Solubilities of the Inert Gases in Water.

By T. J. MORRISON and N. B. JOHNSTONE.

[Reprint Order No. 5273.]

The solubilities of the inert gases in water are accurately represented by an equation of the type proposed by Valentiner. A constant partial molar heat capacity is indicated for all five gases from helium to xenon, though there may be a variation of not more than about 6 cal./deg./mole. Comparison with data obtained by Ostwald's technique suggests that the work of Lannung on helium, neon, and argon is the most reliable, but the temperature ranges he used are too small for reliable estimates of $\bar{c}_p$ to be obtained. The behaviour of the inert gases is compared with that of the paraffin series and other gases. The probable behaviour of carbon tetrafluoride is briefly considered.

DURING a continuation of the salting-out measurements previously reported (*J.*, 1952, 3814, 3819) it became evident that the solubilities obtained in the inert-gas series showed rather considerable deviations from many results obtained by Ostwald's technique. Since these earlier measurements have been used to calculate the thermodynamic characteristics of these important systems, it is of interest to compare the results from two different techniques.

The results are accurately represented by the type of equation due to Valentiner (*Z. Physik*, 1927, **42**, 253), *viz.*,

$$\log_{10} s_0 = -A + B/T + C \log_{10} T$$

(s_0 = absorption coefficient at 1 atm. per 1000 g. of water), but the constant C is approximately the same for all members, whereas in the paraffin series it is not. With $C = 20{\cdot}5$, and the constants A and B shown in Table 1, deviations between experimental and calculated values are generally within $\pm 0{\cdot}5\%$ in s_0 and show little or no trend. In view of the possible error in estimating C, there may be slight differences between the gases, but it is doubtful if these can exceed 3 units from helium to xenon. Fig. 1 shows differences between experimental and calculated values of log s_0 (Δlog s_0) and also deviations of certain recorded values.

TABLE 1.

Gas	He	Ne	A	Kr	Xe
A	58·987	59·412	60·272	60·434	60·836
B	2740	2890	3290	3410	3605

The following comparisons with previously recorded data may be made.

Helium.—The results of von Antropoff (*Z. Electrochem.*, 1905, **14**, 585; 1919, **25**, 269; *Proc. Roy. Soc.*, 1910, **83***A*, 474) and of Estreicher (*Z. physikal. Chem.*, 1899, **31**, 176), which are commonly quoted, show deviations of about +10% and +50%, respectively, and are not included. The results of Lannung (*J. Amer. Chem. Soc.*, 1930, **52**, 68) and of Cady, Elsey, and Berger (*ibid.*, 1922, **44**, 1456) are, however, in reasonable agreement, and suggest from their scatter that the present values in the range 10—30° C are accurate. Individual runs by these workers vary by about ±1% from their mean values. The only recorded measurements of value in the range 30—75° are those at high pressures by Wiebe and Gaddy (*ibid.*, 1935, **57**, 847; 25—1000 atm.) and by Pray, Schweickert, and Minnich (*Ind. Eng. Chem.*, 1952, **44**, 1146; 100—500 lb./sq. in.). Extrapolation to 1 atm. gives rise to slight uncertainty, but suggests that our values in this range are not greatly in error.

Neon.—Our results are in agreement with those of Lannung in the range 10—45°. Data by von Antropoff and by Valentiner, showing very high temperature coefficients in opposite directions, cannot be conveniently included in full in Fig. 1, and there are no other measurements of value above 45°.

Argon.—There is again good agreement with Lannung's results in the range 10—45°. An identical value by Eucken and Herzberg (*Z. physikal. Chem.*, 1950, **195**, 1) at 20° confirms the accuracy. The results of Winkler (*ibid.*, 1906, **55**, 347), Estreicher and Akerlof (*J. Amer.*

FIG. 1.

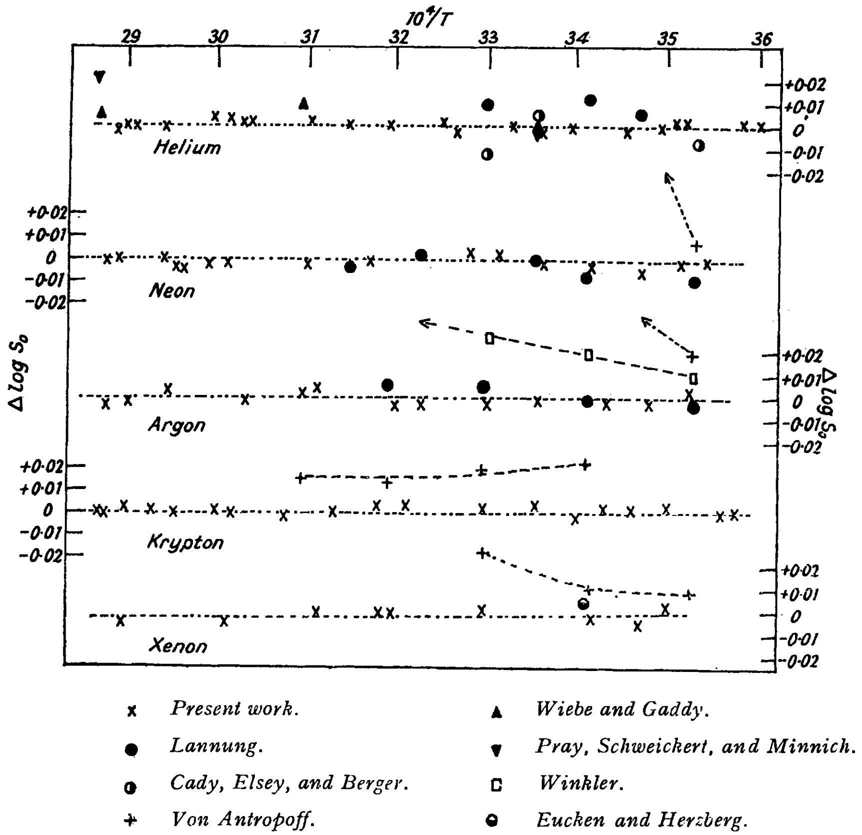
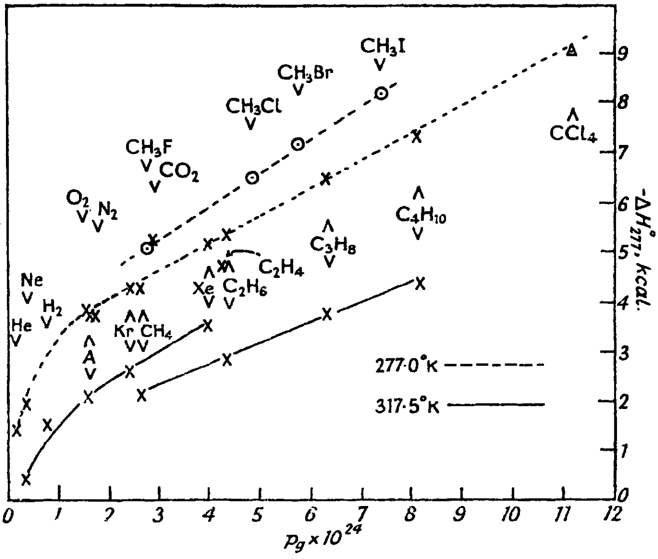

10⁴/T
29
30
31
32
33
34
35
36
Helium
Neon
Argon
Krypton
Xenon
Δ log S₀
+0·02
+0·01
0
-0·01
-0·02
x Present work.
● Lannung.
◐ Cady, Elsey, and Berger.
+ Von Antropoff.
▲ Wiebe and Gaddy.
▼ Pray, Schweickert, and Minnich.
□ Winkler.
⊖ Eucken and Herzberg.

FIG. 2.

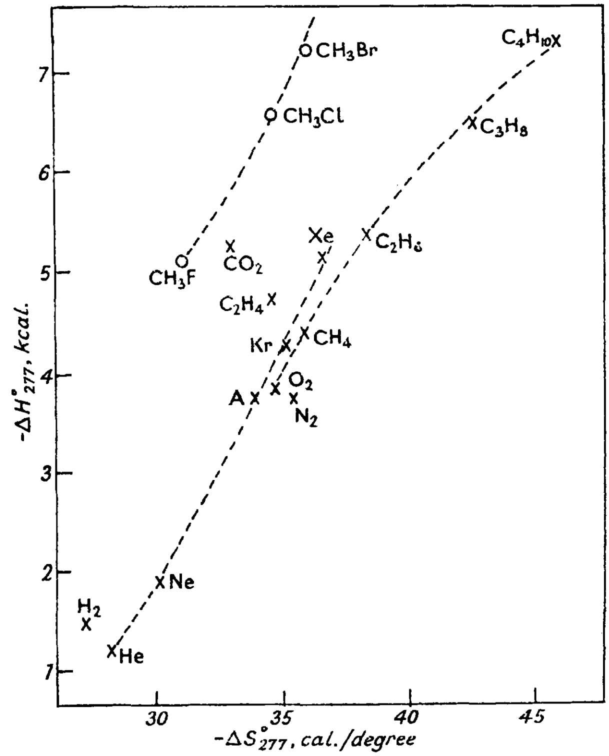

He
Ne
H₂
A
Kr
CH₄
Xe
C₂H₆
C₂H₄
O₂
N₂
CO₂
CH₃F
CH₃Cl
CH₃Br
CH₃I
C₃H₈
C₄H₁₀
CCl₄
277·0°K
317·5°K
-ΔH°₂₇₇, kcal.
Pg × 10²⁴
0
1
2
3
4
5
6
7
8
9
10
11
12

Chem. Soc., 1932, **54**, 4129), and von Antropoff are considerably higher. It is noteworthy also that values in the region of 0—2° by Lannung, Eucken, and Herzberg, and by Sisskind and Kasarnowsky (*Z. anorg. Chem.*, 1931, **200**, 282) are in excellent agreement with our equation.

Krypton and Xenon.—Our results are considerably lower than those of von Antropoff. Eucken and Herzberg, however, record a value for xenon at 20° which is within 1% of our figure.

It therefore appears that the work of Lannung on helium, neon, and argon is the most reliable general investigation in this series by the Ostwald technique, and the solubilities of these gases may be regarded as having been accurately established by two different techniques in the temperature range 10—45°. Little reliance can be placed on the data of von Antropoff which agree neither with those of Lannung nor of ourselves.

FIG. 3.



It is clearly of considerable importance to decide whether the partial molar heat capacity varies in this series by some 40—60 cal./deg. from helium to xenon as calculated by Eley (*Trans. Faraday Soc.*, 1944, **40**, 184) and by Glew and Moelwyn-Hughes (*Discuss. Faraday Soc.*, 1953, **15**, 150), or is approximately constant. It appears that these calculations were based on the experimental results of Estreicher, von Antropoff and Valentiner, and these have been shown to bear little resemblance to more modern values obtained by two different techniques. In the case of helium it can be shown that if the results in the range 10—30° are accepted, a value of $\bar{c}_p$ of 24 cal./deg. (Glew and Moelwyn-Hughes) would lead to discrepancies of the order of 3% at 50° and 8% at 70°. For xenon, $\bar{c}_p = 65$ cal./deg. being used, the corresponding discrepancies would be 7% and 16%. These would, of course, be in opposite directions, and it appears unlikely that some unsuspected source of error at higher temperatures would operate in this way. It seems to us that the variation between helium and xenon does not exceed 6 cal./deg. and is probably less. In the paraffin series there appears to be a real variation of some 20 cal./deg. from methane to *n*-butane.

Although comparisons of thermodynamic characteristics are often made at 25°, the theory put forward by Eley (*Trans. Faraday Soc.*, 1939, **35**, 1421; 1944, **40**, 184) on the mechanism of gas solubilities, suggests that it might be profitable to compare heats and entropies of solution at 4°, the temperature at which, according to Eley, there is little or no energy or entropy change in forming cavities in the solvent. We have therefore calculated values of ΔH°_{277} and ΔS°_{277} (mole-fraction, 1 atm. pressure) using the constants of Table 1, and the corresponding values for the paraffins and other gases (*J.*, 1952, 3814). While a slight extrapolation (not more than about 8°) is necessary, we may relate ΔH°_{277} with Eley's ΔE_A (energy of interaction between gas and water molecules), and ΔS°_{277} with Eley's ΔS_A of interaction, without assumptions about partial molar volumes and the exact mechanism of cavity formation. Fig. 2 shows that ΔH°_{277} is a smooth function of polarisability for all the non-polar gases and becomes almost linear with P_g above argon. A point for carbon tetrachloride (Gross and Saylor, *J. Amer. Chem. Soc.*, 1931, **53**, 1744) also lies on this line. The polar halides, CH_3X (Glew and Moelwyn-Hughes, *Discuss. Faraday Soc.*, 1953,

FIG. 4.

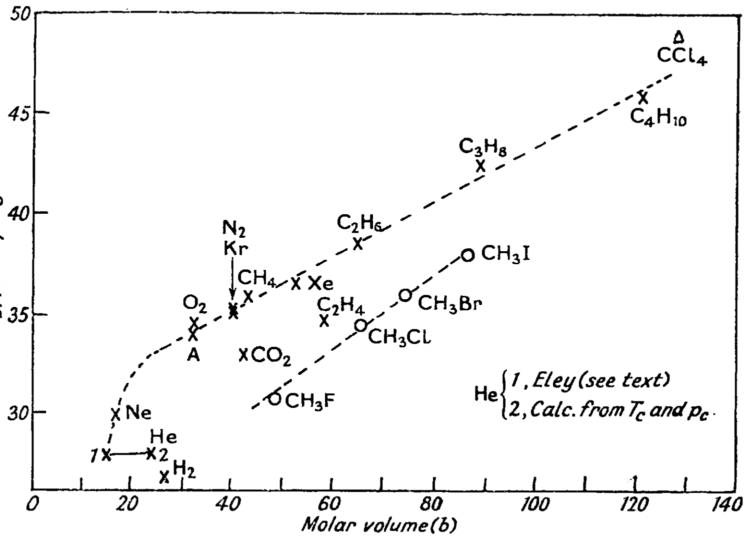
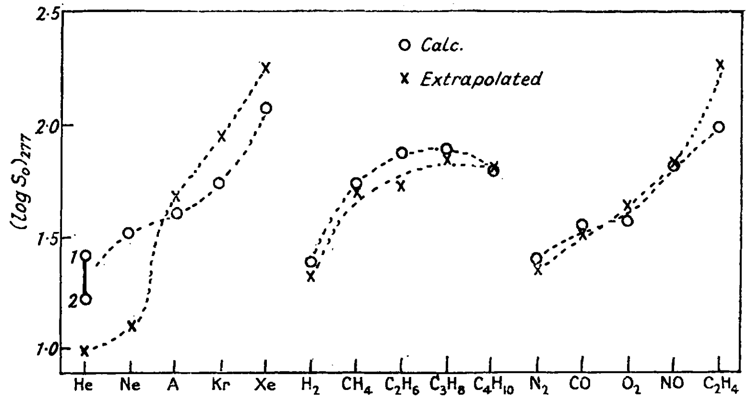


FIG. 5.



15, 150), and carbon dioxide have appreciably higher values of ΔH°_{277}. Eley (*ibid.*, p. 263) has obtained a similar relation by subtracting calculated values of the energy of cavity formation (ΔE_C) from observed values of ΔE°_{298}. Because of the different partial molar heat capacities of the inert gases and the paraffins, the smoothness of the relation shown in Fig. 2 is soon destroyed when the temperature is altered. At 317·5° K, for example ($1/T = 31{\cdot}5 \times 10^{-4}$), Fig. 2 shows that the two series of gases occupy quite distinct lines. It appears to be an interesting confirmation of Eley's views that the smoothest relation with polarisability is obtained for all the non-polar gases in the region of 277° K.

The parallelism between ΔH°_{277} and ΔS°_{277} suggested by the work of Barclay and Butler (*Trans. Faraday Soc.*, 1938, **34**, 1445) and Frank and Evans (*J. Chem. Phys.*, 1945, **13**, 478) is very approximate, and the two series of gases appear to lie on separate curves (Fig. 3). There appears, however, to be a relation between ΔS°_{277} and molecular volume. In the absence of partial molar volumes, we have used the van der Waals constant b as a measure of volume (Fig. 4) and obtain a linear relation from argon upwards.

The relations indicated in Figs. 2 and 4 are sufficiently accurate to reproduce at least qualitatively the essential differences in solubility between the various non-polar gases. Taking the linear portions of these graphs, we find that the solubility at 277° K should be represented by the approximate equation :

$$\log s_0 = 1{\cdot}845 + 0{\cdot}455p_g - 0{\cdot}0309b$$

and in Fig. 5 we have plotted calculated and extrapolated values of log s_0 against arbitrary scales for three groups of gases—the inert gases, the paraffins, and a group of gases of approximately the same molecular weight.

The tendency for solubility to rise with the mass of the molecule in the inert-gas series, while it remains nearly constant in the paraffin series at this temperature, is shown. In the group of miscellaneous gases the relatively low solubility of nitrogen and the high solubility of ethylene are reproduced in the calculated figures. It is somewhat surprising to find that, although the heat and entropy of solution of hydrogen would not be given even to a first approximation by the linear relations of Figs. 2 and 4, yet the calculated solubility is in reasonable agreement with that found. Ethylene behaves rather similarly.

The rather unusual properties of carbon tetrafluoride and similar gases would afford another test of the empirical relations given. Carbon tetrafluoride, for example, has a relatively low electron polarisability, probably about the same as that of methane, while its volume approximates to that of ethane. Using the corresponding heat and entropy of solution, we find that the predicted solubility is of the order of 10 c.c. per 1000 g. of water at 277° K. This will fall fairly rapidly because of the heat of solution of about 4 kcal. and at 25° C should be about 6 c.c. Preliminary experiments have shown that this gas is certainly less soluble than helium with a solubility at 25° C of about 4·5 c.c. The very low solubility at high temperature raises experimental problems which must be overcome before the complete thermodynamic behaviour can be reported, but it appears from the results already available that the solubility is slight less than the predicted value, probably owing to a heat of solution which is somewhat less than would be obtained from the polarisability. A similar treatment applied to sulphur hexafluoride suggests that this gas would have a solubility of the same order.

EXPERIMENTAL

The modified apparatus described by Morrison and Billett (*J.*, 1952, 3819) was used. The inert gases were obtained from the British Oxygen Co. Ltd. and were " spectroscopically pure " in the cases of helium, neon, and argon. The krypton was 99—100% pure, the residue being xenon, while the xenon contained about 1% of krypton. In the case of krypton, the impurity is more soluble and will gradually be removed from the system. For 0·5% of xenon impurity the discrepancy in solubility would not be detected and no correction is therefore applied. The impurity in the xenon may, however, lead to an appreciable error since the krypton will tend to accumulate in the gas. A correction of +0·002 in log s_0, corresponding to 1% of krypton, has been applied to the observed solubilities, and calculations based on the amount of water brought into contact with the gas suggest that the accumulation of krypton was not sufficient to justify further correction. Determinations with helium and with krypton were carried out with two separate samples of each gas (*a* and *b* in Table 2). Temperatures were not systematically raised or lowered for successive runs, but were "scattered" so that any impurity accumulating in the gases might be detected.

TABLE 2. *Solubilities of gases (in c.c. at N.T.P.) per* 1000 *g. of water at a gas pressure of* 1 *atm.* (s_0).

t°, C	s_0	t°, C	s_0	t°, C	s_0	t°, C	s_0	t°, C	s_0
Helium		*Neon*		*Argon*		*Krypton*		*Xenon* (corr. to 100% Xe)	
4·6	9·44 *b*	9·1	11·7	10·7	40·9	6·6	82·0 *a*	12·7	135·5
6·0	9·35 *b*	11·5	11·3	14·3	37·2	8·0	79·4 *b*	15·1	123·6
11·0	9·04 *b*	15·0	10·9	18·2	34·6	12·6	69·5 *a*	15·5	121·1
12·0	8·97 *a, b*	19·8	10·6	24·4	31·1	15·5	65·6 *a*	19·6	110·9
13·2	8·87 *a*	24·4	10·2	29·8	28·3	18·2	61·7 *b*	30·2	84·5
16·6	8·71 *a, b*	28·8	10·1	36·6	25·9	21·2	58·2 *a*	40·0	69·3
21·7	8·53 *a*	31·3	9·93	39·4	25·1	24·7	53·5 *a*	40·5	67·8
24·7	8·47 *a, b*	32·1	9·93	47·8	23·1	30·2	48·9 *a*	47·9	59·4
27·4	8·45 *a*	42·1	9·48	49·5	22·6	35·4	44·3 *a*	59·0	50·8
33·0	8·34 *a*	49·5	9·40	56·3	21·3	41·4	40·6 *a*	71·7	43·8
34·6	8·41 *b*	58·8	9·46	66·3	20·2	46·0	38·3 *b*		
40·4	8·41 *a*	61·0	9·44	71·3	19·4	51·9	35·9 *a*	*Carbon tetrafluoride*	
44·9	8·45 *b*	64·4	9·55	74·1	19·1	57·9	33·3 *a*	6·7	6·5
48·9	8·59 *a*	65·4	9·53			59·8	32·8 *a*	13·1	5·6
54·4	8·71 *b*	66·6	9·57			64·7	31·6 *a*	19·0	5·0
55·9	8·81 *a, b*	72·5	9·84			67·5	30·7 *b*	24·7	4·5
58·6	8·89 *b*	74·1	9·84			71·5	29·7 *a*	38·5	3·7
60·5	9·02 *a*					73·9	29·5 *a*		
67·4	9·23 *a*					74·9	29·3 *b*		
70·5	9·42 *b*								
71·4	9·42 *a*								
73·0	9·46 *b*								

The carbon tetrafluoride used was supplied by Imperial Chemical Industries Limited in the form of "Arcton O." Because of the extremely low solubility, some modification of the apparatus may be required, and the results given are provisional, with possible errors of ±2%.

DUNDEE TECHNICAL COLLEGE.

[*Received, April 2nd,* 1954.]