729. *The Salting-out of Non-electrolytes. Part I. The Effect of Ionic Size, Ionic Charge, and Temperature.*

By T. J. Morrison.

An empirical equation containing three constants is suggested to express the solubilities of gases at various temperatures. Lithium chloride, and probably also barium chloride, lanthanum chloride, and hydrochloric acid, cause a salting-out effect which is uniformly less than that expected when the ionic size is compared with that of sodium chloride. Potassium chloride behaves normally. Potassium iodide causes specific decreases in salting-out as compared with sodium chloride and this effect increases with increasing molecular size. The salting-out of gases generally diminishes with rise in temperature. The partial molar heat capacity of the gas is affected, the greatest diminution being for lithium chloride and the least for potassium iodide. It is therefore suggested that the effect of ions on the structure of the solvent plays an important part in the salting-out effect.

Nearly all recent work on salting-out has been carried out with weak or non-electrolytes of somewhat complex types. Data on simpler non-polar molecules are presented here in an attempt to extend the experimental work in this field. It is generally agreed that the effect varies in an approximately linear manner with concentration, and more attention has therefore been paid to variation in type of electrolyte and temperature.

(i) *Gas Solubilities.*—It has been found that the solubilities of the gases used can be expressed accurately by empirical equations of the type :

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

where s_0 is conveniently expressed as the absorption coefficient at 1 atm. per 1000 g. of water. Values of the constants are given in Table 1, and the validity of the equations is shown by plotting the deviations between experimental and calculated values of $\log_{10}s_0$ ($\Delta \log s_0$) in Fig. 1 and 2. Deviations between recorded values and those obtained by the present method are also shown. Results for oxygen and carbon dioxide are included for comparison with fairly modern determinations, although no salting-out experiments have yet been done on these gases. Deviations generally correspond to not more than $\pm 0{\cdot}5\%$ in solubility so far as the present method is concerned, but some of the older results are almost certainly in error, especially for ethane and nitrogen, where the discrepancy may reach 8% in s_0. Certain modifications (see following paper, p. 3819) in the experimental procedure previously described (*J.*, 1948, 2033) lead to results which are in some cases slightly higher than recorded values, but for oxygen and carbon dioxide the results are in excellent agreement with more recent measurements by different methods. The method appears to be more satisfactory than Ostwald's technique at higher temperatures.

Table 1.

Gas	*A*	*B*	*C*	*A/C*	*B/C*
H_2	36·250	1847	12·65	2·866	146·0
CH_4	77·067	4090	26·20	2·941	156·1
C_2H_6	87·699	4730	29·67	2·956	159·4
C_3H_8	99·629	5445	33·50	2·974	162·6
n-C_4H_{10}	109·258	5995	36·60	2·985	163·8
C_2H_4	69·697	3900	23·70	2·941	164·6
N_2	81·328	4160	27·70	2·936	150·2
O_2	69·053	3685	23·50	2·938	156·8
CO_2	51·375	3280	17·48	2·939	187·6

The theoretical significance of the large values of *C*, which is directly related to the partial molar heat capacity of the gas, has been indicated by Frank and Evans (*J. Chem. Phys.*, 1945, **13**, 478). There is an evident parallelism between the three constants, shown by the ratios given in Table 1, and although the values of *A* and *B* are determined to a large extent by the accuracy with which *C* can be estimated, the ratios *A/C* and *B/C* are little affected by moderate variations in C. The error in C may be about 1·5 units, corresponding to about ± 3 cals. in $\bar{c}_p$. The constancy of C within these limits for each gas suggests that the temperature dependence of $\bar{c}_p$ is small over the range used. It has been found that the type of equation given applies well to most of the data recorded for aqueous solubilities even over much greater temperature ranges, *e.g.*, to the results on the

FIG. 1.

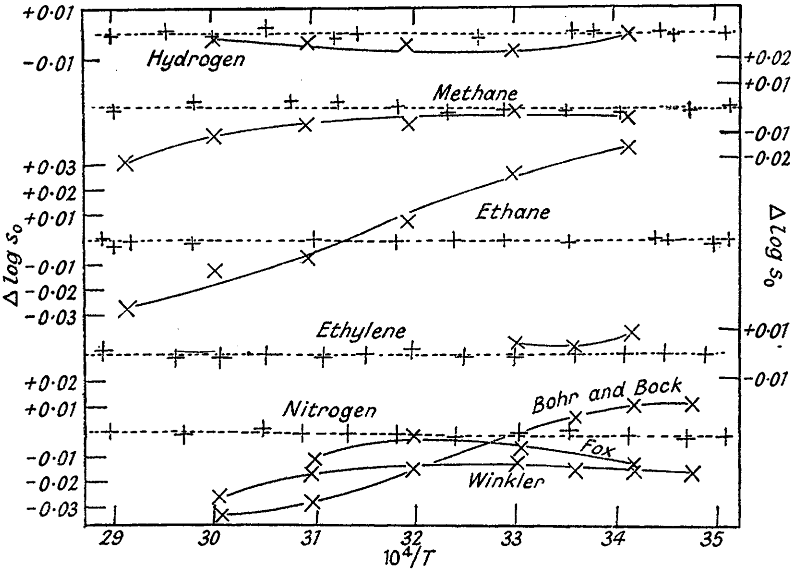
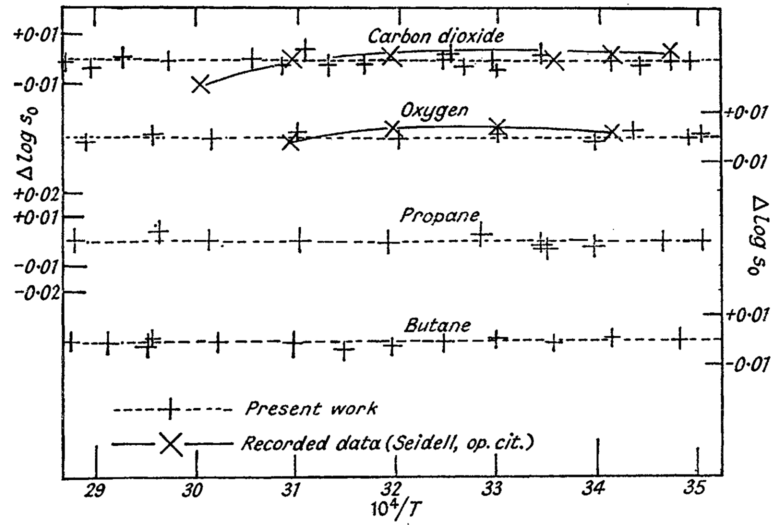


FIG. 2.



solubilities of hydrogen, helium, and nitrogen at high pressures (Seidell, "Solubilities of Inorganic and Organic Substances," van Nostrand, N.Y.)

(ii) *Salting-out.*—(a) *Ionic size and charge.* Since it does not appear to be practicable to calculate theoretical values of $k = (\log_{10} s_0/s)/c$, comparative methods are used. Values of k_X for a given salt are plotted against k_{NaCl} at temperatures corresponding to values of $1/T$ of (1) 0·0035, (2) 0·0033, (3) 0·0031, and (4) 0·0029. All measurements refer to 1000 g. of water. Theories of the salting-out effect generally agree that k should be proportional

FIG. 3.

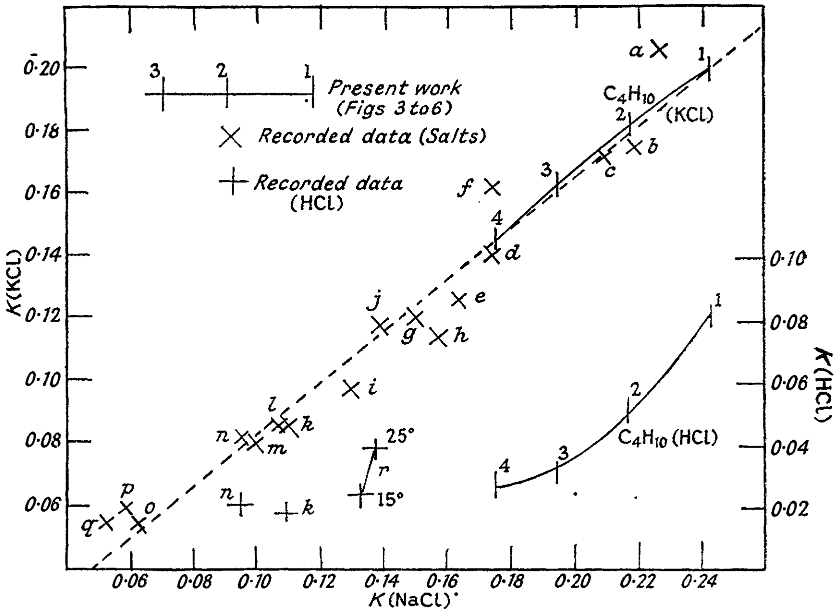
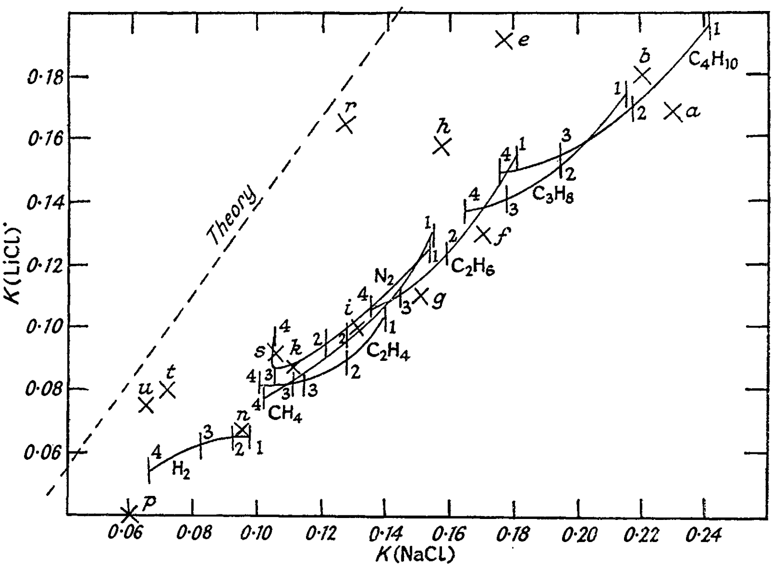


FIG. 4.



Recorded data. (Seidell, *op. cit.*)

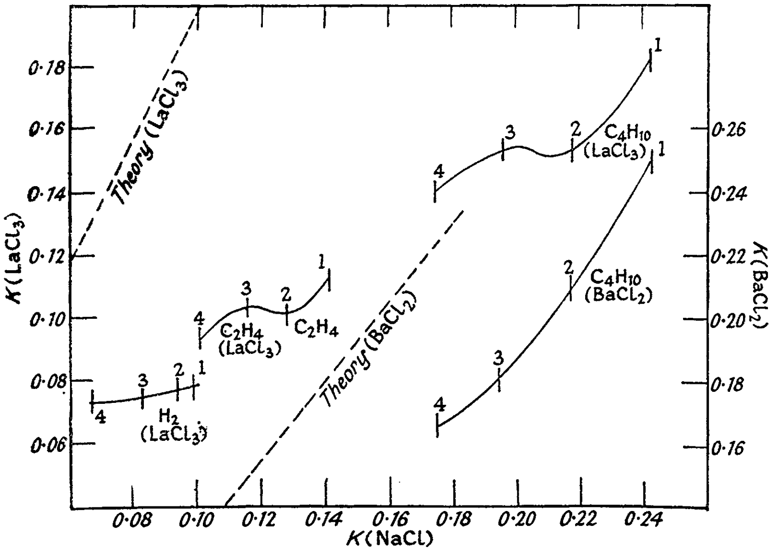
a, Ether.
b, Phenol.
c, Benzoic acid (85°).
d, ,, (60°).
e, ,, (25°).
f, Ethyl acetate.
g, Aniline (25°).
h, Quinol.
i, Phenylthiourea.
j, Diacetone alcohol.
k, N_2O.
l, Acetone.
m, C_2H_2.
n, H_2.
o, H_2S.
p, A.
q, He.
r, O_2.
s, CO_2.
t, Quinone.
u, Acetic acid.

to the quantity $\Sigma ce^2/a$, although the values to be taken for ionic radii may be in doubt. By using crystallographic values (Pauling) the following theoretical ratios of k_X/k_{NaCl} are found:

LiCl	KCl	KI	$\frac{1}{2}BaCl_2$	$\frac{1}{3}LaCl_3$
1·38	0·82	0·76	1·28	1·98

The effect of potassium chloride (Fig. 3), as judged from published data and the present results on *n*-butane, appears to be in accordance with theory, and work on this salt was not carried further. For lithium, lanthanum, and barium chlorides (Figs. 4 and 5) the slopes are less than expected by about 40%, 60%, and 25% respectively, and the reduction is a *general* one, at least for the first two salts. Previous results for lithium chloride in the cases of non-electrolytes lie approximately on the general line, although for weak electrolytes the ratio is usually nearer the expected value. No theoretical ratio has been calculated for hydrogen chloride, but the results (Fig. 3) show that the effect is probably a large general reduction in slope. An entirely different behaviour is found on comparing potassium iodide with sodium chloride (Fig. 6). The variations from the theoretical slope are *specific*. The salting out is slightly high for hydrogen and nitrogen in potassium iodide solutions, but with increasing size in the paraffin series the effect becomes much less than theoretical. Ethylene also showns an abnormally low value. Study of the literature suggests that such a specific effect occurs with other ions, *e.g.*, NO_3'.

FIG. 5.



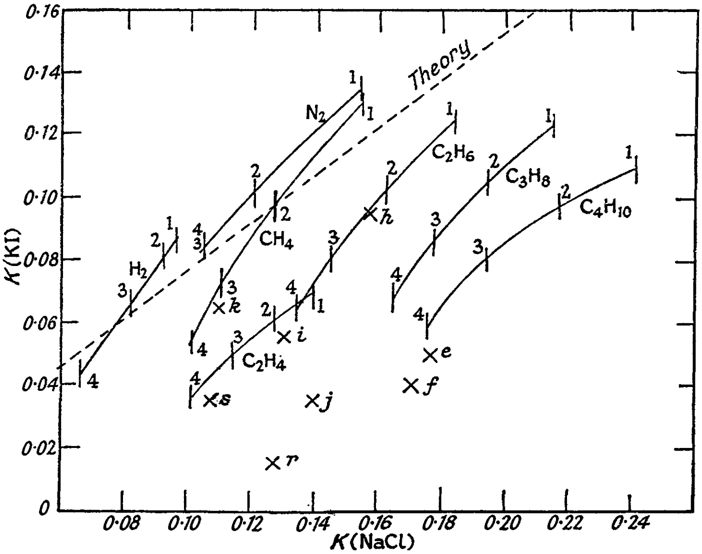
(b) *Temperature.* Figs. 3—6 show that the salting-out generally decreases with rise in temperature, though in some cases (N_2–LiCl) a minimum may be reached, and in others (H_2–$LaCl_3$) the effect is almost independent of temperature. In the case of lanthanum chloride with *n*-butane and ethylene an S-shaped curve is obtained on plotting k against $1/T$, but this may be due to hydrolysis of the lanthanum ion. In other cases plots of this type are not generally quite linear, showing that $\bar{c}_p$ for the gas may be affected, and making comparisons of heats and entropies of solution or even the values of k itself at fixed temperatures of doubtful value. Because of the difficulty of estimating the values of C in the empirical equations with sufficient accuracy, the values of the changes in $\bar{c}_p$ produced by salts presented in Table 2 can only be regarded as very approximate, but the general trend of the results is believed to be significant. The results for lanthanum chloride indicate that in the low-temperature region the changes in $\bar{c}_p$ are negative and

TABLE 2. $\Delta\bar{c}_p$ (*cals./deg./g.-mol.*).

	Gas						
Salt	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4	H_2
LiCl	−23	−15	−14	−12	−12	−8	+5
NaCl	−19	−10	− 7	− 4	− 4	0	+6
KI	−16	− 8	− 5	− 2	+ 6	+3	+8

probably greater than for lithium chloride. Barium chloride and hydrogen chloride appear to have effects of the same order as for lithium chloride, and potassium chloride has approximately the same effect as sodium chloride. The fact that lithium chloride decreases $\bar{c}_p$ to a greater extent than does sodium chloride, while potassium iodide has a more positive effect than sodium chloride is the main reason for the general curvature evident in Figs. 4 and 6 in the lines for individual gases. In Fig. 4 (LiCl–NaCl) the slope generally diminishes with rise in temperature, whereas in Fig. 6 (KI–NaCl) the slope increases. These slopes give, of course, the ratio of the change in heat of solution produced by salt X to that produced by sodium chloride.

FIG. 6.



For key see Fig. 4.

If the views of Frank and Evans (*loc. cit.*) on the origin of the large values of $\bar{c}_p$ for gases in water are correct, the considerable changes produced by salts, which may amount to 40% of the original value, suggest that modification of the solvent structure in the vicinity of the non-electrolyte molecules cannot be neglected in theories of salting-out, at least at the concentrations used. It is noteworthy that ions which, according to Frank and Evans, tend to bring about a "structure building" effect, *e.g.*, Li^+ and La^{3+}, reduce $\bar{c}_p$ to a considerably greater extent than "structure-breaking" ions, *e.g.*, I^-; in fact, it is only potassium iodide which is found to increase $\bar{c}_p$ above the value for water, apart from the case of hydrogen. At the same time any attempt to deal with the problem on the basis of a hypothetical temperature change will be unsuccessful, since $\bar{c}_p$ for the gases in water certainly does not vary with temperature to nearly the same extent as on addition of salts. The considerable difference between the behaviour of nitrogen and of hydrogen supports the suggestion of Frank and Evans, based on rather meagre data, that the nature of the "ice-bergs" responsible for the large thermal characteristics of gases in water, may vary for different gases.

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