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REGULAR SOLUTIONS
OF GASES IN LIQUIDS.
II CONCENTRATED SOLUTIONS
OF HYDROGEN AT HIGH PRESSURE

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Regular Solutions of Gases in Liquids

II. Concentrated solutions of hydrogen at high pressure

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921   In many cases the emergence of high pressure technique into the domain of chemical and physico-chemical processes has facilitated operation with concentrated solutions of gases in liquids. Till now, however, we have not had at our disposal any theory of concentrated solutions of gases in liquids. This is due mainly to the lack of experimental data connected with investigations of the equilibrium concentrations in the liquid and vapour phases. Unfortunately, most investigations of gas/liquid equilibrium are confined to the determination of the solubility of the gas; the error involved in the analysis of the vapour phase makes a perfect interpretation of these data impossible.

The most extensive data we have at our disposal are concerned with solutions of hydrogen in a series of non-polar solvents at low temperatures. These include investigations on the equilibrium H_2-N_2[1,2,3], H_2-CO[1], H_2-CH_4[3,4,5], $H_2-C_2H_4$[6], and $H_2-C_2H_6$[7].

922   For working out the theory of concentrated solutions of gases in liquids at high pressure we shall try to interpret these data.

Another difficulty in the treatment of the results of the experimental investigations arises in the errors in the data on the compressibilities of most mixtures of the gases mentioned. This necessitates calculating the fugacity of the dissolved gases by the Lewis-Randall rule[8] which is only valid for low concentrations of the vapour in the solvent in the vapour phase. This fact reduces still further the amount of data suitable for calculation purposes.

We now consider the thermodynamic equations for solutions of gases in liquids.

For an infinitely dilute solution, Henry's Law is valid at low pressures:-

$$f_1 = K \cdot N_1 \tag{1}$$

where N_1 and f_1 denote the mole fraction and the fugacity of the dissolved gas and K the Henry coefficient.

The behaviour of the infinitely dilute solutions at high pressures is given very satisfactorily by Kritschewsky and Kasarnowsky's Equation:

$$\log \frac{f_1}{N_1} = \log K + \frac{\overline{v}_1(p-p_2^o)}{2.303\,RT} \tag{2}$$

where $\overline{v}_1$ is the partial molar volume of the dissolved gas, p the total pressure, p_2^o the vapour pressure of the solvent.

923   In previous work[10] we attempted to show the applicability of Hildebrand's theory[11] of regular solutions (with certain assumptions) for solutions of gases in liquids at low pressures in the form of eqn. (3).

$$\log \frac{f_1}{N_1} = \log f_1^o + \frac{v_1}{4.58T}\left(\frac{N_2 v_2}{N_1 v_1 + N_2 v_2}\right)^2 \left(\frac{\sqrt{a_1}}{v_1} - \frac{\sqrt{a_2}}{v_1}\right)^2_p \tag{3}$$

where f_1^o denotes the fugacity of the pure gas at the vapour pressure of the liquid gas extrapolated to temperature T, v_1 and v_2 the molar volumes of the liquid gases at p = 1 atm[12], $(a_1)^{\frac{1}{2}}/v_1$ and $(a_2)^{\frac{1}{2}}/v_2$ the square root of the internal pressure of the components.

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It was shown that at $p \to 0$ and $N_1 \ll N_2$

$$\log \frac{f_1}{N_1} = \log f_1^o + \frac{v_1}{4.58T}\left(\frac{\sqrt{a_1}}{v_1} - \frac{\sqrt{a_2}}{v_2}\right)^2_{p=0} = \log K \qquad (4)$$

where $\left(\dfrac{\sqrt{a_1}}{v_1} - \dfrac{\sqrt{a_2}}{v_2}\right)^2_{p=0}$ refers to zero pressure. The calculation carried out

according to eqn. (3) shewed[10] that the value of $\left(\dfrac{\sqrt{a_1}}{v_1} - \dfrac{\sqrt{a_2}}{v_2}\right)^2$ increased with the pressure.

In the present communication we shall try to discuss the dependence of this quantity on the pressure and hence work out in addition the theory of regular solutions on the basis of concentrated solutions of gases in non-polar solvents at high pressures.

To this end we calculate, as in eqn. (2), the change of f_1 with pressure increase and substitute the molar volumes in Hildebrand's equation by the partial molar volumes.

Hence we obtain an equation expressing not only the dependence of $\log f_1/N_1$ value on the pressure but also on the concentration:-

$$\log \frac{f_1}{N_1} = \log f_1^o + \frac{\overline{v}_1}{4.58T}\left(\frac{N_2\,\overline{v}_2}{N_1\,\overline{v}_1 + N_2\,\overline{v}_2}\right)^2\left(\frac{a_1}{\overline{v}_1} - \frac{a_2}{\overline{v}_2}\right)^2_{p=0} + \frac{\overline{v}_1\,(p-p_2^o)}{2.303\,RT} \qquad (5)$$

924   Comparison between eqns. (3) and (5) leads to:-

$$\left(\frac{\sqrt{a_1}}{\overline{v}_1} - \frac{\sqrt{a_2}}{\overline{v}_2}\right)^2_p = \left(\frac{\sqrt{a_1}}{\overline{v}_1} - \frac{\sqrt{a_2}}{\overline{v}_2}\right)^2_{p=0} + \frac{1.982}{82.07}\,(p-p_2^o)\left(\frac{N_1\,\overline{v}_1 + N_2\,\overline{v}_2}{N_2\,\overline{v}_2}\right)^2 \qquad (6)$$

The partial molar volume of the dissolved hydrogen was equated by us to the molar volume of liquid hydrogen at $p = 1$ atm. (as appears probable from the data of Table III). The same goes for the partial molar volume of the solvent. The hypothesis was also advanced of the independence of $\overline{v}_1$ and $\overline{v}_2$ of p and N. If the values of $\overline{v}_1$ and $\overline{v}_2$ are correctly chosen and the assumption is valid, it is evident that we obtain with graphical representation of the values calculated from experimental data of

$\left(^{a_1}/\overline{v}_1 - ^{a_2}/\overline{v}_2\right)^2_p$ against $(p-p_2^o)\left(\dfrac{N_1\,\overline{v}_1 + N_2\,\overline{v}_2}{N_2\,v_2}\right)^2$ a straight line with the

slope:-

$$\beta = 1.982/82.07 = 0.02415$$

From the intercept of this line with the ordinate, the Henry coefficient at p, $N_1 \to 0$ is calculated.

We tested the applicability of eqn. (5) with the data on the equilibrium H_2-CO[1] at $68.1°$, $73.1°$ and $83.1°K$ up to 200-225 atm. and 40.1% hydrogen content, H_2-N_2[1] at $63.1°$, $68.1°$ and $78.1°K$ up to 160-215 atm. and 37.9% H_2, H_2-CH_4[5] at $90.3°$ and $110°K$ up to 190-220 atm. and 15.6% H_2 and $H_2-C_2H_4$ at $188.1°K$ up to 50 atm. and 3.6% H_2.

In the following table are shown, by way of example, the data for the system H_2-N_2. The f_{H_2} value was calculated according to the Lewis-Randall rule and $f_{H_2}^o$ as in the previous paper.[10] The calculating of the fugacities was taken from Newton diagrams.[13]

We now consider the change of the log f_1/N_1 value with the pressure according to the data of this table. At 63.1°K, log f_1/N_1 increases with the pressure so that it appears to follow eqn. (2). At 68.1°K

TABLE I

$p-p_2$ (atm)	N_1	N_1'	$\lg \dfrac{f_1}{N_1}$	$\left(\dfrac{\sqrt{a_1}}{v_1} - \dfrac{\sqrt{a_2}}{v_2}\right)^2_p$	$(p-p_2^0)\left(\dfrac{N_1 \overline{v}_1 + N_2 \overline{v}_2}{N_2 v_2}\right)^2$
	mole fraction				
				$T = 63.1°$ K	
26.6	0.041	0.981	2.768	10.50	28.3
46.0	0.0075	0.982	2.714	10.60	52.0
55.4	0.083	0.984	2.742	11.08	63.8
89.5	0.120	0.963	2.743	11.87	110.0
118.4	0.146	0.968	2.770	12.85	153.7
147.3	0.172	0.957	2.810	13.90	206.5
176.3	0.189	0.937	2.795	14.74	252
205.3	0.216	0.935	2.823	15.46	304
215.0	0.222	0.929	2.835	15.75	321
				$T = 68.1°$ K	
16.9	0.033	0.973	2.684	8.90	17.7
26.3	0.046	0.976	2.724	9.46	28.2
35.7	0.066	0.976	2.691	9.54	39.7
45.6	0.076	0.979	2.728	10.06	51.9
55.6	0.094	0.973	2.709	10.30	65.4
89.4	0.147	0.953	2.687	11.06	116.0
118.2	0.181	0.944	2.704	12.18	165.5
147.1	0.219	0.922	2.700	12.84	218.0
176.1	0.250	0.903	2.718	14.30	284
				$T = 78.1°$ K	
35.5	0.073	0.930	2.633	8.79	40.1
54.4	0.119	0.937	2.600	8.95	66.8
78.8	0.175	0.922	2.577	9.71	109.3
112.5	0.248	0.895	2.594	11.63	186.5
146.3	0.334	0.840	2.495	11.82	292.6
160.8	0.379	0.813	2.493	14.15	381

log $f_1/N_1 \simeq$ const., which can be construed as proof of the applicability of eqn. (1). But at 78.1°K (and at still higher temperature[2]) log f_1/N_1 decreases with increase of pressure i.e. on calculation with eqn. (2), negative values of the partial molar volume of hydrogen arise—which is very doubtful.

In Fig. 1 the data quoted above on the solubility of H_2 in N_2, CO, CH_4 and C_2H_4 are plotted in a co-ordinate system corresponding to eqn. (6).

The straight lines obtained from these prove that the partial molar volumes of hydrogen in one and the same solvent are equal at different concentrations and pressures (within the limits of experimental error).

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In the following table are given the values of $\beta/0.02415$ calculated from these lines.

From the data of these tables it can be concluded that in the neighbourhood of the freezing point of the solvent (65.9°K for CO, 63.1°K for N_2, 90.1°K for CH_4) the partial molar volumes of the dissolved hydrogen are approximately equal to one another and moreover seem also to lie very close to the molar volumes of liquid hydrogen at p = 1 atm. (28.6 cm^3).

Roughly the same values result with the approximate calculation of the solubility data of H_2 in C_6H_6 at 298.1°K[14], (since the data on the composition of the vapour phase are in error.)

TABLE II

solvent	T ($^{\circ}$K)	$\dfrac{\beta}{0.02415}$
CO	68.1	0.987
CO	73.1	0.962
CO	83.1	0.790
N_2	63.1	0.878
N_2	78.1	0.882
N_2	88.1	0.696
CH_4	90.3	0.965*
CH_4	110.0	1.002
C_2H_4	188.1	0.787

*The calculation of these data according to eqn. (2) gave $\overline{v}_{H_2} = 6$ cm^3.

It should be noted that the $\overline{v}_{H_2}$ values calculated according to eqn. (5) are higher than those calculated according to eqn. (2) (where this is possible). This is, perhaps, an explanation of the fact that the partial molar volumes determined by dilatometric methods are also higher than those calculated according to eqn. (2).[15]

It seems to us that the data and calculations outlined above bear out the applicability of the theory of regular solutions to concentrated solutions of hydrogen in non-polar liquids at high pressures.

The constancy of the v_{H_2} values thus obtained with different concentrations and pressures obviously proves that the dependence of the partial molar volumes of the hydrogen on p and N does not lead to errors exceeding the magnitude of experimental error.

The fact that the $\overline{v}_{H_2}$ values under certain conditions lie close to the values of the molar volume of liquid hydrogen is very interesting although an investigation on other gases is also required.

Unfortunately, the paucity of experimental data makes the application of the theory of regular solutions to the solutions of other gases difficult.

In the work of Iljinskaya[15], is to be noted the similarity of the values obtained by her for the partial molar volumes of the gases in water at 273.1°K, to the value of the constant 'b' in the Van der Waals equation. In the following table the mean values of the data obtained by her and other workers by dilatometric methods are compared with the constants 'b' and the molar volumes of the liquid gases at p = 1 atm.

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TABLE III

Gas	$\overline{v}$	L (in cm³)	$\overline{v}$
N_2	36.4	39.1	35.0
H_2	24.3	26.6	28.6
O_2	27.1	32.3	28.1
CH_4	35.3	42.7	37.7
CO	35.7	39.9	36.0

From the data of this table it follows that the $\overline{v}$ values of the gases in water at their freezing point also approach the molar volumes v of the liquid gases at p = 1 atm.

Further investigations are required to deal with this question.

If we knew the partial molar volumes of the dissolved gases it would be possible with the help of these to ascertain all the other quantities in the fundamental equation of the theory of regular solutions. This is apparent from the following simple procedures.

From eqn. (5) we obtain

$$\log \frac{f_1}{N_1} - \frac{\overline{v}_1\,(p-p_2^o)}{2.303\ RT} = \log f_1^o + \frac{\overline{v}_1}{4.58T}\left(\frac{N_2\,\overline{v}_2}{N_1\,\overline{v}_1 + N_2\,\overline{v}_2}\right)^2 \left(\frac{\sqrt{a_1}}{\overline{v}_1} - \frac{\sqrt{a_2}}{\overline{v}_2}\right)^2_{p=0}$$

If we plot graphically the values of $\log \frac{f_1}{N_1} - \frac{\overline{v}_1\,(p-p_2^o)}{2.303\ RT}$ against those

of $\left(\dfrac{N_2\,\overline{v}_2}{N_1\,\overline{v}_1 + N_2\,\overline{v}_2}\right)^2$ we should obtain a straight line whose intercept with

the ordinate gives the value of $\log f_1^o$. From the slope of this line

$\left(\dfrac{\sqrt{a_1}}{\overline{v}_1} - \dfrac{\sqrt{a_2}}{\overline{v}_2}\right)^2_{p=0}$ can be calculated.[16]

In subsequent work we intend to test by this method the applicability of the derived equations above for other gases with help of the most probable $\overline{v}$ values.

Summary

1. An equation was proposed which describes gas/non-polar liquid equilibrium at high concentrations and pressures.

2. The applicability of this equation to solutions of hydrogen in liquid N_2, CO, CH_4 and C_2H_4 at high pressures and concentrations of the dissolved gas was shewn.

3. It was shewn that under certain conditions, the values of the partial molar volumes of the dissolved hydrogen in the solvents investigated lie close to one another and to the molar volume of liquid hydrogen at p = 1 atm.

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4. It has been shewn that the assumption about the independence of the partial molar volume from the concentration and the pressure for the system considered does not give rise to errors in excess of the experimental error.

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12. In the general case v_2 denotes the molar volume of the solvent.

13. Newton, Ind.Eng.Chem., 27, 302 (1935).

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16. If we know the $\bar{v}_1$ value it is also possible to calculate the $a^{\frac{1}{2}}/\bar{v}_1$ values from the Van der Waals constants a when the extrapolation of $a^{\frac{1}{2}}/v$ becomes unnecessary. (See previous paper.)
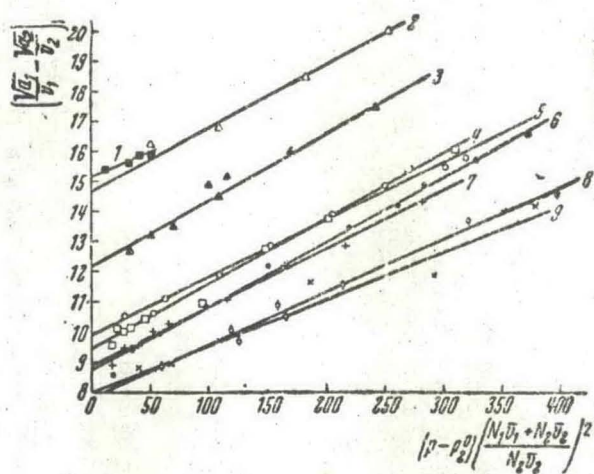
Fig. 1. 1 – H_2 – C_2H_4 (188.1°K); 2 – H_2 – CH_4 (90.3°K);
3 – H_2 – CH_4 (110.0°K); 4 – H_2 – CO (68.1°K);
5 – H_2 – N_2 (63.1°K); 6 – H_2 – CO (73.1°K);
7 – H_2 – N_2 (68.1°K); 8 – H_2 – CO (83.1°K);
9 – H_2 – N_2 (78.1°K).