΔG_{Soln} ΔH_{Soln} ΔS_{Soln} all of which, however, are interconvertible by the addition or subtraction of suitable terms.

$$\Delta G_{Butler} = -RT \ln \gamma + RT \ln \frac{R'T \ x \ 760}{V_1}$$

where $R' = 82 \cdot 1$ cc. atms. deg^{-1}

$$\Delta G_{Bell} = -RT \ln \gamma$$

$$\Delta G_{Eley} = -RT \ln \gamma + RT \ln \frac{R'T}{1000}$$

$$\Delta G_{Frank \ and \ Evans} = -RT \ln \gamma + RT \ln \frac{R'T}{V_1}$$

So for the corresponding entropy terms we find

$$\Delta S_{Frank \ and \ Evans} = \Delta S_{Butler} + R \ln 760.$$

$$\Delta S_{Frank \ and \ Evans} = \Delta S_{Bell} - R \ln R'T - R \ln V_1$$

$$\Delta S_{Frank \ and \ Evans} = \Delta S_{Eley} - R \ln \frac{V_1}{1000}$$

This causes variations of the following order.

H_2 in benzene at $20^{\circ}C$.

$$\Delta S_{Bell} \quad\quad - \ \cdot 34$$

$$\Delta S_{Eley} \quad\quad - 7\cdot1$$

$$\Delta S_{Frank \ and \ Evans} \ -11\cdot6$$

H_2 in water at $25^{O}C$.

ΔS_{Butler} $-39\cdot2$

ΔS_{Eley} $-18\cdot2$

$\Delta S_{Frank\ and\ Evans}$ $-26\cdot0$

———————

CALCULATION OF RESULTS

Due to the change in methanol concentration of
the solvent during degassing the experimental solubility
figures were not obtained at even methanol concentrations.
Because of this the results of six or seven runs at each
temperature were least squared and values at each 20 Mole %
methanol interpolated.

These values were then converted to Ostwald
coefficients since

$$\beta = \Upsilon \frac{T}{273}$$

Values of the free energy of solution may then be obtained
from

$$\Delta G_{Solv} = -RT \ln \gamma + RT \ln \frac{R'T}{V_1} \text{ (Frank and Evans)}$$

or

$$\Delta G_{Solv} = -RT \ln \Upsilon + RT \ln \cdot 082T \text{ (Eley)}$$

The variation of ΔG_{Solv} with temperature can be
expressed in the form of an equation by the method of
least squares which on differentiation gives values of
ΔS_{Solv}. In the present work the equations relating
ΔG_{Solv} to temperature were quadratic so that on
differentiation a straight line relationship was established
between temperature and entropy. This may be criticised,
but when the order of accuracy of the results is considered

($\pm$ 0·5 eu.) it is seen to be quite unimportant.   This
inaccuracy of up to ·5 eu. seems to have been neglected
by workers such as Eley, who strove to obtain theoretically
values within 0·1 eu. of the experimental ones, when the
latter are often possibly several entropy units out.

In the following tables (XVI - XIX) the thermo-
dynamic functions are listed for the standard states of
both Eley, and Frank and Evans.   For purposes of
comparison between different solvents the latter only
should be used as the molal volume of the solvent is
taken into account.

Table XX lists the values used for the vapour
pressure of water-methanol mixtures in the calculation of
the listed Bunsen coefficients.   These were interpolated
from data listed by Vrewski[55], Butler[53] and Bredig and
Bayer[52] and are accurate to $\pm$ 1 mm.   This will introduce
an error into the resulting solubility figures, which will
however be not greater than 1% in the most unfavourable
case, i.e. within the experimental error.

TABLE XVI

Thermodynamic Functions for the System He – H_2O – CH_3OH

Bunsen Coefficient β
Mole % MeOH

Temp.	0	20	40	60	80	100
10	·0098	·0098	·0122	·0170	·0223	·0293
15	·0097	·0097	·0124	·0173	·0235	·0306
20	·0096	·0096	·0126	·0177	·0243	·0319
25	·0095	·0093	·0128	·0181	·0250	·0331
30	·0094	·0091	·0130	·0185	·0258	·0344
35	·0092	·0101	·0138	·0193	·0268	·0356
40	·0091	·0108	·0152	·0213	·0288	·0372

Ostwald Coefficient γ

Temp.	0	20	40	60	80	100
10	·0102	·0102	·0126	·0176	·0236	·0304
15	·0102	·0102	·0131	·0183	·0248	·0323
20	·0103	·0102	·0135	·0190	·0261	·0342
25	·0104	·0102	·0140	·0198	·0273	·0361
30	·0104	·0101	·0144	·0205	·0286	·0382
35	·0104	·0114	·0156	·0218	·0302	·0402
40	·0104	·0124	·0174	·0243	·0330	·0427

Eley and Evan's Standard States

$\Delta G_{Solv.}$ (cals.)

Temp.	0	20	40	60	80	100
10	4352	4340	4223	4037	3874	3734
15	4432	4443	4298	4103	3928	3777
20	4514	4534	4364	4163	3979	3819
25	4599	4610	4422	4217	4027	3861
30	4684	4673	4474	4265	4071	3902
35	4772	4722	4515	4306	4111	3943
40	4862	4757	4550	4341	4148	3987

Mole %
MeOH

$$0 \quad \Delta G_T = -234 + 17\cdot485T - \cdot00666T^2$$

$$20 \quad \Delta G_T = -23,940 + 177\cdot636T - \cdot27461T^2$$

$$40 \quad \Delta G_T = -12,955 + 105\cdot6991T - \cdot15902T^2$$

$$60 \quad \Delta G_T = -9,779 + 83\cdot768T - \cdot12351T^2$$

$$80 \quad \Delta G_T = -4841 + 50\cdot3391T - \cdot06908T^2$$

$$100 \quad \Delta G_T = 245 + 15\cdot9532T - \cdot01282T^2$$

$$0 \quad -\Delta S_T = 17\cdot485 - \cdot00666T$$

$$20 \quad -\Delta S_T = 177\cdot636 - \cdot54922T$$

$$40 \quad -\Delta S_T = 105\cdot699 - \cdot31804T$$

$$60 \quad -\Delta S_T = 83\cdot768 - \cdot24702T$$

$$80 \quad -\Delta S_T = 50\cdot339 - \cdot13916T$$

$$100 \quad -\Delta S_T = 15\cdot953 - \cdot02565T$$

$- \Delta S_{Solv.}$

Mole % MeOH

Temp.	0	20	40	60	80	100
10	17·4	22·2	16·4	13·5	10·9	8·6
15	17·4	19·4	14·6	12·3	10·2	8·5
20	17·3	16·6	12·8	11·1	9·5	8·4
25	17·3	13·8	11·0	9·9	8·8	8·3
30	17·2	11·1	9·3	8·6	8·1	8·1
35	17·2	8·4	7·7	7·4	7·4	8·0
40	17·2	5·7	6·1	6·2	6·7	7·9

$\Delta H_{Solv.}$

Mole % MeOH

Temp.	0	20	40	60	80	100
10	−582	−1945	− 419	+ 216	+ 804	+1379
15	−579	−1146	+ 91	+ 560	+ 990	+1328
20	−575	− 332	+ 612	+ 910	+1195	+1357
25	−554	+ 496	+1144	+1266	+1403	+1387
30	−528	+1308	+1655	+1661	+1616	+1447
35	−526	+2134	+2143	+2026	+1831	+1478
40	−522	+2972	+2640	+2400	+2051	+1513

GRAPH VIII

He – H₂O – CH₃OH
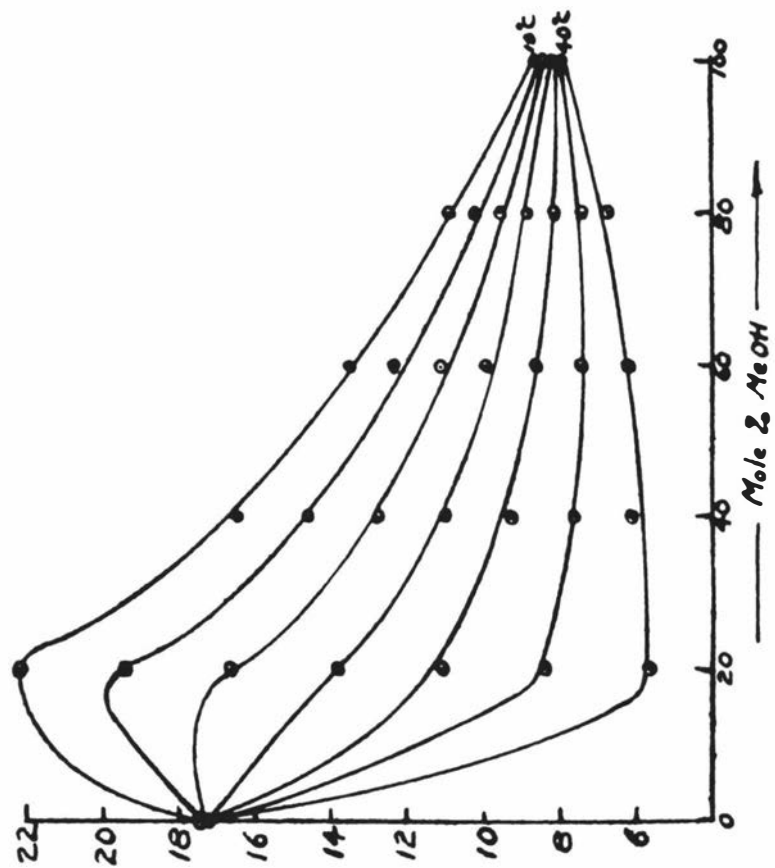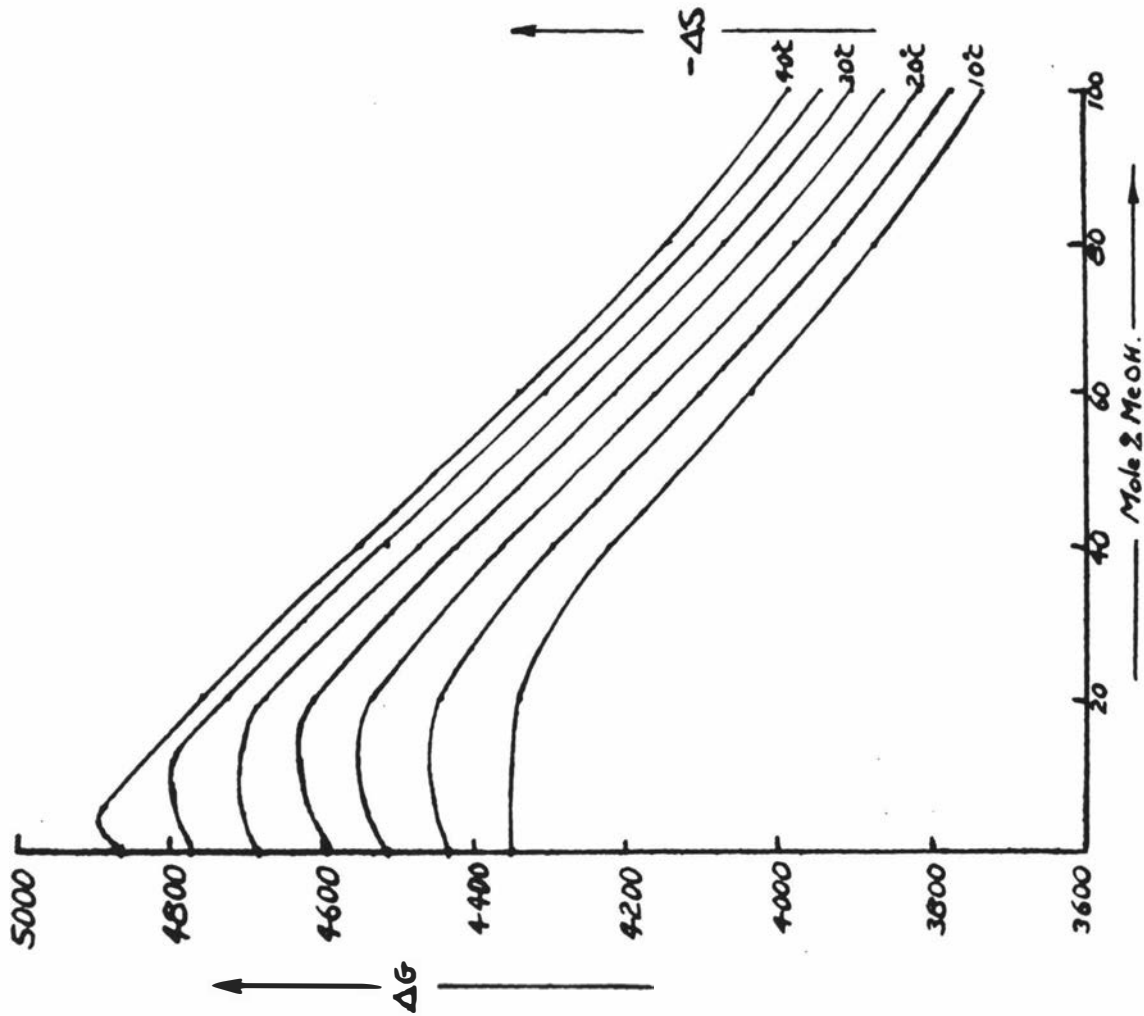
GRAPH IX

He - H$_2$O - CH$_3$OH
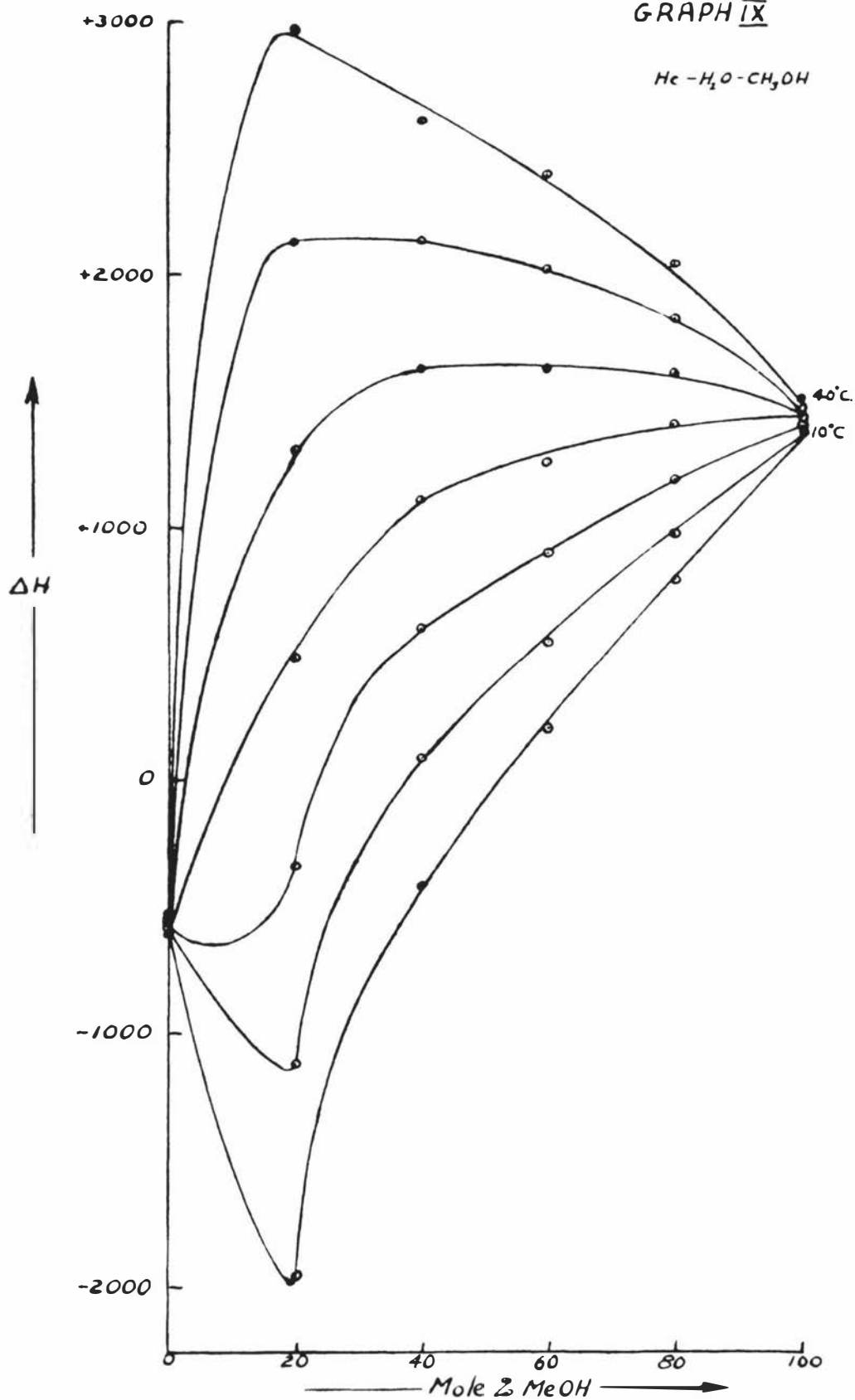
Frank and Evans Standard States

$\Delta G_{Solv.}$

Temp.	0	20	40	60	80	100
10	6614	6498	6285	6004	5760	5547
15	6729	6628	6382	6103	5844	5615
20	6848	6751	6481	6194	5925	5684
25	6976	6870	6580	6280	6003	5757
30	7104	6974	6668	6360	6077	5831
35	7231	7052	6744	6433	6147	5904
40	7353	7120	6805	6498	6214	5961

$- \Delta S_{Solv.}$

	0	20	40	60	80	100
10	25·2	29·4	23·1	19·8	16·9	14·3
15	25·2	26·6	21·3	18·6	16·2	14·2
20	25·1	23·8	19·5	17·4	15·5	14·0
25	25·1	21·0	17·7	16·2	14·8	13·9
30	25·0	18·2	16·0	14·9	14·1	13·7
35	25·0	15·5	14·4	13·7	13·4	13·6
40	25·0	12·8	12·8	12·5	12·7	13·5

$\Delta H_{Solv.}$

Temp.	0	20	40	60	80	100
10	−532	−1835	− 279	+ 376	+ 984	+1589
15	−529	−1036	+ 231	+ 720	+1170	+1588
20	−525	− 222	+ 752	+1070	+1375	+1587
25	−504	+ 606	+1284	+1426	+1583	+1597
30	−478	+1418	+1795	+1821	+1796	+1657
35	−476	+2244	+2283	+2186	+2013	+1688
40	−472	+3082	+2780	+2560	+2231	+1723

TABLE XVII

Thermodynamic Functions for the System Ne – H_2O – CH_3OH.

Bunsen Coefficient β

Mole % MeOH

Temp.	0	20	40	60	80	100
10	·0136	·0113	·0140	·0203	·0290	·0410
15	·0131	·0112	·0142	·0206	·0296	·0422
20	·0126	·0112	·0144	·0211	·C304	·0434
25	·0121	·0112	·0147	·0218	·0313	·0446
30	·0117	·0111	·0152	·0227	·0325	·0458
35	·0115	·0121	·0160	·0238	·0339	·0472
40	·0115	·0130	·0173	·0250	·0357	·0503

Ostwald Coefficient γ

Temp.	0	20	40	60	80	100
10	·0141	·0117	·0145	·0210	·0301	·0425
15	·0138	·0118	·0150	·0217	·0312	·0445
20	·0135	·0120	·0155	·0227	·0326	·0466
25	·0132	·0122	·0160	·0238	·0342	·0487
30	·0130	·0123	·0169	·0252	·0361	·0508
35	·0130	·0137	·0181	·0269	·0383	·0533
40	·0132	·0149	·0198	·0287	·0409	·0577

Eley and Evans' Standard States

$$\Delta G_{Solv.}(Cals.)$$

Temp.	0	20	40	60	80	100
10	4164	4266	4145	3944	3741	3544
15	4265	4356	4221	4004	3796	3593
20	4363	4436	4286	4058	3847	3640
25	4457	4504	4343	4108	3893	3684
30	4547	4561	4391	4152	3936	3725
35	4633	4607	4430	4190	3974	3764
40	4715	4642	4460	4223	4008	3800

Mole %
MeOH

$$0 \qquad \Delta G_T = -8,043 + 65 \cdot 4817 T - \cdot 07899 T^2$$

$$20 \qquad \Delta G_T = -19,069 + 145 \cdot 5044 T - \cdot 22322 T^2$$

$$40 \qquad \Delta G_T = -15,731 + 117 \cdot 4857 T - \cdot 17947 T^2$$

$$60 \qquad \Delta G_T = -8,439 + 74 \cdot 882 T - \cdot 1100 T^2$$

$$80 \qquad \Delta G_T = -6,167 + 58 \cdot 594 T - \cdot 08335 T^2$$

$$100 \qquad \Delta G_T = -3,622 + 40 \cdot 4698 T - \cdot 05354 T^2$$

$$0 \qquad -\Delta S_T = 65 \cdot 482 - \cdot 1580 T$$

$$20 \qquad -\Delta S_T = 145 \cdot 504 - \cdot 4464 T$$

$$40 \qquad -\Delta S_T = 117 \cdot 486 - \cdot 3589 T$$

$$60 \qquad -\Delta S_T = 74 \cdot 882 - \cdot 2200 T$$

$$80 \qquad -\Delta S_T = 58 \cdot 594 - \cdot 1667 T$$

$$100 \qquad -\Delta S_T = 40 \cdot 470 - \cdot 1071 T$$

$$-\Delta S_{Solv.}$$

Mole % MeOH

Temp.	0	20	40	60	80	100
10	20·8	19·1	15·9	12·6	11·4	10·1
15	20·0	16·9	14·1	11·5	10·5	9·6
20	19·2	14·6	12·3	10·4	9·7	9·0
25	18·4	12·4	10·5	9·3	8·9	8·6
30	17·6	10·2	8·7	8·2	8·1	8·0
35	16·8	8·0	6·9	7·1	7·3	7·5
40	16·0	5·7	5·1	6·0	6·4	6·9

$$\Delta H_{Solv.}$$

Mole % MeOH

10	−1724	−1141	− 356	+ 377	+ 514	+ 685
15	−1497	− 513	+ 158	+ 691	+ 771	+ 827
20	−1265	+ 157	+ 681	+1010	+1004	+1002
25	−1028	+ 808	+1213	+1336	+1240	+1126
30	− 788	+1469	+1781	+1667	+1481	+1300
35	− 543	+2142	+2304	+2003	+1725	+1453
40	− 295	+2857	+2863	+2344	+2004	+1640

GRAPH X
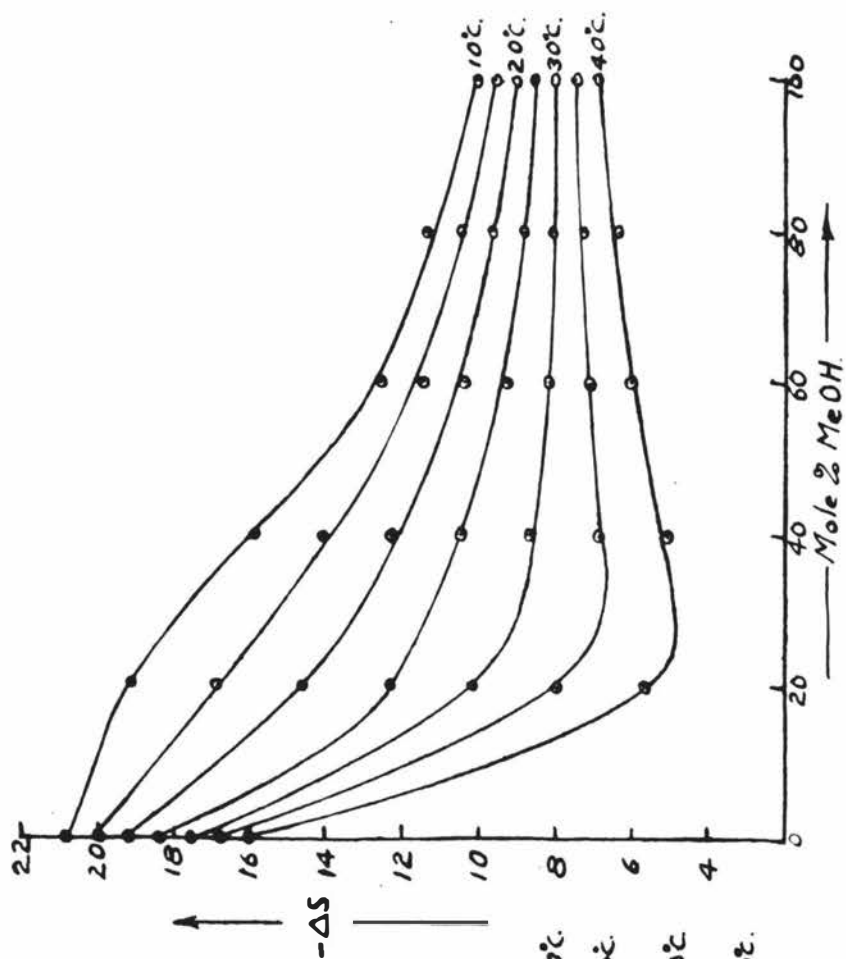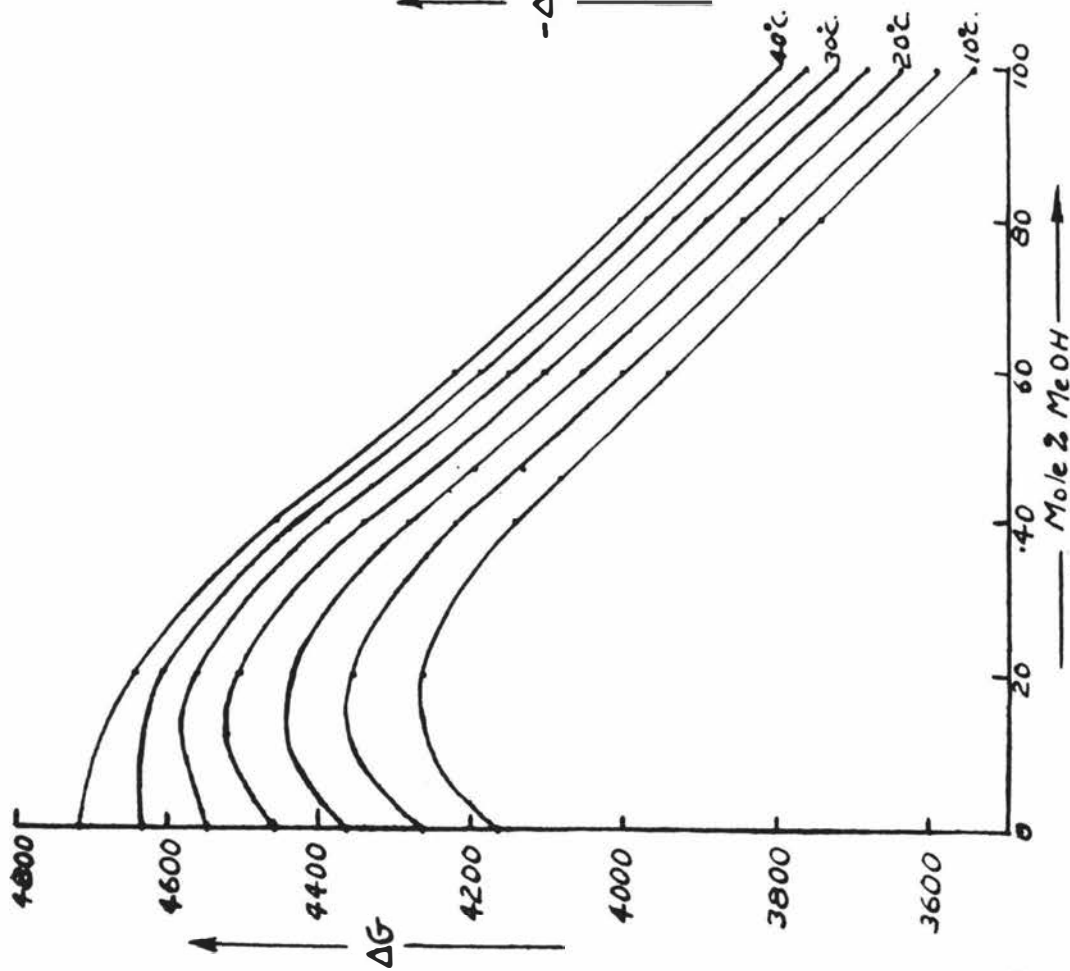
Me-H₂O-CH₃OH

GRAPH XI

$Ne - H_2O - CH_3OH$
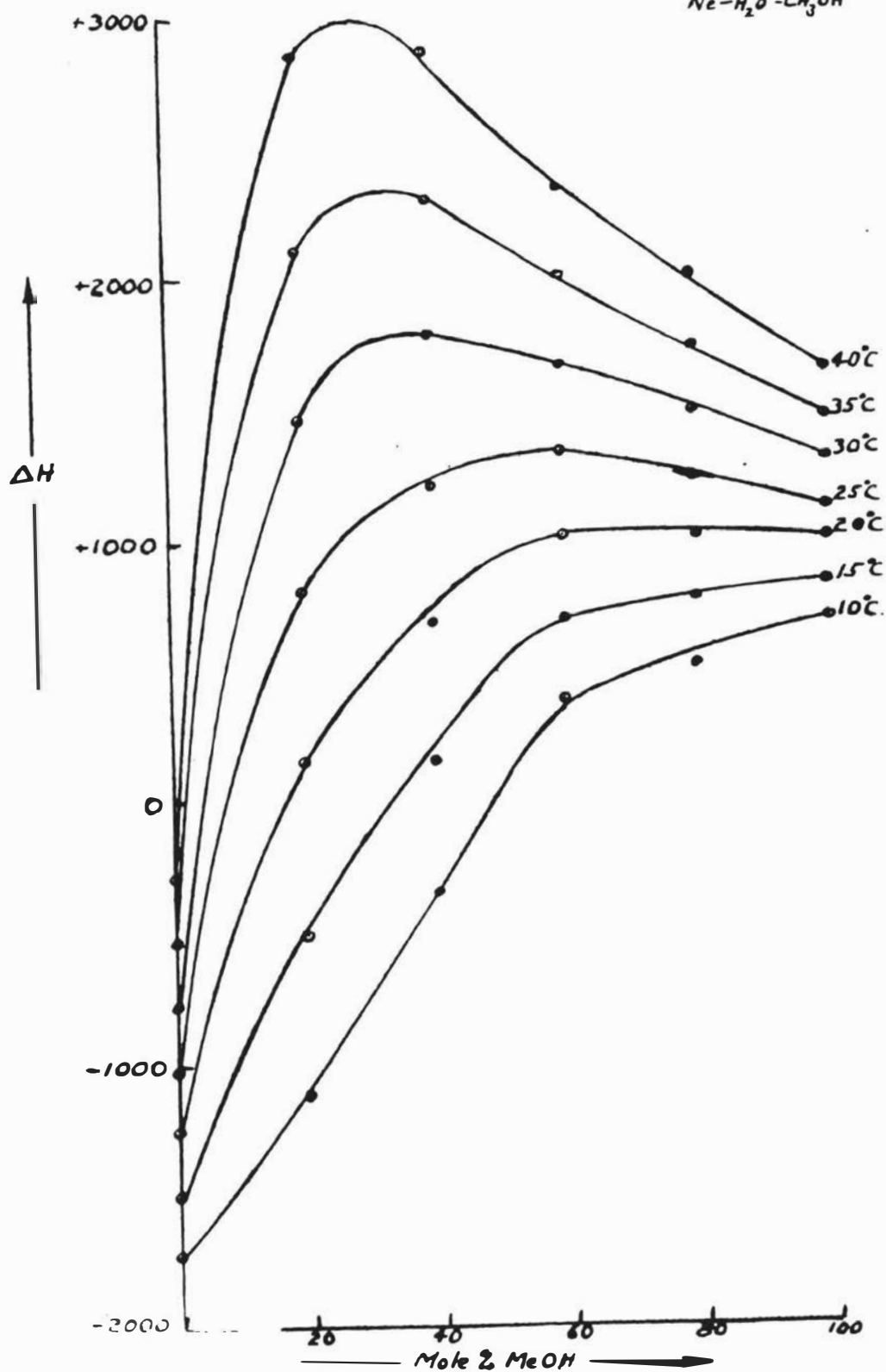
Frank and Evans' Standard States

$\Delta G_{Solv.}$

Temp.	0	20	40	60	80	100
10	6426	6424	6207	5911	5627	5357
15	6562	6541	6305	6004	5712	5431
20	6697	6653	6403	6089	5793	5505
25	6834	6764	6501	6171	5869	5580
30	6967	6862	6585	6247	5942	5654
35	7092	6937	6659	6317	6010	5725
40	7206	7005	6715	6380	6074	5774

$-\Delta S_{Solv.}$

Temp.	0	20	40	60	80	100
10	28·6	26·4	22·6	18·9	17·4	15·9
15	27·8	24·1	20·8	17·8	16·6	15·3
20	27·0	21·9	19·0	16·7	15·8	14·7
25	26·2	19·6	17·2	15·6	15·0	14·2
30	25·4	17·3	15·4	14·5	14·2	13·6
35	24·6	15·1	13·6	13·4	13·3	13·1
40	23·8	12·8	11·8	12·3	12·5	12·5

$$\Delta H_{Solv.}$$

Temp.	0	20	40	60	80	100
10	−1671	−1050	− 191	+ 561	+ 701	+ 856
15	−1448	− 402	+ 313	+ 875	+ 930	+1023
20	−1216	+ 234	+ 834	+1195	+1162	+1197
25	− 976	+ 921	+1373	+1520	+1398	+1347
30	− 731	+1618	+1917	+1851	+1668	+1532
35	− 487	+2285	+2469	+2188	+1912	+1688
40	− 245	+2998	+3020	+2529	+2160	+1860

TABLE XVIII

Thermodynamic Functions for the System A − H_2O − CH_3OH

Bunsen Coefficient β

Mole % MeOH

Temp.	0	20	40	60	80	100
10	·0429	·0446	·0677	·1121	·1779	·2652
15	·0387	·0425	·0663	·1102	·1743	·2585
20	·0348	·0405	·0651	·1088	·1715	·2531
25	·0320	·0386	·0635	·1066	·1682	·2481
30	·0299	·0373	·0633	·1053	·1660	·2443
35	·0281	·0371	·0632	·1055	·1650	·2413
40	·0271	·0381	·0647	·1069	·1648	·2383

Ostwald Coefficient γ

	0	20	40	60	80	100
10	·0445	·0462	·0702	·1162	·1844	·2748
15	·0408	·0448	·0700	·1163	·1839	·2728
20	·0373	·0435	·0697	·1164	·1837	·2717
25	·0349	·0421	·0693	·1164	·1836	·2709
30	·0332	·0414	·0703	·1168	·1842	·2711
35	·0317	·0419	·0713	·1190	·1862	·2722
40	·0311	·0437	·0742	·1237	·1889	·2733

Eley and Evans Standard States

$$\Delta G_{Solv.}(cals)$$

Temp.	0	20	40	60	80	100
10	3532	3494	3258	2978	2720	2496
15	3653	3594	3338	3044	2781	2556
20	3769	3686	3410	3108	2841	2613
25	3881	3771	3475	3168	2898	2668
30	3987	3846	3532	3224	2954	2722
35	4087	3915	3582	3278	3006	2775
40	4182	3975	3624	3328	3057	2826

Mole % MeOH

$0 \quad \Delta G_T = -11,933 + 84 \cdot 4405T - \cdot 10531T^2$

$20 \quad \Delta G_T = -15,484 + 113.1388T - \cdot 16286T^2$

$40 \quad \Delta G_T = -13,727 + 103 \cdot 2117T - \cdot 15265T^2$

$60 \quad \Delta G_T = -6,244 + 51 \cdot 4658T - \cdot 06673T^2$

$80 \quad \Delta G_T = -4,391 + 37 \cdot 6531T - \cdot 04429T^2$

$100 \quad \Delta G_T = -3,508 + 30 \cdot 4535T - \cdot 03265T^2$

$0 \quad -\Delta S_T = 84 \cdot 441 - \cdot 2106T$

$20 \quad -\Delta S_T = 113 \cdot 139 - \cdot 3257T$

$40 \quad -\Delta S_T = 103 \cdot 212 - \cdot 3053T$

$60 \quad -\Delta S_T = 51 \cdot 466 - \cdot 1335T$

$80 \quad -\Delta S_T = 37 \cdot 653 - \cdot 0886T$

$100 \quad -\Delta S_T = 30 \cdot 453 - \cdot 0653T$

$-\Delta S_{Solv.}$

Mole % MeOH

Temp.	0	20	40	60	80	100
10	24·8	20·9	15·8	13·7	12·6	12·0
15	23·7	19·3	14·7	13·0	12·1	11·6
20	22·7	17·6	13·6	12·4	11·7	11·3
25	21·6	16·0	12·6	11·7	11·2	11·0
30	20·6	14·4	11·7	11·1	10·8	10·7
35	19·5	12·7	10·6	10·4	10·4	10·4
40	18·5	11·1	9·6	9·7	9·9	10·0

$\Delta H_{Solv.}$

Mole % MeOH

Temp.	0	20	40	60	80	100
10	-3501	-2423	-1213	-900	-847	-901
15	-3175	-1966	- 896	-701	-687	-786
20	-2884	-1473	- 575	-526	-588	-699
25	-2558	- 999	- 280	-320	-441	-611
30	-2257	- 519	- 13	-140	-319	-521
35	-1921	+ 2	+ 317	+ 74	-198	-429
40	-1610	+ 500	+ 619	+291	- 43	-305

GRAPH XII

A·H₂O·CH₃OH

GRAPH XIII
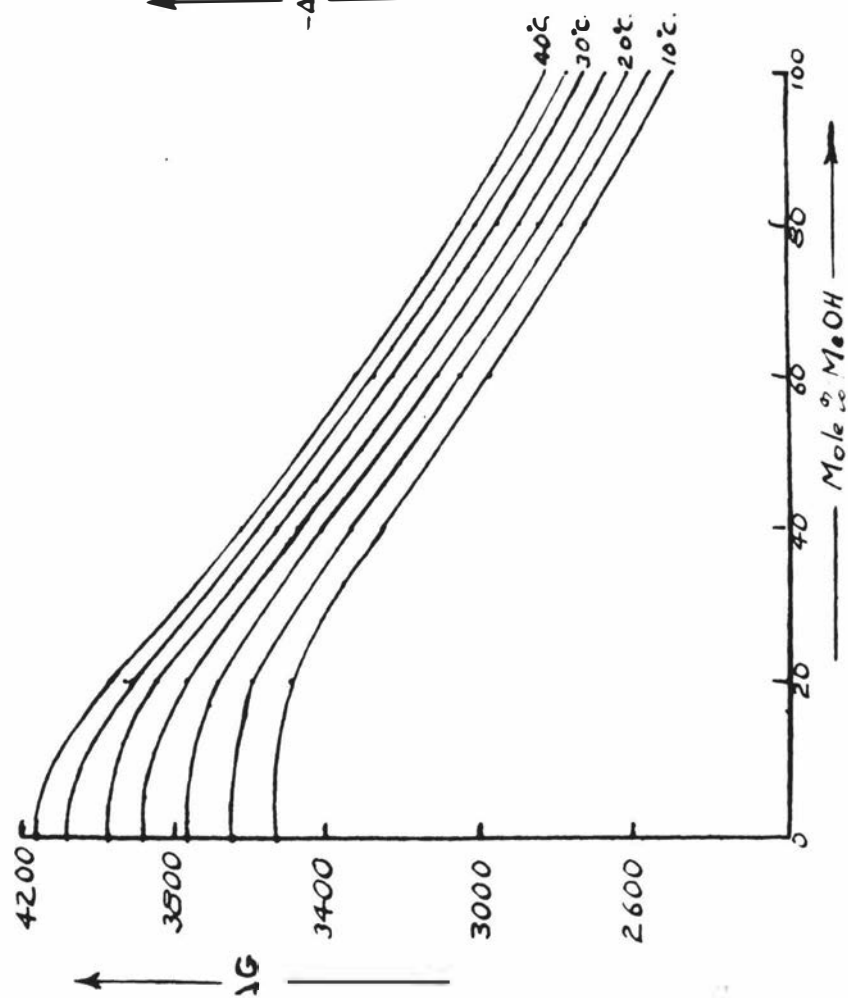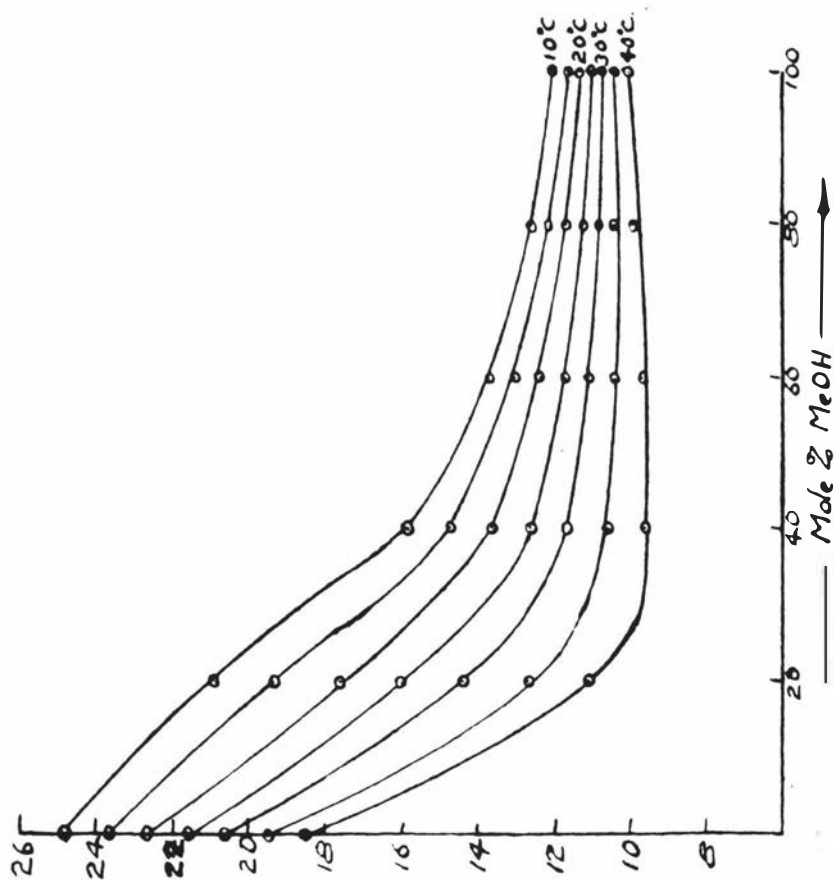
A-H₂O-CH₃OH
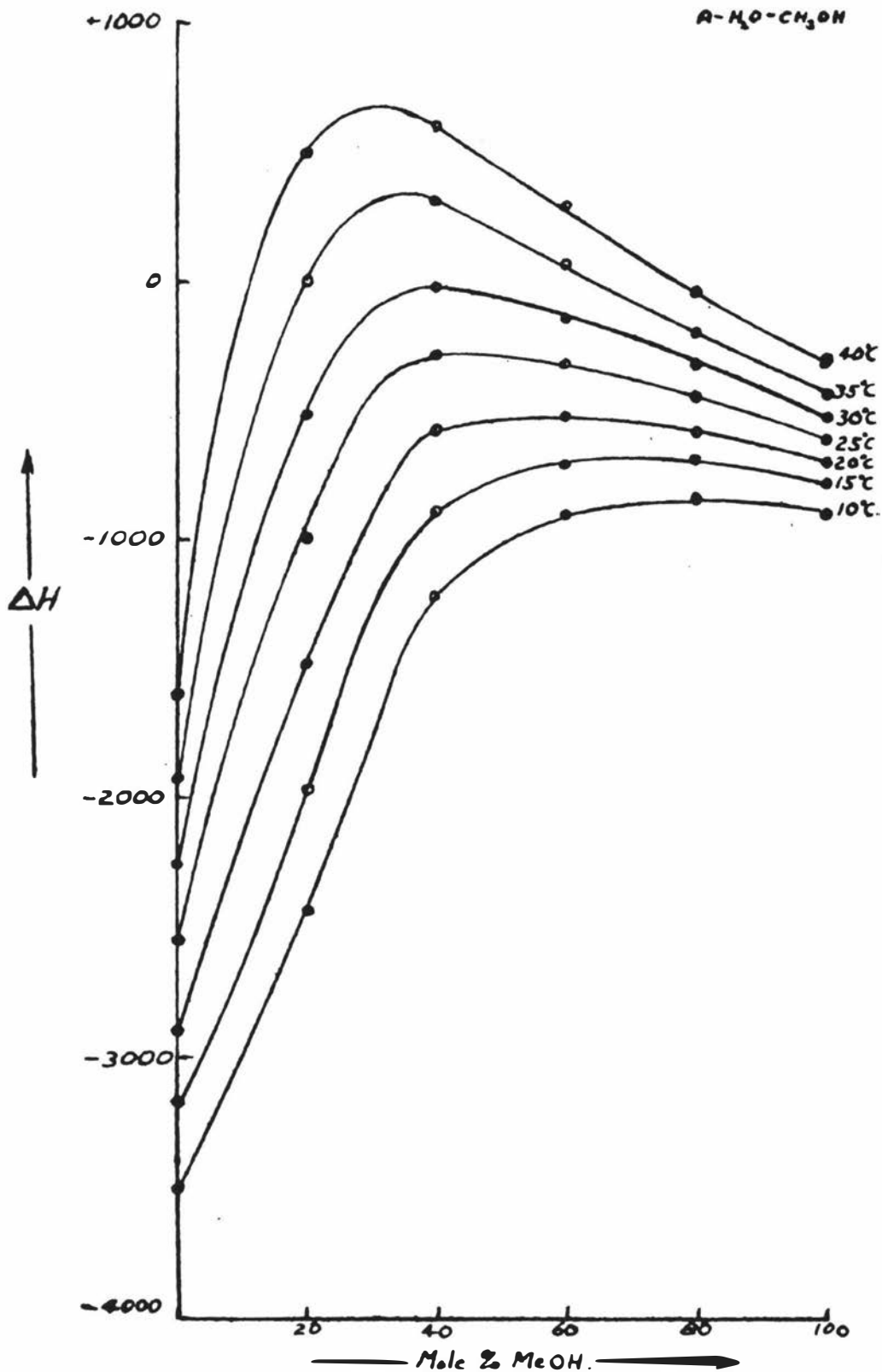
Frank and Evans Standard States

$\Delta G_{Solv.}$

Temp.	0	20	40	60	80	100
10	5794	5652	5320	4945	4606	4309
15	5950	5779	5422	5044	4697	4394
20	6103	5903	5527	5139	4787	4478
25	6258	6031	5653	5231	4874	4564
30	6407	6147	5726	5319	4960	4651
35	6546	6245	5811	5405	5042	4736
40	6673	6338	5879	5485	5123	4800

$-\Delta S_{Solv.}$

Temp.	0	20	40	60	80	100
10	32.6	28.1	22.5	20.0	18.6	17.7
15	31.5	26.5	21.4	19.3	18.1	17.3
20	30.5	24.8	20.3	18.7	17.7	16.9
25	29.4	23.2	19.3	18.0	17.2	16.6
30	28.4	21.5	18.4	17.4	16.8	16.3
35	27.3	19.8	17.3	16.7	16.4	16.0
40	26.3	18.2	16.3	16.0	15.9	15.6

$$\Delta H_{Solv.}$$

Temp.	0	20	40	60	80	100
10	-3451	-2313	-1073	-740	-667	-691
15	-3125	-1856	- 756	-541	-507	-576
20	-2834	-1363	- 435	-366	-408	-489
25	-2508	- 889	- 140	-160	-261	-401
30	-2207	- 409	+ 127	+ 20	-139	-311
35	-1871	+ 113	+ 457	+234	- 18	-219
40	-1560	+ 610	+ 760	+451	+140	-100

TABLE XIX

Thermodynamic Functions for the System H_2 - H_2O - CH_3OH

Bunsen Coefficient β

Mole % MeOH

Temp.	0	20	40	60	80	100
10	·0189	·0218	·0301	·0441	·0632	·0875
15	·0180	·0218	·0306	·0448	·0640	·0885
20	·0172	·0218	·0311	·0456	·0650	·0896
25	·0165	·0218	·0316	·0467	·0667	·0909
30	·0157	·0219	·0325	·0478	·0684	·0927
35	·0151	·0223	·0336	·0489	·0704	·0949
40	·0147	·0235	·0353	·0518	·0744	·1020

Ostwald Coefficient γ

10	·0196	·0226	·0313	·0457	·0656	·0907
15	·0190	·0230	·0323	·0472	·0675	·0933
20	·0185	·0234	·0334	·0490	·0698	·0961
25	·0179	·0238	·0345	·0509	·0728	·0992
30	·0175	·0243	·0361	·0530	·0760	·1029
35	·0169	·0252	·0379	·0552	·0794	·1071
40	·0167	·0269	·0405	·0595	·0853	·1170

Eley and Evans Standard States

$\Delta G_{Solv.}$(cals)

Temp.	0	20	40	60	80	100
10	3974	3898	3717	3505	3301	3115
15	4076	3972	3778	3558	3354	3169
20	4177	4042	3835	3609	3402	3218
25	4276	4107	3887	3657	3446	3262
30	4373	4167	3935	3702	3485	3301
35	4468	4223	3978	3743	3522	3335
40	4561	4274	4017	3782	3554	3364

Mole % MeOH

$$0 \qquad \Delta G_T = -5{,}343 + 44 \cdot 978T - \cdot 04263T^2$$

$$20 \qquad \Delta G_T = -7{,}981 + 67 \cdot 880T - \cdot 0928T^2$$

$$40 \qquad \Delta G_T = -7{,}284 + 64 \cdot 942T - \cdot 09214T^2$$

$$60 \qquad \Delta G_T = -5{,}015 + 48 \cdot 867T - \cdot 06667T^2$$

$$80 \qquad \Delta G_T = -6{,}140 + 55 \cdot 881T - \cdot 07958T^2$$

$$100 \qquad \Delta G_T = -8{,}141 + 68 \cdot 192T - \cdot 1005T^2$$

$$0 \qquad - \Delta S_T = 44 \cdot 978 - \cdot 08526T$$

$$20 \qquad - \Delta S_T = 67 \cdot 880 - \cdot 1856T$$

$$40 \qquad - \Delta S_T = 64 \cdot 942 - \cdot 18428T$$

$$60 \qquad - \Delta S_T = 48 \cdot 867 - \cdot 13334T$$

$$80 \qquad - \Delta S_T = 55 \cdot 881 - \cdot 15916T$$

$$100 \qquad - \Delta S_T = 68 \cdot 192 - \cdot 2010T$$

$$- \Delta S_{Solv.}$$

Mole % MeOH

Temp.	0	20	40	60	80	100
10	20·8	15·4	12·8	11·2	10·9	11·3
15	20·4	14·4	11·8	10·5	10·1	10·3
20	20·0	13·5	10·9	9·8	9·2	9·3
25	19·6	12·6	10·0	9·1	8·4	8·3
30	19·1	11·6	9·1	8·3	7·6	7·2
35	18·7	10·6	8·2	7·5	6·7	6·2
40	18·3	9·8	7·3	6·7	5·8	5·2

$$\Delta H_{Solv.}$$

Mole % MeOH

10	−1915	− 462	+ 93	+ 334	+ 215	− 85
15	−1801	− 178	+ 378	+ 532	+ 442	+ 201
20	−1685	+ 85	+ 640	+ 737	+ 705	+ 492
25	−1561	+ 351	+ 906	+ 945	+ 946	+ 788
30	−1416	+ 651	+1178	+1186	+1182	+1119
35	−1293	+ 957	+1452	+1441	+1457	+1424
40	−1170	+1266	+1732	+1748	+1738	+1736

GRAPH XIV
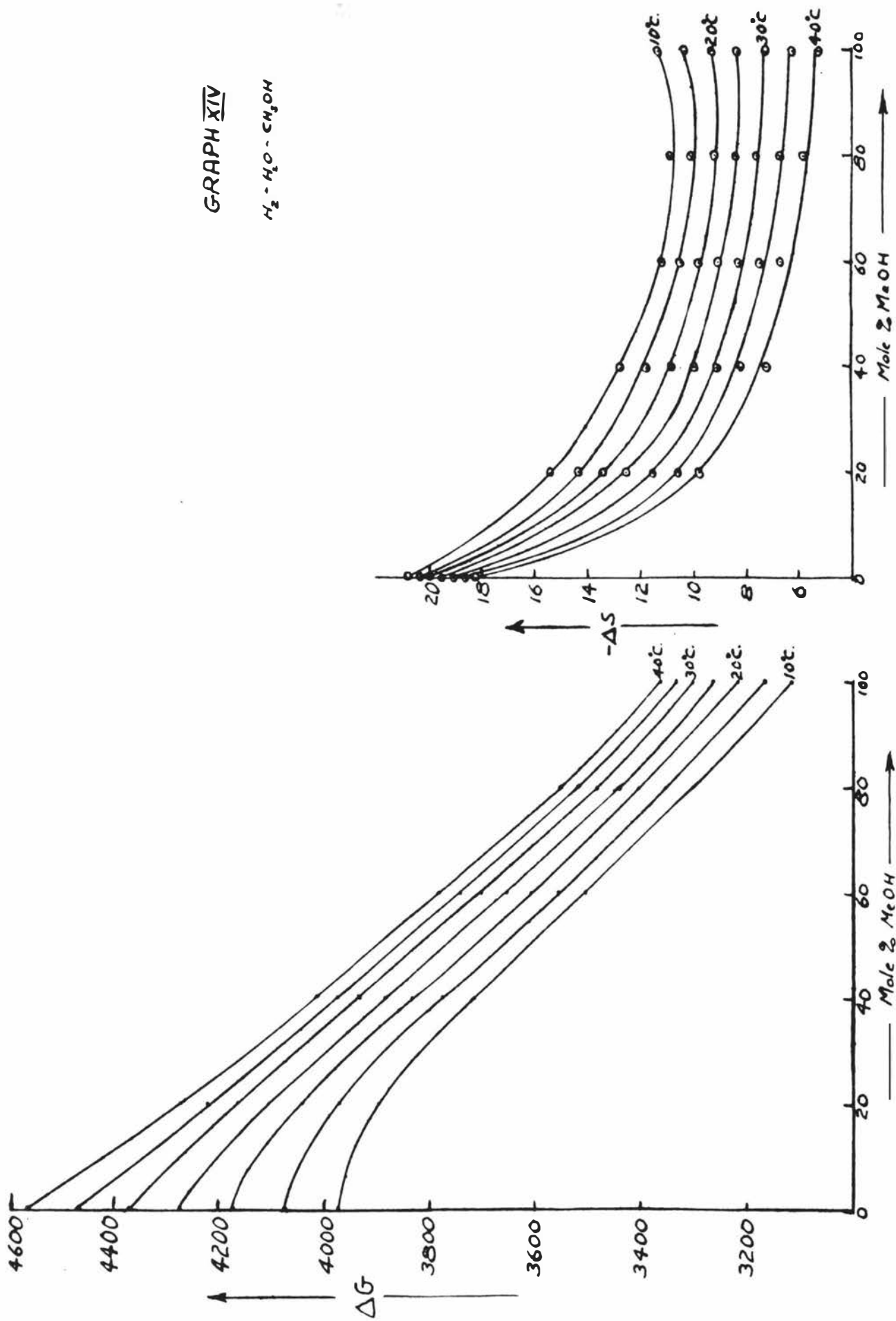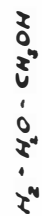
$H_2 - H_2O - CH_3OH$

GRAPH XV

H₂ – H₂O – CH₃OH.
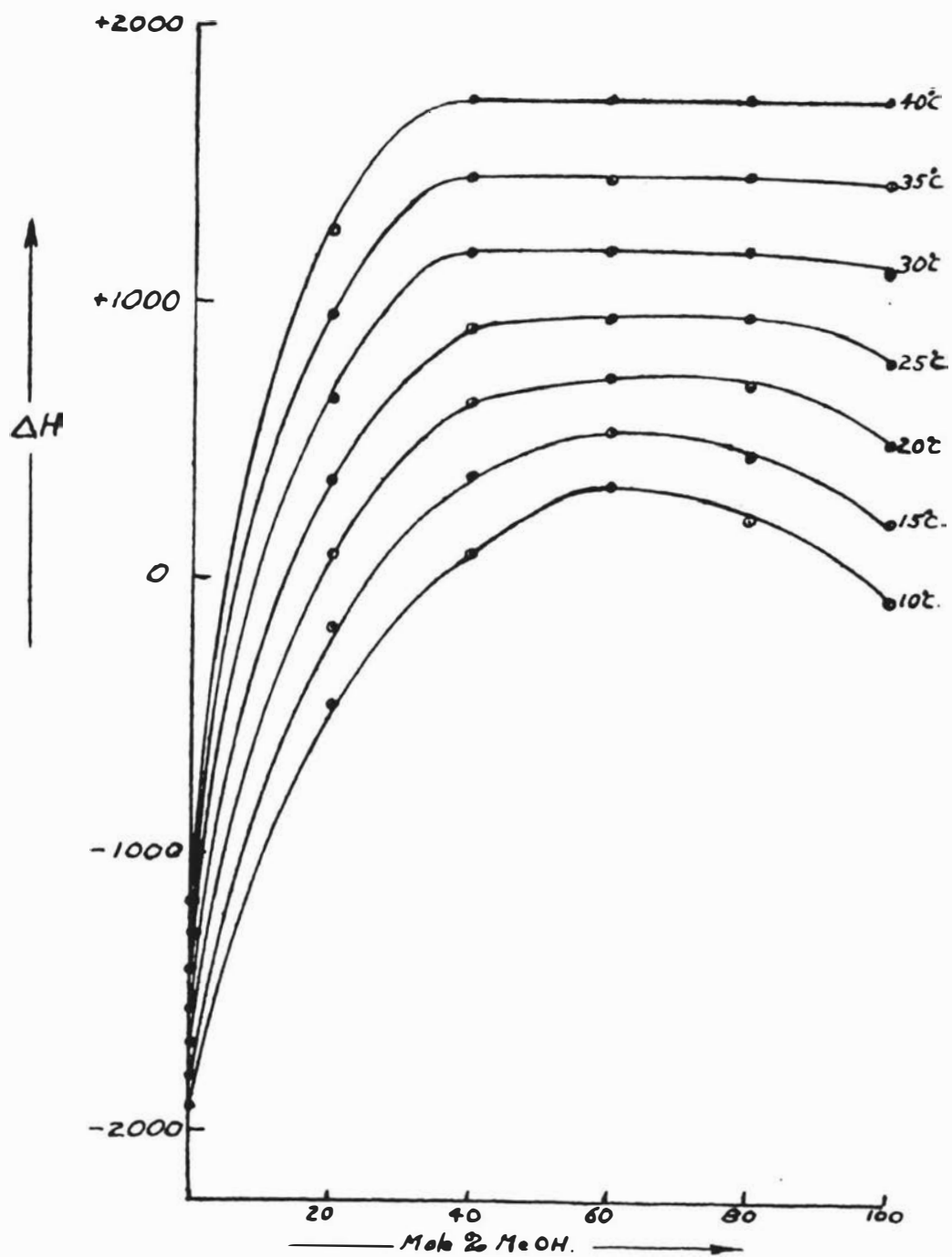
Frank and Evans Standard States

$\Delta G_{Solv.}$

Temp.	0	20	40	60	80	100
10	6236	6056	5779	5472	5187	4928
15	6373	6157	5862	5558	5270	5007
20	6511	6259	5952	5640	5348	5083
25	6653	6367	6045	5720	5422	5158
30	6793	6468	6129	5797	5491	5230
35	6927	6553	6207	5870	5558	5296
40	7052	6637	6272	5939	5620	5338

$-\Delta S_{Solv.}$

Temp.	0	20	40	60	80	100
10	28·6	22·6	19·5	17·5	16·9	17·1
15	28·2	21·6	18·5	16·8	16·1	16·1
20	27·8	20·7	17·6	16·1	15·2	15·1
25	27·4	19·8	16·7	15·4	14·4	14·1
30	26·9	18·8	15·8	14·6	13·6	13·0
35	26·5	17·8	14·9	13·8	12·7	12·0
40	26·1	17·0	14·0	12·8	11·8	11·0

$$\Delta H_{Solv.}$$

Temp.	0	20	40	60	80	100
10	−1865	− 352	+ 233	+ 494	+ 395	+ 125
15	−1751	− 68	+ 518	+ 692	+ 622	+ 411
20	−1635	+ 195	+ 780	+ 897	+ 885	+ 702
25	−1511	+ 461	+1046	+1105	+1126	+ 998
30	−1366	+ 761	+1318	+1346	+1362	+1329
35	−1243	+1067	+1592	+1601	+1637	+1634
40	−1120	+1376	+1872	+1908	+1918	+1946

TABLE XX

Vapour Pressure of Water-Methanol Mixtures

Mole % Methanol

Temp.	0	10	20	30	40	50	60	70	80	90	100
10	9·2	16·0	23·0	29·2	35·0	38·1	42·8	46·0	49·3	51·7	54·2
15	12·8	21·8	31·2	39·0	45·8	49·2	54·8	59·8	64·4	68·0	72·2
20	17·5	31·0	43·0	52·2	60·3	66·3	72·2	78·0	84·1	90·0	95·1
25	23·8	40·2	55·0	66·6	75·7	83·0	92·1	100·4	109·1	117·8	124·0
30	31·8	54·7	70·6	84·4	96·0	105·7	115·9	127·8	137·7	149·2	160·3
35	42·2	72·1	92·8	110·0	124·0	138·9	150·0	163·6	177·3	189·6	205·2
40	55·3	90·5	119·5	143·0	160·5	176·5	192·8	209·0	225·2	242·8	260·5

D I S C U S S I O N

(a) ACCURACY OF GAS SOLUBILITY METHODS IN GENERAL

The wide variations in published gas solubility data are shown in Table XXI and Graphs XVI and XVII.

TABLE   XXI

Solubility of Helium in Water.

Temp.	Present Work	Lannung[79]	Akerlof[27]	Cady, Elsey and Berger[80]	Antropoff[99]	Estreicher[76]
10	·0098			·0089-·0090	·0098	·0144
15	·0097	·0089				
20	·0096	·0088				·0138
25	·0095	·0087		·0086		
30	·0094	·0086	·0087	·0084-·0080	·0100	·0137
35	·0092					
40	·0091				·0102	·0138

Solubility of Neon in Water

Temp.	Present Work	Lannung[79]	Antropoff[83]	Valentiner[98]
10	·0136	·0111-·0115	·0117	·0185
15	·0131			
20	·0125	·0104	·0146	·0164
25	·0121	·0102		
30	·0118	·0098	·0158	·0145
35	·0115	·0097		
40	·0115	·0096	·0166	·0126

GRAPH XVI   Helium in Water.

Estreicher.

Antropoff.

Present Work.
Lannung.

Cady, Elsey & Berger.

Neon in Water.

Antropoff.

Valentiner.
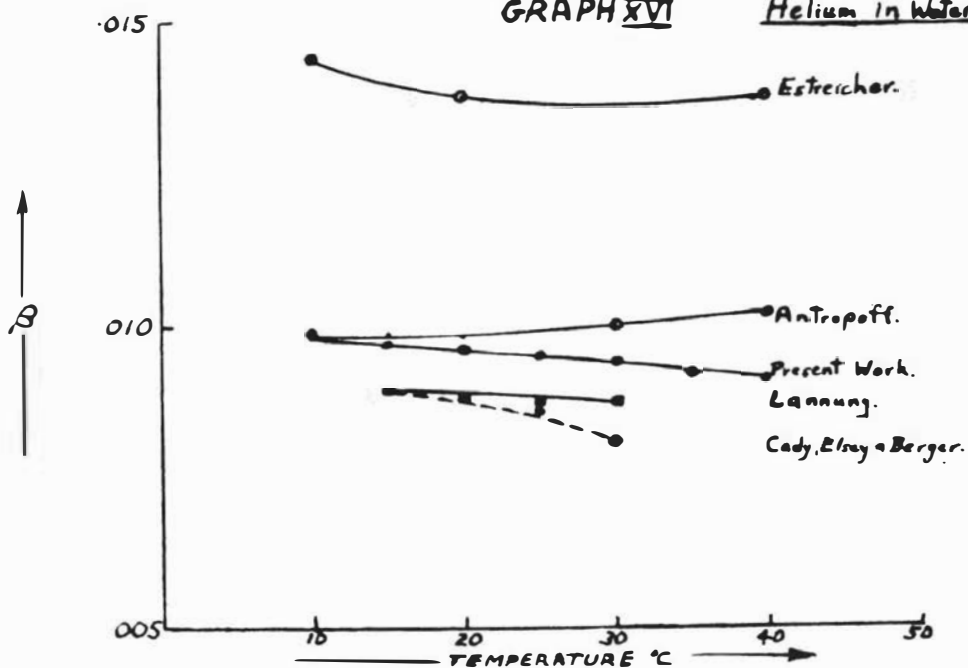
Present Work.
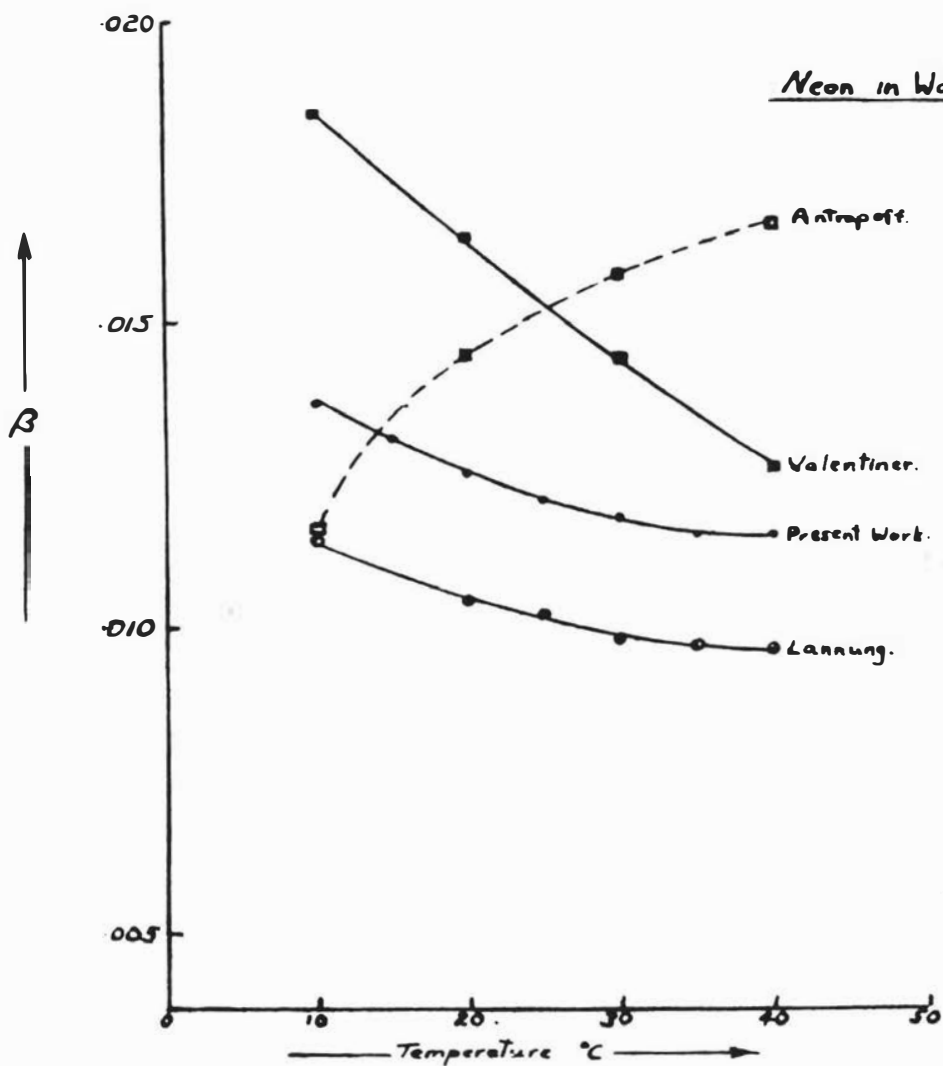
Lannung.

Solubility of Argon in Water

Temp.	Present Work	Lannung[79]	Estreicher[76]	Winkler[100]	Akerlof
10	•0428		•0453	•0425	
15	•0387	•0371	•0410		
20	•0350	•0336	•0379	•0351	
25	•0322	•0315	•0347		•0332
30	•0301	•0289	•0326	•0300	
35	•0282	•0271	•0305		
40	•0271	•0254	•0287	•0271	

Solubility of Hydrogen in Water

Temp.	Present Work	Winkler[101]
10	•0190	•0195
15	•0181	•0188
20	•0172	•0182
25	•0164	•0175
30	•0157	•0170
35	•0150	•0166
40	•0146	•0164

GRAPH XVII

Argon in Water.

Estreicher
Winkler and Present Work.
Lannung.

Hydrogen in Water

Winkler
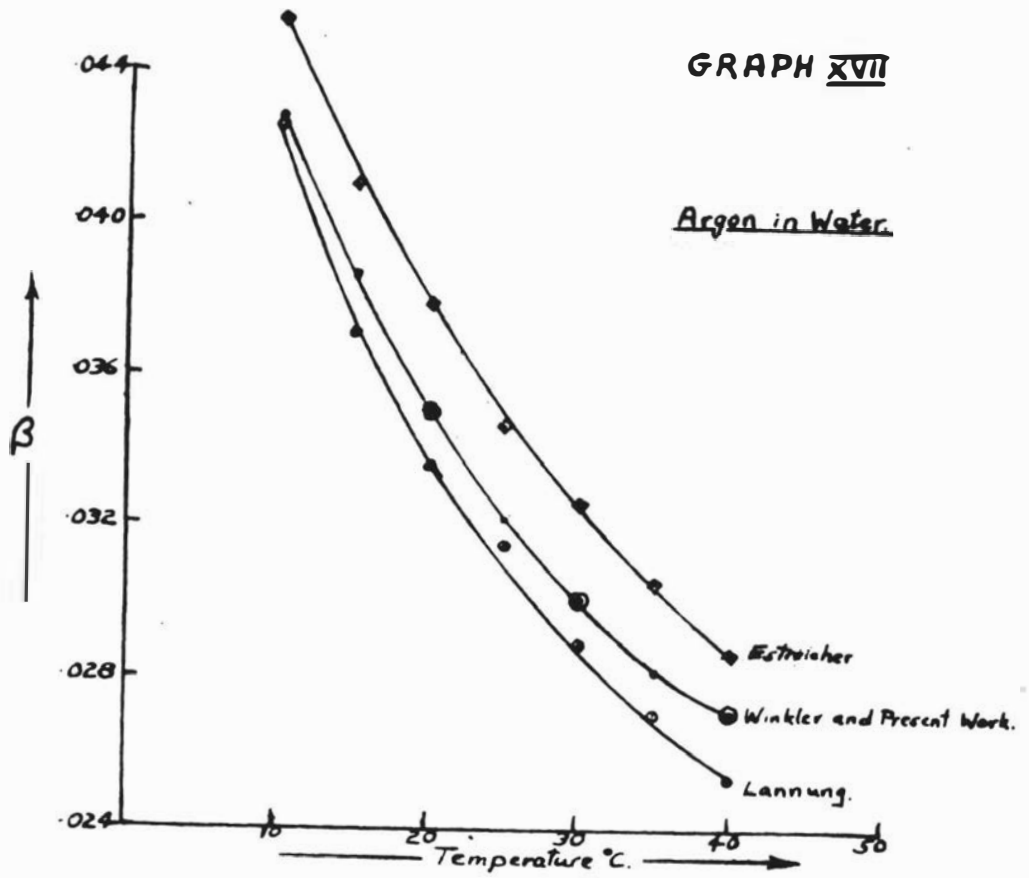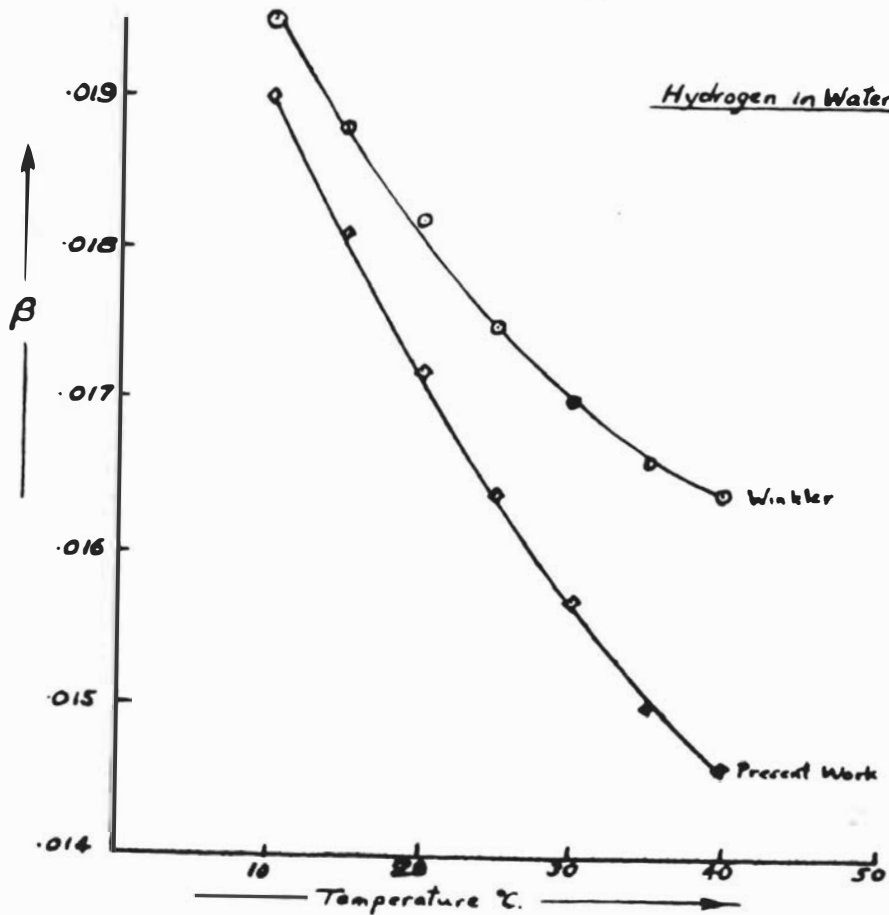
Present Work

Solubility of Hydrogen in Organic Solvents at 20°C.

(Ostwald Coefficient)

Solvent	Horiuti [86]	Maxted & Moon [73]	Just [36]	Christoff [38]	Present Work
CCl_4	·0780				·0798
Benzene	·0685	·0660	·0707		
Ether	·1398			·1350	
Acetone	·0950		·0703		
Methanol			·0902		·0961

.

.

It is seen that differences of up to 2% in the value of the Bunsen coefficient are not uncommon, so that the reliability of the derived thermodynamic functions is somewhat open to question.

In calculating the Ostwald coefficient from:

$$\gamma = \frac{v_0}{V} \; \frac{760}{p} \; \frac{T}{273}$$

where v_0 is the volume of gas dissolved, reduced to N.T.P.

V is the volume of solvent,

p is the vapour pressure of the solvent,

T is the temperature of the measurement,

the only appreciable errors introduced are in the measurement of v_0, and in the accuracy of listed vapour pressure data.

If the former of these is ·002 cc. the fourth figure of γ is unaffected but variations of up to 1 mm. in the listed vapour pressure data are often found and this can quite easily cause errors of up to 1% in γ .

Neither of these, however, would normally cause errors as great as 5% in the solubility and these divergencies must be attributed to one of the following:

(a) Incomplete degassing of solvents.

(b) Impure gases.

(c) Lack of attainment of true equilibrium.

(a)   Complete degassing of solvents, as we have seen, is quite a difficult process and the comparatively low results of some early workers may be attributed to this factor.   Once the solvent has been degassed it must be kept in contact only with its own vapour until the process of solution is commenced.   This, and the fact that no allowance is made for the increase in solvent volume when the gas dissolves probably explains why Lannung's results are all lower than those obtained in the present work.

(b)   The high results of both Estreicher[76] and Valentiner[98] are clearly due to impure gas.   Antropoff[83] probably had pure helium and neon, but he found after he had finished his work that his method contained a serious source of error.   He measured the gas in the burette in a dry condition, brought a small part of it through a long glass spiral into contact with the water in the absorption vessel, shook the latter for ten minutes and assumed that equilibrium had been reached and that the gas in the measuring system was completely saturated with water vapour.   In his work on krypton he showed that the diffusion of water vapour was so slow that this assumption was wrong and that the error was great enough to change the entire shape of the solubility curve, giving an apparent

minimum of solubility when none exists.   Antropoff also
points out that with his method the results at lower
temperatures are in error because in the absence of liquid
water in the gas burette and since he went from a higher
to a lower temperature, the gas at lower temperatures
would be supersaturated with water vapour.   Thus only the
results in the middle of his series are "correct".

The method used in the present work for mixed solvents
is somewhat similar to that of Antropoff[83], in that dry
gas is taken initially and each run proceeds from a higher
to a lower temperature.   We have seen that it is impossible
to use saturated gas, and the alternative to the present
method (which consists in saturating all the gas in the
apparatus) is to put a stopcock in the gas line between
the burette and the pipette.   When this is done no gas
should be allowed to pass back into the burette but as
the volume of gas over the solvent must expand as it
becomes saturated, more mercury must be run out of the
pipette to maintain atmospheric pressure above the solvent
or when the tap connecting the burette to the pipette is
opened saturated gas will pass back into the former.   This
will only occur when the expansion of the gas over the
solvent is greater than the amount required for saturation
and thus depends on the free gas space above the solvent
and also on how often the connecting tap is opened.   If

this is done frequently, reasonably accurate results should be obtained, but on the whole the method seems very likely to give results that are too low and so Horiuti's[86] results must be open to some doubt.

In the present work the saturation of the gas took anything up to 12 hours, compared with 1 to 2 hours for the saturation of the solvent.   Use of this method however should give quite reliable results.

(c)   Possibly the most serious error in Estreicher[76] and Antropoff's[83] work is the way in which equilibrium was secured between the gas and the liquid.   Gas is absorbed very slowly by a liquid unless the surface of the latter is changed constantly.   Estreicher and Antropoff secured this by connecting the burette to the absorption vessel by a flexible spiral of glass tubing and shaking the absorption bulb violently with a motor.   This enabled them to reach a static condition in 10 minutes.   Violent hammering, however, results when a vessel partly filled with solvent and free from air or other gases is shaken, this being used as a test for the presence of air in the vessel because even a small quantity of gas will so cushion the blow that no such effect is found.   When a gas is acting to stop the blow between a solvent and the glass it is put under a pressure greater than that exerted by the rest

of the gas and is driven into the solvent, forming a supersaturated solution. All measurements made in this manner will be in error as it is much easier to get a gas into solution than it is to get it out again, so that allowing the apparatus to stand for 1 to 2 hours after violent shaking is of little use and the fact that gas does not come out of solution during this period does not show that the solution is not supersaturated.

(b) THE EFFECT OF CHANGING METHANOL CONCENTRATION ON

GAS SOLUBILITY

From the gas solubility figures listed in
Tables XVI - XIX we see that the solubility passes through
a minimum for the two smallest gases - helium and neon.
This effect which is not found for hydrogen or argon in
water-methanol mixtures does occur for the former in water-
ethanol mixtures as shown in Graph VI.   It may also be
noted that as we pass from helium to neon the minima occur
at a   lower Mole % methanol, but not at the higher
temperatures.

We saw in an earlier section on the structure
of water-alcohol mixtures that the free volume of water-
methanol passes through a minimum at about 18 Mole % MeOH,
so that the undisturbed liquid at 25°C. is close packed at
this concentration.   Raising the temperature will cause
the molecules to move more freely and therefore increase
the free volume.   It also seems logical that if large
uncharged gas molecules are forced between the solvent
molecules the structure of the liquid will be broken down.
This probably explains why the solubility of helium passes
through a minimum at about 18 Mole % MeOH but for larger
gases the minimum is either shifted to a lower methanol
concentration or disappears entirely.   This shift in
minima is shown in Graph XVIII where the Bunsen coefficient

GRAPH XVIII

A.

H₂

Ne.

He.

β_{25}
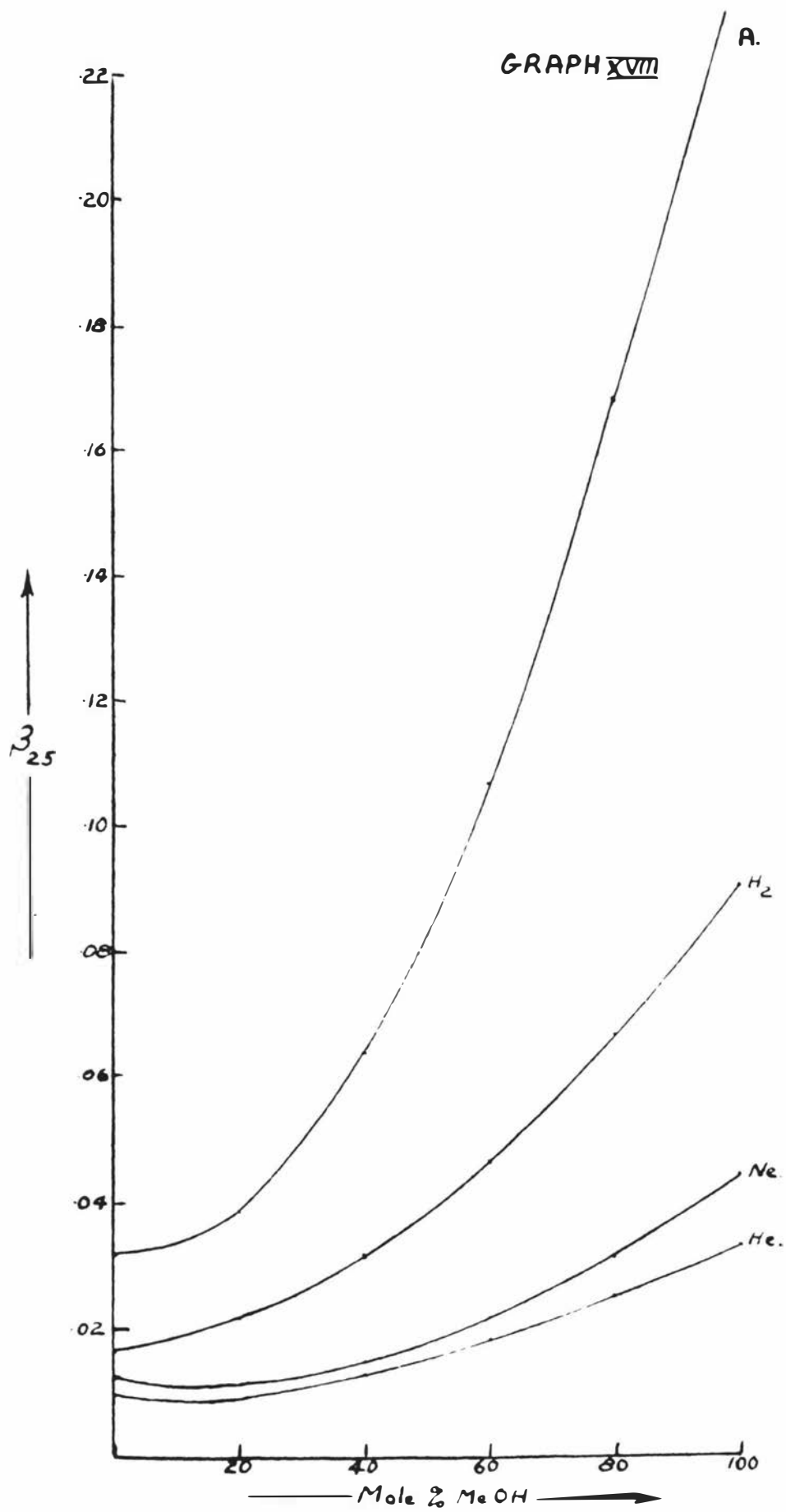
Mole % MeOH

for He, Ne, H_2 and A at 25°C. is plotted against Mole %
MeOH.

The solubility of helium even at 40°C. shows
a minimum while none is found for any of the larger gases
at this temperature.   This again is due to a breakdown
of the liquid structure caused both by increasing gas
size and increasing temperature.   In water-ethanol
mixtures it would be expected that neon would show
minima up to 40°C. since both the free volume V_f and the
product $\delta_3 V_f$ are much smaller at low ethanol concentrations
than at the corresponding methanol concentrations.

Summarising we see that either increasing
temperature or molecular gas size shifts the minimum, when
it exists, in the direction of decreasing methanol
concentration.

(c) THE TEMPERATURE COEFFICIENT OF GAS SOLUBILITY

Bunsen[70] applied a purely empirical equation to the data that he found for the solubilities of a number of gases in water and ethanol.   This was of the form:

$$\beta = a + bt + ct^2$$

Carius[102], Than[103], and Timofejew[75] used similar equations. The constants a, b, and c are obtained by substituting experimental data at several temperatures.   This is similar to the method employed in the present work where a quadratic equation is fitted to a function of the Ostwald Coefficient by means of the method of least squares. Winkler[101] added a further term in t^3, but this appears unnecessary when the accuracy of the data is considered. Wiedeman[104] showed that while a, b and c for different gases in water were very different the ratios b/a and c/a were nearly the same for all gases.   Similar results were obtained for ethanol.

Bohr[105] proposed that at constant partial gas pressure the osmotic pressure of a dissolved gas was constant.   Thus βT would be constant, but on substituting experimental values he found that such was not the case, but that $\beta(T - a) =$ constant.   He found a to be a constant which for the four diatomic gases, hydrogen, oxygen, nitrogen and carbon monoxide in water was a linear

function of the molecular weight.   He later attempted
to find a theoretical basis for these empirical equations
by equating the rate of solution of a gas to its rate of
escape and making measurements of each.

He established an empirical relation for the
rate of escape which proved to give the equation that he
sought.   The empirical nature of his result however
remained.   Later Kofler showed that the same equation
fitted his results for radon in water over the temperature
range 0 - 75°C.

Kofler[106] later stated that there is a connection
between the critical temperature of a gas and its solubility
in a given solvent.   He plotted T/T_c for a number of gases
in water against β and found they fell on a smooth curve.

Meyer[107] applied the equation

$$\beta = b + \epsilon^{-a\theta}$$

to the solubility of a number of gases in various solvents.
The equation fits better if it refers to the amount of
gas dissolved per unit weight of solvent. θ is a measure
of the temperature, on a scale such that for a given solvent
there are a hundred degrees between the melting point and
the boiling point.   Thus in the case of water it is the
Centigrade scale.   Meyer found a to be nearly the same
for all gases and all solvents.   For the system radon-water
the equation fits the results very well.

Jaeger[10] from kinetic considerations derived
the equation,

$$\gamma = e^{-\frac{A}{RT}}$$

Empirically he found that:-

$$A = a\left[1 + bt(1 - ct)^2\right]$$

He found that the equation represented the experimental
values within 2 to 3%, c being constant for all gases and
equal to the capillarity constant of water.

The Clapeyron equation has been used as a basis
for the derivation of several equations relating gas
solubility and temperature.   If the heat of solution of
the gas in the liquid is not a function of the temperature
over the interval used, the Clapeyron equation gives:-

$$\ln\frac{\gamma_1}{\gamma_2} = -\frac{A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where the subscripts refer to temperatures 1 and 2.
Graphically log γ is a linear function of $1/T$.   More
frequently the exponential form is used.

$$\gamma = ae^{-\frac{A}{RT}}$$

Tammann[108] and Lannung[79] have used this form
which may be compared with the above equation of Jaeger.
Lannung, working with the rare gases, found that log γ
was almost a linear function of $1/T$ for organic solvents
but not for water.

If, as is normally the case, the heat of
solution is a function of the temperature, an equation
of the form of the isochore results which may be shortened
to the form used by Valentiner:

$$\log \gamma = \frac{a}{T} + b \log T + c$$

This was used by Valentiner[98] for the available data on
the rare gases in water which it fitted quite well.

Experiment has shown that the solubility of all
gases in water decreases with increasing temperature until
a minimum is reached after which it often increases quite
rapidly. When the solubility is expressed as the Bunsen
coefficient the minimum occurs for hydrogen at $60^{\circ}C$,
nitrogen at $90^{\circ}C$. and helium at about $50^{\circ}C$. When the
Ostwald coefficient is used these minima occur at much
lower temperatures, e.g. helium about $10^{\circ}C$.

For organic solvents with small gas molecules
such as helium, neon, hydrogen, the solubility increases
with the temperature, at least above $10^{\circ}C$. The temperature
coefficient is found to be greater for smaller gas mole-
cules and also for higher pressures. e.g. For the
system H_2 - liquid ammonia at 1000 atms. there is a
sevenfold increase in solubility from $0^{\circ}— 100^{\circ}C$.

For larger molecules the position is somewhat
obscure, but work on radon by Ramstedt[109] and the present
work on argon seems to indicate that here, as in water,

the solubility falls off with increasing temperature. This would lead us to expect that for a given solvent there is some critical gas size where the temperature coefficient of the solubility changes sign.

Apparently the generally accepted idea that the solubility of gases decreases with rise of temperature is due to most measurements having been made with water as a solvent and over a limited temperature range. As water in the liquid state, is highly associated at low temperatures, one would expect anomalies in the temperature coefficient of many of its properties including its dissolving power of gases.

From the above remarks we might expect the solubility of all gases in all solvents to pass through a minimum, the position of which is solely dependent on the particular gas and solvent. For increasing gas size in both water and organic solvents the minimum occurs at progressively increasing temperatures. We have seen that this is true for several gases in water while in ether the minimum occurs for oxygen at $-40^{\circ}C$. and for nitrogen at $-106^{\circ}C$.

From the standpoint of Eley's theory, this means that the relative values of ΔE_A and ΔE_C have changed. He stated that when $-\Delta E_A > \Delta E_C$ the temperature coefficient is negative and when $\Delta E_C > -\Delta E_A$ the temperature coeffi-

cient is positive. If this is true, then the minimum must occur at the temperature where $\Delta E_C = -\Delta E_A$. Eley showed that the value of the energy of cavity formation (ΔE_C) in water increased smoothly from zero at $277^{\circ}K$ to about 1 Kcal at $340^{\circ}K$. This would mean that since the minima for larger gas molecules occur at higher temperatures, so will the energy of interaction ($-\Delta E_A$) be greater for larger gases, and in fact this is what is found on calculation:-

Gas	$-\Delta E_A$ (K.cal)
He	·256
Ne	·166
A	·416
Kr	·436
Xe	·445

The small value for neon is somewhat unexpected, but may be due to inaccurate data. These values are all much lower, however, than those obtained by equating ΔE_C to $-\Delta E_A$ at the position of the minimum in the solubility plot. This is not unexpected as there must be a strong temperature dependence of $-\Delta E_A$, especially for larger gas molecules. If accurate calculations of the energies of interaction and cavity formation were possible we would be able to predict the position of the solubility minima.

Tammann[108] interpreted the minimum of gas solubility in water by postulating that the gas had a stronger interaction with water I than the other water species. Eley, however, prefers to say that solution occurs on to those points in a hypothetical "static water structure" where modifications of structure in the direction I→ II→ II'→ III can occur. This classification of water was suggested by Bernal and Fowler. Water I exists below $4^{\circ}C$. but at this temperature it changes to a quartz-like structure water II. Above $4^{\circ}C$. thermal expansion occurs through the formation of holes in quartz water II together with a modification towards close packed water III. A significant modification of water structure occurs around $50^{\circ}C$. (see Magat[110]) which might be called a modified quartz stuucture II'. Over $0^{\circ}C$. to $50^{\circ}C$. a continual breakdown I→ II→ II' occurs but above $50^{\circ}C$. behaves as a close packed organic liquid.

If this theory of the minima in the solubility is true, similar changes must occur in organic liquids to explain the results obtained. This may not be unlikely as at very low temperatures (e.g. $-80^{\circ}C$.) the liquids are probably not close packed. In fact the main difference between water and organic solvents could be due to the freezing point of water occuring much nearer the temperatures where most experimental work is done,

i.e. 10 - 50°C.

A much better approach than Eley's to this problem seems to be that from the viewpoint of free volume. We saw earlier that the solubility of a gas at a particular temperature is largely determined by the free volume and the free angle ratio of the solvent so that the temperature coefficient of solubility must be controlled by the temperature coefficient of these two factors.

$$\gamma = \frac{\delta_3 V_f V_g}{V_1}$$

The temperature coefficient of solubility is then given by

$$\frac{d\gamma}{dT} = \left(\frac{d}{dT}\ \delta_3 V_f\right)\frac{V_g}{V_1} + \delta_3 V_f \cdot \frac{d}{dT}\left(\frac{V_g}{V_1}\right)$$

so that its sign is determined by the relative temperature dependence of the free volume V_f, the free angle ratio δ_3, the molal volume V_1, and the volume of the gaseous molecule V_g.

For benzene using $\delta_3 V_f$ = ·240   at 25°C.

$$= ·246 \quad \text{at } 26°C.$$

$$V_1 = 87·7 \text{ at } 25°C.$$

$$= 87·75 \text{ at } 26°C.$$

$$r_{H_2} = 1·9 \ \overset{o}{A}$$

we find γ_{25} = ·0720, γ_{26} = ·0723, and $\frac{d\gamma}{dT}$ = +·0003 compared with γ_{25} = ·0716 experimental. The error in

the value of the solubility is reasonable when the accuracy of the free volume figures is considered, while the temperature coefficient is of the correct sign and order.

A similar calculation for water using

$$\delta_3 V_f = \cdot 0150 \quad \text{at } 25^{\circ}\text{C.}$$
$$= \cdot 0152 \quad \text{at } 26^{\circ}\text{C.}$$
$$V_l = 18 \cdot 08 \quad \text{at } 25^{\circ}\text{C.}$$
$$= 18 \cdot 15 \quad \text{at } 26^{\circ}\text{C.}$$
$$r_{h_2} = 1 \cdot 9 \text{ Å}$$

gives $\gamma_{25} = \cdot 0218$, $\gamma_{26} = \cdot 0217$, and $\frac{d\gamma}{dT} = -\cdot 0001$. Here again the temperature coefficient is of the correct sign and order.

Calculations on a large number of liquids are unfortunately not possible because of lack of $\delta_3 V_f$ data, but the basic idea employed appears to be not unreasonable. This also gives a possible explanation for the greater variation with temperature of the solubility of large gas molecules as there the factor V_g would be expected to vary to a greater extent with temperature than for small gases such as helium. When more free volume data is available, it should be possible to predict gas solubilities over wide temperature ranges, and also the positions of the minima.

The temperature dependence of $\delta_3 V_f$ is due to

the fact that as the temperature is raised the potential
barriers between the cells in the liquid become smaller
and so the effective free volume increases.   At the
same time the molecules are able to rotate more freely,
and the free angle ratio must in the limit tend to unity.

As the temperature is raised, the Ostwald
coefficient will approach unity, which will be reached
at the critical temperature of the solvent: at this
point the concentration of gas in the liquid and gaseous
phases will be the same.

Winkler[111] proposed an equation relating vis-
cosity to solubility:

$$\frac{\beta_1 - \beta_2}{\beta_1} = \frac{\eta_1 - \eta_2}{\eta_1} \frac{\sqrt[3]{M_g}}{k}$$

The subscripts refer to temperatures 1 and 2.
From this he predicted the existence of minima in the
solubility temperature plots since:
With increasing temperature the increasing volume of the
solvent will cause an increase in β while the decreasing
viscosity will cause a decrease in β .

In the present work a minimum in the temperature
coefficient would be expected to occur for each gas at
some definite methanol concentration since in pure water
$-\Delta E_A > \Delta E_C$ (negative temperature coefficient) while
in methanol the reverse is true.   Thus, at some inter-

mediate point it is logical from the Eley viewpoint
to expect that $\Delta E_C = -\Delta E_A$. That this does occur
may be shown by examining the solubility data in
Tables XVI - XIX where it is seen that, when larger gas
molecules are dissolved, the minima occur at higher
methanol concentrations.

(d)   <u>ENTROPY OF SOLUTION</u>

The transfer of a molecule from the gas phase
to a solution is completely characterised from a thermo-
dynamic point of view by the change in any two of the
three partial molal quantities heat content $(\bar{H})$, free
energy $(\bar{G})$ and entropy $(\bar{S})$, these changes being related
by the equation

$$\Delta G = \Delta H - T \Delta S.$$

If we consider a series of systems in which
the forces acting are qualitatively similar, it might be
possible to derive some further relation between ΔG,
ΔH and ΔS which would be valid for any system in this
series and would thus make a knowledge of one of these
quantities sufficient to determine the other two.   Such
relations might be of two kinds, namely:

(a)   A relation valid for a given solute in a series
of different solvents.

(b)   A relation valid for a series of different
solutes in the same solvent.

Evans and Polanyi[112] suggested that such
relations might exist and examined the available experi-
mental data for the solubility of solids in liquids.   They
came to the conclusion that a relation of type (a) is
valid:

$$\text{i.e.} \quad T \Delta S = \alpha \Delta H + \beta$$

where α and β are independent of the solvent. On the other hand the corresponding relation for a series of different solutes in the same solvent was found to be of very limited validity. All the solutes considered by Evans and Polanyi were either solid or liquid so that it should be of interest to analyse the data for gases. This was done by Bell[113] who, from the data of Horiuti[86] and Lannung[79], found that a linear relation existed between $T \Delta S$ and ΔH for a number of gases in a given solvent which both in range and in accuracy between the observed and calculated values was comparable to that found by Evans and Polanyi. When this type of plotting is used, deviations of up to 3 eu from the straight line are found. If, however, ΔH is replaced by ΔG much better plotting is obtained as shown by Graph XIX. This type of relationship is not unexpected when it is remembered that:

$$\Delta S_{Solv.} = R \ln \frac{V_g'}{\delta_3 V_f} \qquad \text{(Frank and Evans)}$$

or more correctly,

$$\Delta S = R \ln \frac{V_g^{n_B} (\gamma V_f)_A^{o \, n_A}}{(\gamma V_f)^{n_B} (\gamma V_f)^{n_A}}$$

for the removal of n_B moles of solute from dilute solution.

$$\Delta G_{solv.} = -RT \ln \gamma = -RT \ln \frac{\delta_3 V_f}{V_l V_g},$$

GRAPH XIX
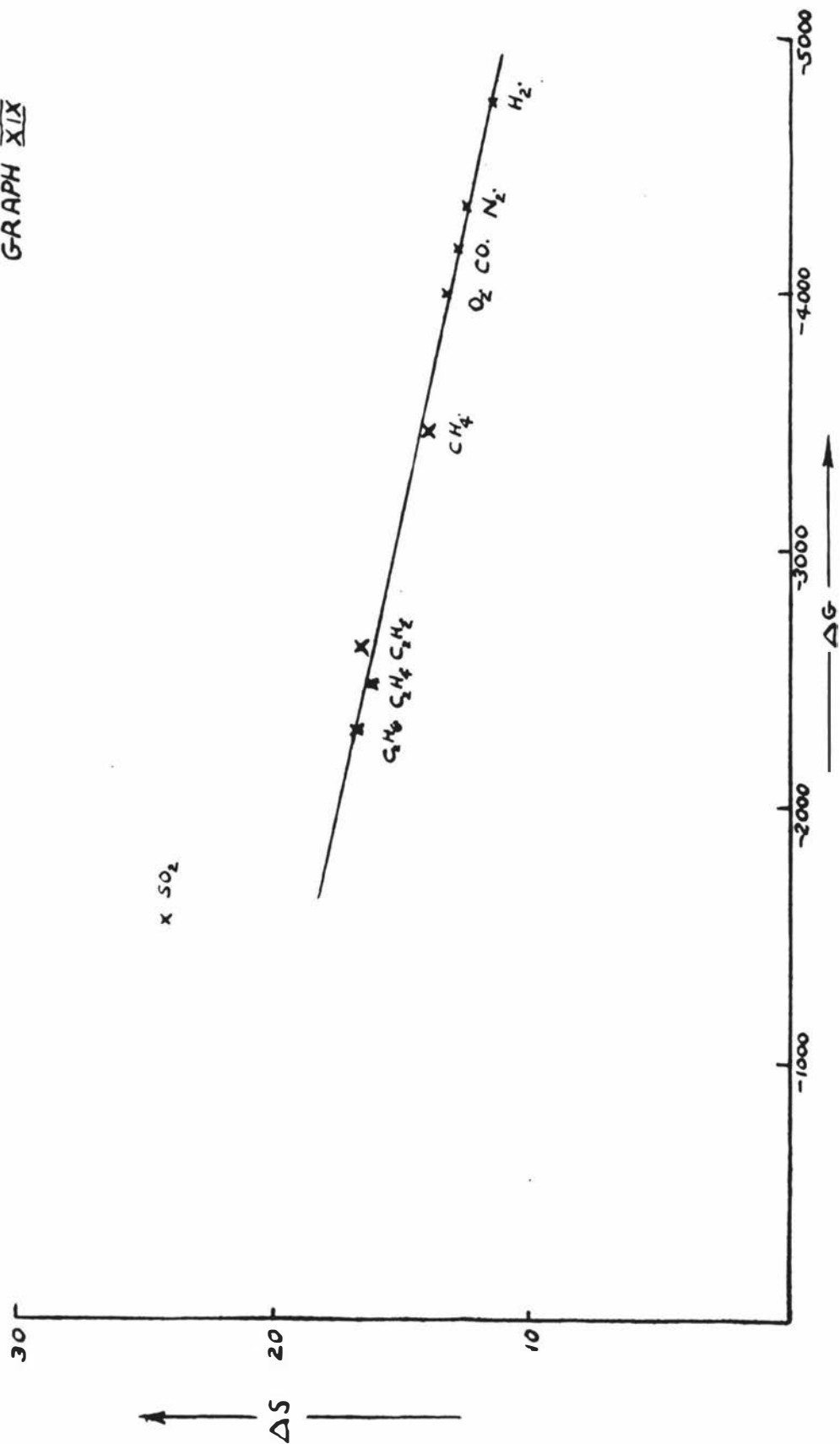
From this we see that for a number of gases in any liquid, or for one gas in a series of liquids, a straight line will be obtained whose slope is proportional to the free volume of the gas, or to the free volume of the liquid.

A strong decrease in $-\Delta S_{solv.}$ with increase of temperature, for the inert gases in water and in 20 Mole % methanol is attributable according to Eley to a strong increase of ΔS_c with temperature, mainly arising from an increase in α, the thermal expansion coefficient. The other factor which might vary significantly with temperature is the free volume of the gas molecule in the solvent, V_G . However, for $V_G = cT^{3/2}$ we should only expect an alteration in $\Delta S_{solv.}$ of 0·9 eu over 0 to 100°C. from this source. In 20 Mole % methanol a large temperature coefficient is not unexpected, as here we have a very close packed solvent at lower temperatures which rapidly changes its characteristics as the temperature is raised.

A large part of the difference between entropies of solution of a gas in an organic solvent and in water is to be attributed to the relatively large increase in the entropy of the organic solvent associated with the formation of a cavity in it, in which to put the gas molecule. That other factors, such as the restriction of

the solvent in the field of the gas molecule are important is shown by the fact that variations in $\frac{3}{2} R \ln \frac{m'G}{m}$ will by no means account for the variations in the observed ΔS_{solv}. These restrictions, in order to give the observed variations in ΔS_{solv} must increase rather more rapidly with increase of size of the gas molecule than the corresponding increase in ΔS_C. Polyatomic gases will be expected to restrict the solvent molecules to the same extent as inert gases of similar size and polarisability. However, polyatomic gases are frequently more restricted themselves than the corresponding inert gas.

If the entropy of vaporisation of a solute gas from water is greater than from an organic solvent, its entropy in the aqueous solution must be abnormally low. The partial entropy of a substance in solution (the change of entropy per mol caused by adding some of the solute to the solution) includes not only the entropy of the solute molecules, but also any changes of entropy which the solute molecules bring about in their action on the solvent. Thus the partial entropy of a solute in water may be abnormally low if the presence of a solute molecule diminishes the entropy of the solvent molecules about it. It might do this merely by the formation of the cavity, which by reducing the number of ways in which they can

unite with each other, restricts the number of config-
urations open to water molecules, or by reducing their
ability to rotate.   Either of these would reduce the
product $\delta_3 V_f$ and so increase the entropy of vaporisation.

The abnormal drop in entropy, however, diminishes
rapidly as the temperature rises.   Frank and Evans give
the following explanation for this.   They suggest that
when a rare gas atom or non-polar molecule dissolves in
water at room temperature it modifies the water structure
in the direction of greater crystallinity, i.e. the water
builds a microscopic iceberg around it.   The extent of
this iceberg is greater the larger the foreign atom.
This "freezing" of water produced by the rare gas atom
causes heat and entropy to be lost, beyond what would
normally have been expected.   The heat adds on to the
heat of solution of the gas, producing the considerable
positive ΔH_{vap}.   The loss of entropy causes the entropy
of vaporisation to be so remarkably large.   As the
temperature is raised the "icebergs" melt giving rise to
the enormous partial molar heat capacity of these gases
in water, which may exceed 60 cal. deg^{-1} mol.$^{-1}$ The
magnitude of this effect naturally depends on the size of the
iceberg originally present, so it is greatest for radon,
and at the higher temperatures the order of ΔS for the
rare gases has actually reversed itself, ΔS of vaporisation

of radon being smaller than that of helium.

This presumably means that here the expansion
of the system by intrusion of a radon atom loosens the
water considerably more than with helium and the resulting
gain in entropy shows up in the lower entropy of vapor-
isation.   Such a tendency should also exist in cold
water where, however, it is overshadowed by the iceberg
effect.

The assumption that the rare gases form icebergs
when they dissolve in water at low temperatures receives
some support from the existence of crystalline hydrates
of these substances.   There is obviously no general
correlation between solute species and solid phases but
in the case of the rare gases work by de Forcrand[114] on
their solid hydrates indicates that at any rate the
geometric relations between the non-polar solute and the
water molecules do not preclude the existence of complexes.

A possible cause of iceberg formation was
suggested by Frank and Evans as being due to a microscopic
operation of the Le Chatelier principle.   Any solute
molecule occupies a space that is large compared with
what would be required if it were not there, and therefore
even helium causes the water to expand somewhat. Cold
water as we saw is unique in that there exists in it a
mobile equilibrium between different structures in which
there are probably several structures represented by

moderately large populations. One of these structures must be more open than any other and it seems reasonable to imagine that at the edge of a patch of this material there is a greater proportion of "available" space than elsewhere. We might therefore expect a foreign molecule to find its way to such an edge location and to stabilise it to such effect as to increase the population of the iceberg material.

Considering the entropy of solution of helium, neon, and argon, we find that as the size of the gas molecule increases, the region of maximum temperature dependence of entropy moves towards higher methanol concentration.

Gas	Mole % MeOH for max. $\frac{\delta \Delta S}{\delta T}$
He	19
Ne	25
A	30

This is doubtless due to the fact that larger gas molecules affect the solvent structure to a greater extent than do smaller ones. The entropy of the small molecule helium, in 20 Mole % methanol at 10°, 15° and $20^{\circ}C$. is seen to be even lower than in water and this could be due to the large amount of restriction placed on it by the close

packed solvent structure at this composition, if the
gas molecules were sufficiently small to fit into the
interstices of the solvent structure.   This structure
will break down as the temperature is raised, so that it
is not surprising to find the "normal" type of plot at
higher temperatures.

At higher temperatures a minimum exists for
each gas, the size of which decreases with the gas size.
e.g.   at 40°C. we have,

Gas	Mole % MeOH for minimum.	Depth of minimum (eu)
He	20	2·0
Ne	28	1·8
A	40	0·5

These figures are all for entropies calculated on the
basis of Eley's standard state.   Strictly, when comparing
entropies in different solvents we should use Frank and
Evans stand state which takes account of the varying
molal volume of the solvent.   When this is done the size
of the minimum is greatly reduced but its position remains
practically unaltered except in the case of argon where
it disappears.

Gas	Mole % MeOH for minimum	Depth of minimum (e.u)
He	20	1·0
Ne	28	0·8
A	—	0

The occurrence of these minima means that here we have the maximum amount of freedom of the dissolved gas molecule. They are to some extent unexpected, but it is noteworthy that for increasing size of gas molecules more methanol is required to produce the minima which occur only at the higher temperatures. The temperature of occurrence decreases as the size of the gas molecule is increased. Thus for helium the only minimum occurs at 40°C., for neon and for argon there is one at 40°C. and a less well defined one at 35°C., while for hydrogen well defined minima are shown at 10°, 15° and 20°C. This would indicate that a larger gas molecule such as neon causes a sufficient breakdown of the solvent structure even at 35°C. that its freedom of movement is considerably enhanced. By these remarks we tacitly imply that the temperature coefficient of $\delta_3 V_f$ is greatest at the point of occurrence of the minima so that for mixed solvents in the presence of large gas molecules $\delta_3 V_f$ must refer to the free volume of the solvent modified by the presence of the gas molecules.

Measurements on krypton and xenon should show the existence of minima at methanol concentrations above 40 Mole % and at temperatures down to 10° and 15°C.

The results obtained for hydrogen do not fit into this general scheme but this may be explained on the

basis of its diatomic nature.   If its disrupting effect is greater than would be expected from its size as given by electron diffraction work, the shape of the curves obtained essentially fit the above scheme.   Here the minima are occurring at about 80 - 90 mol % methanol at 10°, 15° and $20^{\circ}C$. while at higher temperatures they have disappeared completely.   Thus generalizing for all the gases studied we may say:-

(a) Minima in the entropy-alcohol concentration plots occur for all gases if studied over a wide enough temperature range.

(b) The position of the minimum moves towards the alcohol rich solutions as the size of the gas molecule is increased.

(c) The position of the minimum moves towards the alcohol rich solutions for any one gas as the temperature is lowered.

(e) HEAT AND FREE ENERGY OF SOLUTION.

The large difference between $\Delta H_{solv.}$ for water and for methanol which is of the order of 2 Kcal mole^{-1} may be attributed to the difference in the energy of cavity formation, since $\Delta E^O = \Delta H^O - RT$, and a given gas has much the same value of ΔE_A in all solvents including water. Calculated values of $\delta \Delta H_C$ are of the order $2 - 3$ Kcal mole^{-1} i.e. approximately the same as $\delta \Delta H_{solv}$. The fact that ΔE_A is about the same in water as in organic solvents is due to the fact that the polarisation energy arising from a water dipole is negligible.

Some interesting facts about the structure of the water-methanol solvent may be deduced from the $\Delta H_{solv.}$ results more especially for helium which has the least disturbing effect. For this gas at 10°, 15° and 20^OC. we find minima which occur at progressively lower methanol concentrations as the temperature is raised. These indicate close packing of the solvent and may be correlated with the entropy values which indicated a large amount of restriction on the gas molecules at these compositions.

Maxima are found to occur for all gases, but at progressively lower temperatures as the size of the gas molecule increases. This also causes the maxima to move

into the region of greater methanol concentration.   All these changes may be correlated with the corresponding entropy changes which were discussed in the previous section.

The values of the free energy of solution which for Eley's standard states are dependent only on the solubility of the gas show the expected characteristics. Maxima are found for helium and neon at decreasing methanol concentration as the temperature is raised but at a higher methanol concentration for helium than neon.   Here again the maxima are mainly due to the type of standard states used.   If we convert the values of $\Delta G_{solv.}$ to Frank and Evans' basis, i.e. per mole of solvent rather than per c.c., these maxima vanish completely and we are left with a smooth curve over the whole range which, however, does show a definite change of slope from 30 % methanol down to pure water.

RATE OF SOLUTION OF GASES IN LIQUIDS

INTRODUCTION

The rate at which a gas dissolves in a liquid
is dependent on the size of the gas molecule and the free
volume of the liquid. Therefore, rate measurements on
a gas in a series of solvents should give a method of
determining the product $\delta_3 V_f$.

The earliest work on rates in heterogeneous
systems was done by Noyes and Whitney[115] who proposed a
two step process:-

1. Rapid reaction at interface.

2. Slow diffusion from interface

for the reaction at solid-liquid interfaces.

This was generalised to all heterogeneous systems
by Nernst[116]. Adeney and Becker [117, 118, 119] studied
the rate of solution of air, oxygen, and nitrogen from
bubbles of known magnitude into water and obtained an
empirical equation:

$$\frac{dW}{dt} = SA_p - f\frac{S}{V}W$$

A is the initial rate of solution per unit area.

f   the coefficient of escape from the liquid per unit
    volume and unit area.

S   the area of boundary surface.

V   the liquid volume.

p   the gas pressure.

W   the weight of gas dissolved.

Donnan and Masson[120] modified Adeney and Becker's equation and proposed:

$$\frac{dW}{dt} = k_2 (kc_g - c_1)$$

c_g concentration of absorbable gas in vapour phase.

c_1 concentration of absorbable gas in liquid phase.

k   Henry's Law coefficient.

k_2 a constant.

This is similar to the equation of Lewis, Whitman and Keats[121]

$$\frac{dW}{dt} = k_p (p_g - p_1)$$

p_g and p_1 are the partial pressures of the absorbable component in the gas and liquid phases respectively.   In deriving this equation stationary gas and liquid films at the boundary were postulated.   Davis and Crandall [124] assumed that the upper surface of the liquid film is almost instantaneously saturated with the gas and interpreted their work on the rate of solution of oxygen into water by the equation:

$$\frac{1}{S} \left(\frac{dn}{dt} \right) = k_1 (c_d - c_1)$$

C_d saturation concentration of dissolved gas.

C_l concentration of gas in the liquid phase.

k_1 constant.

n number of moles of gas in the liquid phase.

S area of boundary of surface.

This theory of Davis and Crandall is similar to that of Nernst, and Noyes and Whitney, all being based on two assumptions:-

(i) Existence of a stationary film of liquid or stationary films of liquid and gas.

(ii) Instantaneous saturation of the upper layer of the stationary film with the gas.

Miyamoto[122] neglects these assumptions which will obviously not hold when the main body of the liquid is kept well stirred. He separates the process of solution into two steps:-

(i) Penetration of gas molecules into the liquid phase.

(ii) Escape of gas molecules from the liquid phase, and obtains from general kinetic theory the equation

$$\frac{dn}{dt} = \frac{P}{\sqrt{2\pi MRT}} \, S \, e^{-\frac{Mu_o^2}{2RT}} - \frac{C_1 N}{1000} \, \frac{\sqrt{RT}}{2\pi M} \, e^{-\frac{Mu_o'^2}{2RT}}$$

C_1 concentration of gas in the liquid phase.

p partial pressure of the gas.

u_0 the threshold velocity at right angles to the interface which must be exceeded by the entering molecules.

u_0' the threshold velocity at right angles to the interface which must be exceeded by molecules escaping from the solution.

Miyamoto uses his equation to calculate values of u_0 rather than rates of solution.

All the above equations either involve assumptions of a questionable nature or involve parameters whose values cannot be determined with any great accuracy.

A more rigorous treatment of rates of solution has been made by Stearn, Irish and Eyring[123] who use Eyring's theory of absolute reaction rates.

The diffusion coefficient D is defined by the relationship:

$$ds = - DA \frac{dc}{dx} dt$$

This is negative as diffusion occurs in the direction of decreasing concentration. ds is the quantity of solute which crosses a boundary of cross section A in time dt, when the concentration gradient is $\frac{dc}{dx}$; the distance x being measured in the direction of diffusion.

Stearn, Irish and Eyring then obtain an equation,

$$D = \lambda^2 \frac{kT}{h} \frac{h}{(2 \pi mkT)^{\frac{1}{2}} V_f^{\frac{1}{3}}} e^{- \Delta E_{vap}/n RT}$$

where λ is the equilibrium distance between molecules
in the liquid.

The process of diffusion is very similar to
that of viscosity (which was considered earlier) except
that in the former case unlike molecules are involved.
In order to diffuse into solution, a molecule of solute
and one of solvent are required to slip past each other.

Suppose λ is the distance between two successive
equilibrium positions, so that this is the distance through
which a molecule of solute is transported in each jump.
The change of the standard free energy with distance can
then be represented by the curve:
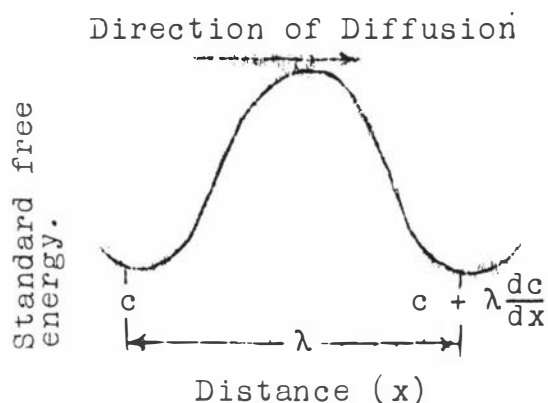
If k' is the number of times per second that a particular
molecule is engaged in passing a neighbour in the direction
of diffusion then from absolute reaction rate theory we
may write:-

$$k' = \frac{kT}{h} \frac{F^{*}}{F} e^{-E_{0}/RT}$$

$$= \frac{kT}{h} e^{-\Delta G^{*}/RT} = \frac{kT}{h} e^{-\Delta S^{*}/R} e^{-\Delta H^{*}/RT}$$

where F^* and F are the partition functions of the reacting system in the activated and normal states respectively. ΔG^*, ΔH^* and ΔS^* are respectively the standard free energy, heat, and entropy increases when the activated complex is formed from the reactants.

E_0 is the difference in energy between the lowest state in the normal and in the activated states.

k Boltzmann constant.   h Planck constant.

It can also be shown[125] that $D = \lambda^2 k'$

So $D = \lambda^2 \dfrac{kT}{h} \dfrac{F^*}{F} e^{-E_0/RT}$

If we assume that the degree of freedom corresponding to flow is a translational one and that the partition functions for other degrees of freedom are the same for the initial and activated states

$$\frac{F^*}{F} = \frac{h}{(2\pi mkT)^{\frac{1}{2}}} \frac{1}{v_f^{\frac{1}{3}}}$$

v_f is the free volume.

If the unit process in diffusion is the passing of two molecules in the sense of a partial rotation of a double molecule[21], extra space must be provided though this may not necessarily have to be a hole the full size of a molecule.   Therefore the energy of activation for diffusion per mole may be taken as some fraction of the energy of vaporisation.

$$\Delta E_{Act} = \Delta E_{vap}/n$$

$$\therefore \quad D = \frac{\lambda^2}{v_f^{\frac{1}{3}}}\left(\frac{kT}{2\pi M}\right)^{\frac{1}{2}} e^{-\Delta E_{vap}/nRT}$$

Values of the parameter n, which varies from 2 - 4 can be obtained from the temperature coefficient of the viscosity of the solvent. Ewell and Eyring[35] assumed that the average activation energy of flow for a liquid was given by:

$$\Delta E_{Act.} = R \, d \, \ln \eta / d \, (1/T)$$

and found values of the ratio $\Delta E_{vap}/ \Delta E_{act.}$ listed below.

Liquid	n	Liquid	n
Water	2.4	Acetone	4
Ether	4	Carbon Tetrachloride	3
Methyl Alcohol	3	Carbon Disulphide	4

In this equation for diffusion as in his corresponding one for viscosity, Eyring assumed that $\lambda = (V/N)^{\frac{1}{3}}$ where V is the molal volume, so that

$$D = \left(\frac{V}{N}\right)^{\frac{2}{3}}\frac{1}{v_f^{\frac{1}{3}}}\left(\frac{kT}{2\pi M}\right)^{\frac{1}{2}} e^{-\Delta E_{vap}/nRT}$$

Here, however, for the same reasons as before, λ is probably much closer to $\left(\frac{V}{N}\right)^{\frac{1}{3}} - b \left(\frac{V_f}{N}\right)^{\frac{1}{3}}$ so that the corrected equation for D is

$$D = N^{-\frac{2}{3}} v_f^{-\frac{1}{3}} \left(V^{\frac{2}{3}} + b^2 V_f^{\frac{2}{3}} - 2bV^{\frac{1}{3}}V_f^{\frac{1}{3}}\right)\left(\frac{kT}{2\pi M}\right)^{\frac{1}{2}} e^{-\Delta E_{vap}/nRT}$$

It must be remembered, however, that in general diffusion involves molecules of two types, solvent and solute; hence mean values of λ, V_f and ΔE_{vap} should be employed.

For λ and V_f weighted arithmetic means of the values for the two pure components are obtained from:

$$\lambda = N_1\lambda_1 + N_2\lambda_2$$
$$V_f^{\frac{1}{3}} = N_1 V_{f1}^{\frac{1}{3}} + N_2 V_{f2}^{\frac{1}{3}}$$

while the mean value of ΔE_{vap} was calculated from the equation

$$\Delta E_{vap.}^{\frac{1}{2}} = N_1 \Delta E_1^{\frac{1}{2}} + N_2 \Delta E_2^{\frac{1}{2}}$$

The mass M in the equation for D is the reduced mass of the two constituent molecules treated as a combined unit. For gases of low solubility such as hydrogen the error introduced by the use of values of λ, V_f and $\Delta E_{vap.}$ for the pure solvent will be negligible.

Ewell and Eyring found no significant difference in the values of the free volume calculated from sound velocity or energy coefficient data except in the case of water. For five organic liquids the ratio $\dfrac{V_f(S.V.)}{V_f(E.V.C.)}$ averaged 0·95 and varied from 0·85 to 1·07 whereas for water this ratio was 2·5.

These workers tested their equation for diffusion on a number of compounds. For the diffusion of tetrabromo-ethane in tetrachloroethane the calculated values are all twice as big as the experimental ones while for diffusion

into water the ratio $D_{obs.}/D_{calc.}$ ranges from 4·5 to 1·7. For the diffusion of gases into water they obtained the following values:

Gas	Temperature	$D_{obs.}$ x 10^5	$D_{calc.}$ x 10^5
C_2H_2	291	1·76	·391
CO_2	291	1·46	·367
N_2	291	1·62	·396
H_2	291	3·59	1·04

Their explanation for this deviation is that in the case of a liquid such as water (i.e. with considerable structure) rotation in the normal state will be hindered to a greater extent than in the activated state. Thus in cancelling out all but the translational term in the partition functions corresponding to the two states this factor is overlooked resulting in too low a calculated value.

If, however, the corrected equation for D is used, these deviations are reduced to a certain extent. The essential difference between the two is the existence of the factor $(b^2 V_f^{2/3} - 2b V_f^{\frac{1}{3}} V_f^{\frac{1}{3}})$ in the corrected form and it is apparent that if $2b V^{\frac{1}{3}} V_f^{\frac{1}{3}} > b^2 V_f^{2/3}$ the resulting values of D will be less than those calculated from the equation of Stearn, Irish and Eyring, while if $b^2 V_f^{2/3} > 2b V^{\frac{1}{3}} V_f^{\frac{1}{3}}$ the values will be greater. This change in the value of D

may be illustrated by the following calculations for
benzene and water.

Using a value of 10 for the factor b we have:-

	Benzene	Water
V_l	87·7	18·1
V_f	·27	·42
$V_f^{\frac{1}{3}} V^{\frac{1}{3}}$	2·9	1·9
$V^{2/3} + b^2 V_f^{2/3} - 2b V^{\frac{1}{3}} V_f^{\frac{1}{3}}$	6·4	24·8
$V^{2/3}$	19·4	6·8

From this we see that the ratio $D_{Eyring}/D_{corr.}$ for
benzene is 3·0 while for water it is 0·23. These factors
are almost identical with those by which Eyring's
calculated values deviated from the experimentally
observed ones. This is shown in Table XXII where values
calculated from Eyring's and the corrected equation are
compared with the observed values.

TABLE XXII

Substance	$D_{Eyring} \times 10^5$	$D_{corr.} \times 10^5$	$D_{obs.} \times 10^5$
Nitrogen – water	·396	1·72	1·62
Hydrogen – water	1·04	·4·52	3·59
Carbon Dioxide – water	·367	1·60	1·46
Phenanthrene – benzene	3·34	1·11	0·95
Octyl Bromide – benzene	3·29	1·10	1·17
Iodoform – benzene	3·04	1·01	1·12

The fact that the corrected equation gives values in good agreement with the observed ones does not in itself prove that the equation is correct, but the improved agreement seems to indicate that the inclusion of b and V_f is not unreasonable. This is particularly shown by the increase in the values for water and the decrease for organic solvents.

TEMPERATURE COEFFICIENT OF DIFFUSION

In the older treatments of diffusion in liquid systems the effect of temperature on the data has normally been represented by linear functions. This doubtless arose from the limited material available, measurements of the diffusion coefficient often being only available at two temperatures. The data was then represented by an equation of the form:-

$$D_2/D_1 \quad = \quad 1 \quad + \quad \alpha \ (T_2 \ - \ T_1)$$

Precision work by Cohen and Bruins[126] however, showed that diffusion was an exponential function of temperature.

Although data for the temperature variation of diffusion coefficients is meagre there are generalisations possible which are readily understandable from the standpoint of diffusion as a velocity process depending upon hole formation in the liquid medium. Thus Oholm[128] on the basis of data at two temperatures with a wide variety of media pointed out that substances showing a high value for the diffusion coefficient always showed a small temperature coefficient and vice versa.

This is to be anticipated on the basis of Eyring's theory since the more slowly diffusing particles require larger holes than the faster species and the activation

energies to produce larger holes are correspondingly greater.

Riecke[127] attempted to formulate a kinetic theory of diffusion in dilute solutions and obtained an expression for the diffusion coefficient,

$$D = \text{const.} \ (1/M)^{\frac{1}{2}} l$$

where M is the molecular weight and l the mean free path. Values for l of the order of $0\cdot1$ $\overset{o}{A}$ were obtained with this equation, but Oholm showed that for molecules with molecular weights between 50 and 300, the diffusion coefficients varied quite randomly on the molecular weight basis. This may be compared with Eyring's concept which shows that it is the shape and volume of the diffusing molecule rather than its mass which determines the diffusion velocity in a given medium.

Work by Barrer[129], and Newitt and Weale[130], on the rate of diffusion of gases into high polymers has shown that the values of D obtained are comparable to those for diffusion of gases into organic liquids. The values for hydrogen were much greater, at a given temperature, than those for nitrogen. The diffusion coefficients of gases in various liquid and solid substances were shown by Barrer to increase exponentially with temperature according to the relation:

$$D = D_O \, e^{-\,E_D/RT}$$

where D_O is a constant and E_D is the heat of activation of diffusion.

DISCUSSION.

Some approximate rate measurements were carried out which showed that the rate of solution of hydrogen decreased in the following order -

Ether $\longrightarrow$ carbon disulphide $\longrightarrow$ n-hexane $\longrightarrow$ carbon tetrachloride $\longrightarrow$ methyl alcohol $\longrightarrow$ water.

This is the order that would be expected from values of D calculated from the corrected equation.

Further work is now being carried out in this laboratory on rate measurements, using the apparatus that has been built for equilibrium measurements. The object of this work will be, not so much to add to the already large amount of unrelated diffusion data existing but to give an alternative method of calculating free volumes. Thus if the rate of solution of any one gas in a solvent is measured it will be possible to calculate the equilibrium solubility of any other gas in the same solvent.

SUMMARY.

1.   A gas solubility apparatus has been designed and
      constructed.

2.   The solubility of helium, neon, argon and hydrogen
      in water-methanol mixtures over the range $10^{\circ} - 40^{\circ}C$.
      has been measured and the derived thermodynamic
      properties calculated.

3.   An equation has been suggested which relates
      simply the solubility of a gas to the product $\delta_3 V_f$
      for the solvent.   Quite good agreement was found
      for the large number of gases and solvents tested.

4.   A corrected form of Eyring's viscosity equation has
      been shown to represent the experimental data more
      accurately and also to give the correct relationship
      between viscosity and free volume.

5.   The structure of methanol-water mixtures has been
      examined and the solvent shown to be closest packed
      at about 20 Mole % and values of the free volume
      and free angle ratio calculated from several sets
      of data listed.   Corresponding values for ethanol-
      water mixtures were also calculated and compared
      with the work of Matsuyama.

6.   The correction employed in the viscosity equation
     has been extended to the corresponding equation
     for diffusion and a method suggested for the
     evaluation of free volumes.

7.   An explanation has been offered for the varying
     temperature coefficient from water to organic solvents
     on the basis of free volume.   Calculations made
     with the limited data available show good agreement
     with experiment.

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