

CCLII.—*The Equilibrium between Acetone and Salts.*

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IN the present communication are given solubilities of salts in absolute acetone, compositions of solid phases in equilibrium with the saturated solutions, transition temperatures, and dissociation pressures of acetonates. The methods employed are similar to those already described in connexion with alcoholic systems (J., 1926, 318, 321; 1928, 658; 1929, 1440).

## E X P E R I M E N T A L.

The purest procurable acetone was fractionally distilled through a 12-pear column, and the first runnings and the residue were rejected. The middle fraction (about 75% of the original sample) was allowed to stand, with occasional shaking, in contact with potassium permanganate for 24 hours, and was then fractionally redistilled. The distillate was purified through the sodium iodide compound as described by Shipsey and Werner (J., 1913, 103, 1255). The product was dehydrated by either calcium chloride or potassium carbonate, and distilled, the first and the last portions being rejected. The acetone thus purified, b. p.  $56.1^{\circ}/760$  mm.,  $d_4^{20}$  0.79081 (compare 0.79082, Price, J., 1919, 115, 1116), did not decolorise dilute permanganate solution even in 30 minutes, and was used in the present work.

The salts were purified first chemically and finally by recrystallisation from water. They were then thoroughly dried by heating in a vacuum (Turner and Bissett, P., 1913, **29**, 233). Their degrees of purity were:  $\text{CoCl}_2$ , 99.5%;  $\text{NiBr}_2$ , 99.7%;  $\text{CoBr}_2$ , 99.8%;  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{BaBr}_2$ ,  $\text{MgCl}_2$ ,  $\text{ZnBr}_2$ , each 99.9%;  $\text{CaBr}_2$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{NaI}$ ,  $\text{CaCl}_2$ ,  $\text{SrBr}_2$ , each 100.0%. Great care was exercised to exclude atmospheric moisture during the purification of the salts and of the acetone, and in the subsequent work.

The dissociation pressures were determined by the dynamical method, and the experimental arrangements were precisely similar to those adopted for the alcoholates (J., 1926, 321), except that a U-tube filled with silica gel was used as desaturator in place of that filled with phosphoric oxide and glass wool. The mass of the acetone removed by the current of air could be determined either by the loss in weight of the mixture of acetonates in the saturator or by the gain in weight of the silica gel in the desaturator. Experiments in which both loss and gain were measured demonstrated that, within the limits of experimental error, these were equal. Before use, the silica gel was activated by several hours' heating at  $150^\circ$  in a vacuum.

Whenever possible, the results obtained by the dynamical method were confirmed by the method of Bagster (J., 1917, **111**, 494).

*Results.*—In the following tables solubilities (all directly determined) are given as g. of salt per g. of acetone, and pressures in mm. of mercury.

*Solubilities in absolute acetone.*

Temp.	LiCl.	LiBr.*	CaI <sub>2</sub> .	Ca(NO <sub>3</sub> ) <sub>2</sub> .	NiBr <sub>2</sub> .	ZnBr <sub>2</sub> .
0°	0.0173	—	0.726	0.209	0.0166	—
10	0.0148	0.134	0.805	0.170	0.0116	—
20	0.0118	0.182	0.888	0.168	0.0081	3.64
30	0.0087	0.213	0.972	0.171	0.0055	3.63
40	0.0069	0.263	1.056	0.172	0.0036	3.80
50	0.0061	0.346	1.129	0.184	0.0027	3.81
60	—	0.397	1.196	—	—	—

  

Temp.	NaI.	CaCl <sub>2</sub> .	CaBr <sub>2</sub> .	SrBr <sub>2</sub> .	BaBr <sub>2</sub> .	CoCl <sub>2</sub> .	CoBr <sub>2</sub> .
0°	0.115	0.000062	0.0290	0.00869	0.000287	0.0447	0.541
10	0.182	0.000073	0.0282	0.00753	0.000275	0.0332	0.543
15	0.232	0.000086	—	—	—	—	—
20	0.299	0.000101	0.0274	0.00599	0.000262	0.0289	—
22.5	—	—	—	—	—	0.0340	—
25	0.401	0.000118	0.0272	—	0.000261	0.0371	0.650
27	—	—	—	0.00454	—	—	0.687
28.5	—	—	—	0.00429	—	—	—
30	0.389	0.000131	0.0272	—	0.000258	0.0451	0.696
35	0.367	0.000154	0.0279	0.00359	—	—	—
40	0.348	0.000173	0.0292	0.00323	0.000254	0.0601	0.924
45	0.329	0.000190	—	—	—	—	—
50	0.309	0.000213	—	0.00274	0.000246	0.0725	—
55	0.293	—	—	—	—	—	—

\* The solubilities at  $32^\circ$ ,  $35^\circ$ , and  $37^\circ$  were respectively 0.221, 0.224, and 0.237.

In the cases of lithium chloride, nickel bromide, and barium bromide the solid phases in equilibrium with the saturated solutions were the non-solvated salts throughout. The calcium salts and cobalt bromide were acetonated, the compositions of the solid phases being as follows :

Solid phase.	Salt in solid phase, %.	
	Found.	Calc.
$\text{CaI}_2, 3\text{C}_3\text{H}_6\text{O}$ .....	63.3	62.8
$\text{Ca}(\text{NO}_3)_2, \text{C}_3\text{H}_6\text{O}$ .....	73.2	73.9
$\text{CaBr}_2, 2\text{C}_3\text{H}_6\text{O}$ .....	63.3	63.3
$\text{CoBr}_2, \text{C}_3\text{H}_6\text{O}$ .....	79.0	79.0

*Calcium bromide diacetate* forms short transparent needles, *calcium nitrate monoacetate* long needle-shaped crystals, and *cobalt bromide monoacetate* large deep-blue crystals. Bagster (*loc. cit.*) has shown that calcium chloride in contact with its saturated solution is diacetate.

Transition points were observed with lithium bromide, zinc bromide, sodium iodide, strontium bromide, and cobalt chloride, and were confirmed in every case by the use of dilatometers. *Lithium bromide diacetate* at  $35.5^\circ$  is transformed into the non-solvated salt. The transition point of *zinc bromide hemiacetate* into zinc bromide lies at about  $31^\circ$ . At  $25.5^\circ$  sodium iodide triacetate is transformed into the non-acetonated salt. The transition temperature of *strontium bromide sesquiacetate* into the *monosolvated* form is  $32.5^\circ$ . Above  $19.5^\circ$  *cobalt chloride monoacetate* breaks down, yielding cobalt chloride. Results of analyses are as follows :

Solid phase.	Salt in solid phase, %.	
	Found.	Calc.
$\text{LiBr}, 2\text{C}_3\text{H}_6\text{O}$ .....	42.7	42.8
$\text{ZnBr}_2, \frac{1}{2}\text{C}_3\text{H}_6\text{O}$ .....	87.3	88.6
$\text{SrBr}_2, 1\frac{1}{2}\text{C}_3\text{H}_6\text{O}$ .....	73.8	74.0
$\text{SrBr}_2, \text{C}_3\text{H}_6\text{O}$ .....	79.9	81.0
$\text{CoCl}_2, \text{C}_3\text{H}_6\text{O}$ .....	69.1	69.1

Cobalt chloride monoacetate forms fine, pale-blue crystals.

In the present measurements the solutions and the solid acetates were freshly prepared from the pure components immediately before use. Considerable decomposition was apparent in saturated solutions of calcium iodide, of zinc bromide, and of calcium bromide kept in the dark for 3 months; on preservation in the dark for 6 months the solid acetates of zinc bromide, strontium bromide, calcium bromide, and calcium iodide had all become brown, and on addition of water yielded precipitates or turbid solutions.

The values of the solubilities of lithium chloride given above do not agree with those of Laszczynski (*Ber.*, 1894, **27**, 2287), *viz.*, 0.046 at  $0^\circ$  and 0.0214 at  $58^\circ$ . Moreover, we have failed to confirm

the existence of his monoacetate. The present solubility determinations for calcium nitrate do not accord with that of D'Ans and Siegler (*Z. physikal. Chem.*, 1913, **82**, 35), *viz.*, 1.41 at 25°. The solubilities of sodium iodide given agree well with those of Macey and Thomas (*J. Amer. Chem. Soc.*, 1926, **48**, 1547), and excellently with those of Wadsworth and Dawson (*J.*, 1926, 2784). The acetates of sodium iodide and of calcium chloride have already been described by Patten (*Chem. News*, 1909, **100**, 321) and by Bagster (*loc. cit.*) respectively. The present results accord fairly well with Naumann's value for cobalt chloride at 18°, *viz.*, 0.0275 g. per g. of acetone (*Ber.*, 1904, **37**, 4328), but not with those of Laszczynski (*loc. cit.*) and of Krug and McElroy (*J. Anal. Appl. Chem.*, 1892, **6**, 184).

Below are given the compositions of the solid phases, the successive stages of de-acetone on dissociation being indicated, and the dissociation pressures at various temperatures.

*Dissociation pressures of acetates.*

Acetates.	Pressures at given temperatures.					
	0°.	10°.	15°.	20°.	25°.	30°.
NaI, 3C <sub>3</sub> H <sub>6</sub> O : NaI .....	36.4	77.1	114.1	156.3	—	—
MgCl <sub>2</sub> , 3C <sub>3</sub> H <sub>6</sub> O : MgCl <sub>2</sub> .....	—	14.5	25.8	41.2	62.1	—
CoBr <sub>2</sub> , C <sub>3</sub> H <sub>6</sub> O : CoBr <sub>2</sub> .....	—	4.0	7.5	11.7	17.2	25.2
CoCl <sub>2</sub> , C <sub>3</sub> H <sub>6</sub> O : CoCl <sub>2</sub> .....	—	103.6	125.0	—	—	—
Ca(NO <sub>3</sub> ) <sub>2</sub> , C <sub>3</sub> H <sub>6</sub> O : Ca(NO <sub>3</sub> ) <sub>2</sub> ...	—	30.0	43.9	63.4	87.4	126.8
SrBr <sub>2</sub> , 1½C <sub>3</sub> H <sub>6</sub> O : SrBr <sub>2</sub> , C <sub>3</sub> H <sub>6</sub> O	—	113.7	137.6	154.6	—	—

The variations of the dissociation pressures of these acetates with temperature are such that over the above range the logarithm of the pressure is a rectilinear function of the reciprocal of the absolute temperature. This being the case, heats of dissociation per mol. of acetone,  $Q$ , can be calculated by means of the relation,  $I - \log_e p = Q/RT$ , wherein  $I$  is a constant for a given acetate. For instance, in the range of temperature between 0° and 20° the absorption of heat in the dissociation of sodium iodide triacetate to sodium iodide and acetone vapour amounts to 11,600 cal. per mol. of acetone liberated.

These data can also be used to calculate the affinities of salts for acetone. The loss of free energy per mol. of acetone on formation of an acetate from its components is given by  $RT \log_e P/p$ , wherein  $P$  is the saturated vapour pressure of liquid acetone, and  $p$  the dissociation pressure of the acetate at  $T^\circ$  absolute. For instance, the loss of free energy when 1 mol. of liquid acetone combines at 20° with ½ mol. of sodium iodide to form the triacetate is 102 cal., the saturated vapour pressure of acetone at 20° being 186.3 mm. (Price, *loc. cit.*).

The only previous investigation of the dissociation pressures of acetates is that of Bagster (*loc. cit.*), who worked with the mono- and di-acetates of calcium chloride.

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