

XC.—*Equilibrium between Alcohols and Salts.*
Part II.

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INVESTIGATION has been continued on the lines already described (J., 1926, 318, 321). The compositions of the solid phases have also been investigated by Bagster's method (J., 1917, **111**, 494).

The density, without correction of the weighings to vacuum, of the methyl alcohol used was d_4^{25} 0.78661, and that of the ethyl alcohol 0.78505. In the case of the higher aliphatic alcohols, the purest commercial product was first fractionally distilled and then further purified by the method employed by Orton and Jones (J., 1919, **115**, 1194) for *n*-butyl alcohol. The alcohol thus purified was dried, first by standing over anhydrous potassium carbonate, and then by refluxing over calcium turnings until further boiling effected no change in the density of a sample distilled off, whereupon the distillate was accepted for use. The boiling points at 760 mm. and densities (d_4^{25}) were: *n*-propyl alcohol, 97.3°, 0.79970; *n*-butyl alcohol, 117.7°, 0.80569; *n*-amyl alcohol, 137.2°, 0.80942; *iso*amyl alcohol, 130.8°, 0.80484. The benzyl alcohol, purified by fractional distillation under reduced pressure, had d_4^{25} 1.0402.

The salts were purified by the method previously described, with the exception of the magnesium chloride and nitrate, both of which were prepared in the form of their alcoholates by crystallisation from the filtered alcoholic extracts of the ignited salts, the whole preparation being conducted in a closed apparatus out of contact with the air. The degree of purity of the salts was: CoCl₂, HgBr₂, each 99.4%; CaI₂, 99.6%; CdBr₂, CdI₂, CuCl₂, NiBr₂, each 99.8%; LiCl, CaCl₂, CaBr₂, SrBr₂, BaBr₂, Ba(NO₃)₂, MgCl₂.6CH₃.OH, MgCl₂.6C₂H₅.OH, CdCl₂, CoBr₂, FeCl₃, each 99.9%; NaBr, NaI, KBr, Mg(NO₃)₂.6CH₃.OH, Mg(NO₃)₂.6C₂H₅.OH, Ca(NO₃)₂, HgCl₂, NiCl₂, AlCl₃, each 100.0%.

2) Determinations of solubility in methyl alcohol over ranges of temperature have been carried out by Menshutkin (*Z. anorg. Chem.*, 1907, **52**, 9) on calcium chloride, magnesium bromide, and magnesium iodide; by Étard (*Compt. rend.*, 1892, **114**, 112; *Ann. Chim. Phys.*, 1894, **2**, 555) on mercuric and cupric chlorides; by Lemoine (*Compt. rend.*, 1897, **125**, 604) on lithium chloride; and by Centnerszwer (*Z. physikal. Chem.*, 1910, **72**, 431) and Tyrer (*J.*, 1910, **97**, 621) on potassium iodide.

The solubilities of strontium bromide and of sodium iodide in ethyl alcohol have been determined, respectively, by Fonzes-Diacon (*J. Pharm. Chim.*, 1895, **1**, 59) and by King and Partington (*J.*, 1926, 20).

The higher alcoholates have been but little investigated. Étard (*loc. cit.*) measured the solubilities of mercuric and cupric chlorides in *n*-propyl, *isopropyl*, *isobutyl*, *amyl*, and *allyl* alcohols. Menshutkin (*loc. cit.*) prepared the hexa-alcoholates of magnesium bromide and iodide with *n*-propyl, *isobutyl*, and *isoamyl* alcohols, and he also investigated the solubility of the bromide in these alcohols. Loeb (*J. Amer. Chem. Soc.*, 1905, **27**, 1019) described a sodium iodide *n*-propyl alcoholate. Turner and Bissett (*J.*, 1913, **103**, 1904; 1914, **105**, 1783) prepared the tetra-alcoholates of the lithium halides with various higher alcohols, and made determinations of the solubilities of the alkali halides at 25°.

As regards solvent power for salts, methyl alcohol was placed intermediate between water and ethyl alcohol by Dumas and Péligot (*Ann. Chim. Phys.*, 1835, **58**, 18), whilst von Weimarn (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1126) placed the alcohols in the order: methyl, ethyl, propyl, butyl, and *amyl*. These rules, however, are liable to exceptions; *e.g.*, the greater solubility of calcium chloride and bromide in *n*-butyl alcohol than in *n*-propyl alcohol.

In the calculation of dissociation pressure in the gas-current method adopted in the present investigation, Dalton's law is assumed to hold for a mixture of air and alcohol vapour at pressures of alcohol which are below the saturation point. In order to see how far the alcohol vapour in the mixtures deviates from the ideal, we have compared the value of pv (p denoting the pressure of alcohol in mm. of mercury, and v its molecular volume in c.c.) given by the ideal-gas equation with that given by the van der Waals equation, which, despite molecular association on the part of the alcohol, gives the order of magnitude of the deviation. Thus, even in the experiment in which the deviation is greatest, for a pressure of methyl alcohol of 95.2 mm. at 60°, the value of pv given by the ideal-gas equation is 2.0773×10^7 , whilst that given

by $(p + 7.224 \times 10^9/v^2)(v - 66.91) = 62,364T$, the van der Waals equation for methyl alcohol, is 2.0747×10^7 , an agreement which justifies the application of Dalton's law. Further, it is assumed that the vapour which passes over in the current of air is the alcohol itself, and not one of its products of decomposition. This point was tested by condensing the alcohol carried away from an ethyl-alcoholate by the passage of dry air under the conditions of the experiments. The condensed alcohol was found to be free from ether and water, and to contain only a negligible trace of aldehyde. The influence of total pressure on the dissociation pressure in the present experiments can be safely ignored. In the following tables, each value of a dissociation pressure given is the mean of several determinations.

The maximum work, A , obtainable by the isothermal vaporisation of a liquid to give 1 g.-mol. of a vapour which conforms with the van der Waals equation, followed by the expansion of the vapour to the dissociation pressure in a univariant system with two solid phases and by the combination of the vapour with one of the solids in the system, is given by the equation

$$A = RT \log_e \frac{V - b}{v - b} + \frac{RTb(V - v)}{(V - b)(v - b)} - \frac{2a(V - v)}{vV} - Pv' - \frac{p(v_1 - v_2)}{n}.$$

Here v denotes the molecular volume of the vapour in equilibrium with the liquid, V that of the vapour in equilibrium with the two solid phases, a and b the constants in the van der Waals equation, P the saturated vapour pressure, p the dissociation pressure, n the number of g.-mols. of the vapour which combine with one formula-weight (in grams) of the solid to give the addition compound, and v' , v_1 , and v_2 the volumes occupied by the formula-weight (in grams) of the liquid, reacting solid, and solid addition compound, respectively. Thus, for the dissociation of magnesium nitrate hexa-methyl-alcoholate at 60° , the value of the pressure, 95.2 mm., on being substituted in the van der Waals equation gives $V = 217,927$ c.c., and the vapour pressure of methyl alcohol, 624.3 mm., gives 32,992 c.c., the value of n is 6, and the volumes of the condensed phases are $v' = 41$, $v_1 = 66$, and $v_2 = 274$; whence A is calculated by the above equation to be 3.8896×10^7 (mm. of mercury) \times (c.c.), or 1240.0 cal. If terms of low magnitude be ignored, the loss of free energy per g.-mol. of vapour on formation of the addition compound is given by $RT \log_e (P/p)$. In the case of the above example this expression has the value 1245.5 cal.

The variation of the dissociation pressure of an alcoholate with

temperature is, in general, such that over a moderate range the logarithm of the pressure is sensibly a rectilinear function of the reciprocal of the absolute temperature. Thus for magnesium nitrate hexa-methyl-alcoholate, the equation $\log_{10} p = 11.02341 - 3006.63/T$ gives at 30°, 40°, and 50° the pressures 12.7, 26.3, and 52.2 mm., respectively, whilst the direct determinations from the results of which the equation has been calculated give the respective values, 12.7, 26.3, and 52.3 mm. This form of variation is consequent on the fact that, when the heat of dissociation is great in comparison with the molecular heats of the substances involved, it is practically independent of temperature. If Q denote this heat per g.-mol. of alcohol vapour, and if it be assumed constant, integration of Clapeyron's equation gives the relation $\log_e p = I - Q/RT$, wherein I is the constant of integration. Thus for the given example, Q , which may be assumed to be the true heat of dissociation at the middle temperature, 40°, of the range, has the value 13,766 cal.

Between alcohols and salts there occur in many cases more profound reactions than solvation, ionisation, and alcoholysis. Such reactions are marked by their difficultly reversible character, and they often result in decomposition of both salt and alcohol. Thus, aluminium chloride when added to either methyl or ethyl alcohol gives an immediate violent evolution of hydrogen chloride. Ferric chloride does not react so vigorously, but its saturated solutions in both alcohols on standing at temperatures above 50° yield chloroform and deposit a red ferric precipitate, whilst they evolve hydrogen chloride on boiling. Below 50° the solubility of ferric chloride in these alcohols can be determined, although there is evidence of the slow formation of ethyl chloride in the ethyl-alcoholic solution. Even cupric chloride, when its saturated solution in ethyl alcohol is boiled, yields traces of chloroform.

EXPERIMENTAL.

Results.

In the following tables solubility is given as g. of salt per g. of alcohol, and pressure as mm. of mercury.

Solubility in methyl alcohol.

Temp.	LiCl.	NaBr.	KBr.	CuCl ₂ .	BaBr ₂ .	Ba(NO ₃) ₂ .	CaI ₂ .
0°	0.452	0.173	0.0182	0.565	0.444	0.00070	1.164
10	0.442	0.170	0.0193	0.574	0.431	0.00065	1.211
15	0.440	0.169	0.0200	—	0.425	—	1.237
20	0.438	0.168	0.0208	0.586	0.419	0.00057	1.261
30	0.438	0.165	0.0223	0.600	0.409	0.00052	1.312
40	0.441	0.161	0.0237	0.618	0.402	0.00048	1.368
50	0.444	0.158	0.0255	0.644	0.394	0.00042	1.422
60	0.446	0.153	0.0274	0.664	0.388	0.00040	1.488

Temp.	CaBr ₂ .	MgCl ₂ .	Mg(NO ₃) ₂ .	CdCl ₂ .	CdBr ₂ .	CdI ₂ .	NiBr ₂ .
0°	0.504	0.155	—	—	0.099	—	—
10	0.520	0.157	0.157	—	—	2.068	0.330
15	0.536	—	—	—	0.135	—	—
20	0.562	0.160	0.173	0.0215	0.162	2.067	0.351
25	—	—	—	—	0.184	—	—
30	0.629	0.167	0.209	0.0266	0.211	2.067	0.381
40	0.719	0.178	0.233	0.0344	0.245	2.060	0.433
50	0.832	0.190	0.269	0.0444	0.310	2.081	0.491
60	0.978	0.204	0.350	—	0.439	2.086	0.537
65	1.056	—	—	—	—	—	—
70	—	—	—	—	—	2.120	0.596
Temp.	NaI.	Ca(NO ₃) ₂ .	SrBr ₂ .	HgBr ₂ .	CoCl ₂ .	CoBr ₂ .	
10 ⁵	0.650	1.341	1.150	0.535	—	—	—
20	0.729	—	1.194	0.653	0.385	0.430	—
22	—	—	—	0.703	—	—	—
25	0.780	—	—	—	0.436	—	—
27	0.813	—	—	0.716	—	—	—
28	0.818	—	—	—	0.465	—	—
30	0.814	—	1.234	0.721	0.488	0.586	—
35	—	—	—	—	0.555	0.800	—
37	—	—	—	—	0.589	0.943	—
38	—	—	—	—	0.588	—	—
40	0.807	1.442	1.255	0.760	0.582	1.248	—
50	0.801	—	1.296	0.819	0.589	1.419	—
60	0.794	1.580	1.361	0.851	—	1.531	—
70	—	1.685	1.446	—	—	1.690	—
72	—	1.707	—	—	—	—	—
73	—	1.711	—	—	—	—	—
80	—	1.693	—	—	—	1.906	—

The solubility of ferric chloride in methyl alcohol is 1.31 at 0°, 1.43 at 15°, and 1.61 at 30°. These figures, however, should be accepted with reserve (see p. 661).

The following solubilities in methyl alcohol have been recorded: lithium chloride at 1°, 0.055; at 23°, 0.170 (Lemoine, *loc. cit.*); at 25°, 0.4236 (Turner and Bissett, *loc. cit.*): sodium bromide at 18.5°, 0.170 (Lobry de Bruyn, *Z. physikal. Chem.*, 1892, **10**, 782): potassium bromide at 25°, 0.0151 (Lobry de Bruyn), 0.0217 (Turner and Bissett): cadmium chloride at 25°, 0.0171 (Lobry de Bruyn): cadmium iodide at 20°, 2.20 (Timofejeff, *Compt. rend.*, 1891, **112**, 1224): sodium iodide at 22.5°, 0.777 (Lobry de Bruyn); at 25°, 0.913 (Herz and Kuhn, *Z. anorg. Chem.*, 1908, **60**, 154), 0.9035 (Turner and Bissett).

Dissociation pressures of methyl-alcoholates (A denotes CH₃·OH).

	10°.	15°.	20°.	25°.	30°.	40°.	50°.	60°.
CuCl ₂ , 2A	36.0	50.7	68.0	—	—	—	—	—
MgCl ₂ , 6A	34.4	48.6	—	—	—	—	—	—
Mg(NO ₃) ₂ , 6A	—	—	5.6	—	12.7	26.3	52.3	95.2
CdCl ₂ , 3A	—	—	93.5	—	—	—	—	—
CdBr ₂ , 3A	52.2	—	—	—	—	—	—	—
NiBr ₂ , 6A	8.5	—	17.4	—	34.8	68.9	—	—
NaI, 3A	18.8	27.5	38.7	—	—	—	—	—
Ca(NO ₃) ₂ , 2A	—	11.4	15.2	—	29.4	52.4	74.0†	—
SrBr ₂ , 1½A	12.8	18.3	24.7	—	43.9	—	—	—
HgCl ₂ , A	—	44.7	59.2	87.6	—	—	—	—
HgBr ₂ , A	52.0	—	—	—	—	—	—	—
CoCl ₂ , 3A	—	—	29.4	40.9	59.0	81.9*	—	—
CoBr ₂ , 6A	14.4	—	31.0	—	64.1	—	—	—

* At 35°. † At 45°.

In the following table and in the corresponding table relating to the ethyl alcoholates are given (1) the compositions of the solid phases, the successive stages of de-alcoholation being indicated, (2) the dissociation pressures at 20° measured by the static method of Bagster (*loc. cit.*), and (3) the transition points. The solid phase in equilibrium with the saturated solution at 20° is in each case marked with an asterisk. In the case of each salt the alcoholate given last in the column headed "Solid phase" is the lowest, and on dissociation yields the non-alcoholated salt, *e.g.*, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{CH}_3 \cdot \text{OH}$ on further withdrawal of alcohol yields $\text{Mg}(\text{NO}_3)_2$ directly. Results of analysis are given only where the alcoholates are described for the first time.

Methyl-alcoholates.

Solid phase.	Salt in solid phase, %.		Dissoc. press. in mm. at 20°.	Transition point.
	Found.	Calc.		
$\text{LiCl} \cdot 3\text{CH}_3 \cdot \text{OH}$	—	—	—	0·1°
* $\text{CuCl}_2 \cdot 2\text{CH}_3 \cdot \text{OH}$	65·0	67·7	—	—
* $\text{CaI}_2 \cdot 6\text{CH}_3 \cdot \text{OH}$	60·3	60·5	47	—
$\text{CaI}_2 \cdot 2\text{CH}_3 \cdot \text{OH}$	81·2	82·1	20	—
* $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{CH}_3 \cdot \text{OH}$	46·9	43·6	—	—
* $\text{CdCl}_2 \cdot 3\text{CH}_3 \cdot \text{OH}$	64·9	65·6	94	21·8
$\text{CdCl}_2 \cdot 2\text{CH}_3 \cdot \text{OH}$	74·3	74·1	29	—
$\text{CdCl}_2 \cdot 1\frac{1}{2}\text{CH}_3 \cdot \text{OH}$	79·4	79·2	19	—
* $\text{CdBr}_2 \cdot 3\text{CH}_3 \cdot \text{OH}$	74·5	74·0	94	29·0
$\text{CdBr}_2 \cdot 2\text{CH}_3 \cdot \text{OH}$	80·8	80·9	26	—
$\text{CdBr}_2 \cdot 1\frac{1}{2}\text{CH}_3 \cdot \text{OH}$...	84·5	85·0	15	—
* $\text{NiBr}_2 \cdot 6\text{CH}_3 \cdot \text{OH}$	53·0	53·2	17	48
* $\text{NaI} \cdot 3\text{CH}_3 \cdot \text{OH}$	60·3	60·9	—	27·4
* $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{CH}_3 \cdot \text{OH}$...	71·6	71·9	—	72·2
* $\text{SrBr}_2 \cdot 1\frac{1}{2}\text{CH}_3 \cdot \text{OH}$	84·1	83·7	25	45·7
$\text{SrBr}_2 \cdot \frac{1}{2}\text{CH}_3 \cdot \text{OH}$	94·2	93·9	11	—
* $\text{HgCl}_2 \cdot \text{CH}_3 \cdot \text{OH}$	89·7	89·5	55	—
* $\text{HgBr}_2 \cdot \text{CH}_3 \cdot \text{OH}$	93·4	91·8	74	22
* $\text{CoCl}_2 \cdot 3\text{CH}_3 \cdot \text{OH}$	57·3	57·5	30	37·1
$\text{CoCl}_2 \cdot 2\text{CH}_3 \cdot \text{OH}$	66·9	67·0	15	—
* $\text{CoBr}_2 \cdot 6\text{CH}_3 \cdot \text{OH}$	53·6	53·2	31	40
$\text{CoBr}_2 \cdot 3\text{CH}_3 \cdot \text{OH}$	69·5	69·5	17	—
$\text{CoBr}_2 \cdot 2\text{CH}_3 \cdot \text{OH}$	78·0	77·4	10	—

Throughout the investigated ranges of temperature, sodium bromide, potassium bromide, barium bromide, barium nitrate, and cadmium iodide exist in equilibrium with their respective saturated solutions as the non-alcoholated salts. So also does lithium chloride above 0·1°. In the case of magnesium chloride, the solid phase consists of $\text{MgCl}_2 \cdot 6\text{CH}_3 \cdot \text{OH}$, which dissociates directly into MgCl_2 . Calcium bromide in contact with the alcohol gives the tetra-alcoholate, the dissociation of which has already been investigated (J., 1926, 326). The tri-alcoholate of cobalt chloride is coloured amethyst, and the di-alcoholate a light purple-pink. The hexa-alcoholate of cobalt bromide forms reddish hexagonal columns, the tri-alcoholate is light blue, whilst the di-alcoholate is pale pink.

Solubility in ethyl alcohol.

Temp.	CuCl ₂ .	MgCl ₂ .	Mg(NO ₃) ₂ .	CdCl ₂ .	HgBr ₂ .	CoCl ₂ .
0°	0.423	0.0361	0.0147	—	0.273	0.450
10	0.460	0.0434	—	0.0130	0.282	0.486
20	0.500	0.0560	0.0307	0.0148	0.286	0.544
30	0.541	0.0740	0.0539	0.0166	0.316	0.626
40	0.583	0.1000	0.1086	0.0191	0.340	0.674
50	0.639	0.1280	0.1653	0.0228	0.362	0.651
60	0.708	0.1589	0.2423	0.0278	0.423	0.668
65	—	0.1720	—	0.0286	—	—
70	—	0.1863	0.3402	0.0253	0.463	0.729
80	—	—	0.3263	—	—	0.703

Temp.	Ca(NO ₃) ₂ .	SrBr ₂ .	CdBr ₂ .	CdI ₂ .	CoBr ₂ .
10°	0.462	0.636	0.269	—	0.706
20	0.514	0.639	0.300	1.105	0.771
30	0.562	0.649	0.335	1.081	0.849
40	0.629	0.735	0.378	1.038	0.959
45	—	—	0.393	—	—
50	0.735	0.752	0.381	1.027	1.050
60	0.821	0.755	0.303	1.033	1.208
70	0.901	0.757	0.223	1.034	1.271
80	0.918	0.778	—	1.037	1.294

In the case of ferric chloride and ethyl alcohol, a retroflex region is encountered, the solid phases consisting of FeCl₃·2C₂H₅·OH and FeCl₃. The congruent melting point of the di-alcoholate is 50°. The eutectic point for FeCl₃ and the di-alcoholate is 20.6°. The di-alcoholate crystallises in flat prisms. Details regarding this region are given in the following table.

Temp.	Solubility (g. FeCl ₃ per g. of C ₂ H ₅ ·OH) and solid phase.		
	FeCl ₃ .	FeCl ₃ ·2C ₂ H ₅ ·OH.	FeCl ₃ ·2C ₂ H ₅ ·OH.
0°	—	—	1.36
15	—	—	1.41
20.6	*1.99	*1.99	*1.44
30	2.03	*1.94	*1.49
40	2.07	*1.87	*1.55
50	—	*1.76	*1.76

* The values thus marked were obtained by thermal analysis, the remaining values being determined by direct analysis. These results are somewhat imprecise (see p. 661).

Previously recorded solubilities are: cobalt chloride at 13°, 0.56 (Bourion, *Compt. rend.*, 1902, **134**, 555, who describes the solid phase as 2CoCl₂·5C₂H₅·OH); cadmium chloride at 15.5°, 0.0152 (Lobry de Bruyn, *loc. cit.*); at 20°, 0.0391 (Jahn, *Ann. Physik*, 1891, **43**, 296); cadmium bromide at 20°, 0.349 (Jahn); cadmium iodide at 20°, 1.13 (Timofejeff, *loc. cit.*, who notes that no compound is formed); strontium bromide, about 0.645 and nearly constant between 0° and 40° (Fonzes-Diacon, *loc. cit.*, who gives the formula of the alcoholate as 2SrBr₂·5C₂H₅·OH).

Dissociation pressures of ethyl-alcoholates (A denotes $C_2H_5 \cdot OH$).

	10°.	20°.	25°.	30°.	35°.	40°.	50°
CuCl ₂ ,2A	19.6	31.3	—	43.3	—	62.0	—
MgCl ₂ ,6A	—	1.02	—	3.2	—	8.95	—
Mg(NO ₃) ₂ ,6A	2.4	6.2	9.7	14.5	22.5	32.3	—
CdCl ₂ ,1½A	20.5	29.6	—	40.5	—	54.0	—
CoCl ₂ ,3A	0.85	2.21	3.67	5.54	—	—	—
Ca(NO ₃) ₂ ,2A	—	13.8	—	27.8	—	55.3	—
SrBr ₂ ,½A	8.0	15.2	—	—	—	—	—
CdBr ₂ ,1½A	—	40.8	—	50.1	—	60.9	—
CoBr ₂ ,3A	1.51	4.16	—	10.5	—	25.6	50.6

Ethyl-alcoholates.

Solid phase.	Salt in solid phase, %.		Dissoc. press. in mm. at 20°.	Transition point.
	Found.	Calc.		
*CuCl ₂ ,2A	57.1	59.4	—	—
*Mg(NO ₃) ₂ ,6A	—	—	6	67.5°
*CdCl ₂ ,1½A	75.3	72.7	30	63.5
*CdBr ₂ ,1½A	79.7	79.8	41	47.2
*CoCl ₂ ,3A	48.4	48.5	2	38
CoCl ₂ ,2A	57.9	58.5	1	—
*CoBr ₂ ,3A	63.0	61.3	4	65
CoBr ₂ ,2A	70.7	70.4	2	—
*Ca(NO ₃) ₂ ,2A	—	—	14	65.5
*SrBr ₂ ,½A	92.3	91.5	14	40.5

Within the ranges of temperature investigated, neither cadmium iodide nor mercuric bromide is ethyl-alcoholated. In the case of magnesium chloride, the solid phase consists of the hexa-alcoholate, which on withdrawal of alcohol dissociates directly to MgCl₂. In the above table in the case of every salt the formula of the lowest alcoholate is given. The tri- and the di-ethyl-alcoholates of the chloride and bromide of cobalt are blue.

Solubility in higher alcohols.

Alcohol.	Cupric chloride.					
	10°.	20°.	30°.	40°.	50°.	60°.
<i>n</i> -Propyl ...	0.200	0.247	0.294	0.342	0.377	0.411
<i>iso</i> Amyl	0.107	0.121	0.142	0.166	0.210	0.252
Benzyl	0.0140	0.0165	0.0214	0.0302	0.0440	0.0612

Alcohol.	Calcium chloride.							
	0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.
<i>n</i> -Propyl ...	0.083	0.119	0.158	0.200	0.245	0.291	0.349	—
<i>n</i> -Butyl	0.162	0.214	0.257	0.291	0.316	0.335	0.348	—
* <i>n</i> -Amyl	—	0.070	0.115	0.170	0.226	0.285	0.344	0.413
<i>iso</i> Amyl	—	0.030	0.072	0.121	0.170	0.228	0.269	0.316
Benzyl	—	0.0210	0.0182	0.0164	0.0145	0.0134	0.0125	—

Alcohol.	Calcium bromide.							
	0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.
<i>n</i> -Propyl ...	0.066	0.130	0.225	0.350	0.492	0.634	0.768	—
<i>n</i> -Butyl	0.183	0.253	0.339	0.437	0.543	0.648	0.752	—
<i>n</i> -Amyl	—	0.174	0.253	0.340	0.430	0.515	0.623	0.745
<i>iso</i> Amyl	—	0.217	0.256	0.299	0.369	0.434	0.500	0.562
Benzyl	—	0.129	0.150	0.170	0.177	0.174	0.172	0.170

Higher alcoholates.

In contact with the alcohol, cupric chloride forms green, needle-shaped crystals of the di-alcoholate, except with *n*-propyl alcohol, with which it forms no alcoholate under the conditions of the present experiments, whilst calcium chloride and bromide form tri-alcoholates ($\text{CuCl}_2, 2\text{iso-C}_5\text{H}_{11}\cdot\text{OH}$: Found, CuCl_2 , 42.2; calc., 43.3%. $\text{CuCl}_2, 2\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH}$: Found, CuCl_2 , 39.6; calc., 38.4%. $\text{CaCl}_2, 3n\text{-C}_3\text{H}_7\cdot\text{OH}$: Found, CaCl_2 , 36.1; calc., 38.0%. $\text{CaCl}_2, 3n\text{-C}_4\text{H}_9\cdot\text{OH}$: Found, CaCl_2 , 31.7; calc., 33.3%. $\text{CaCl}_2, 3n\text{-C}_5\text{H}_{11}\cdot\text{OH}$: Found, CaCl_2 , 27.0; calc., 29.5%. $\text{CaCl}_2, 3\text{iso-C}_5\text{H}_{11}\cdot\text{OH}$: Found, CaCl_2 , 27.0; calc., 29.5%. $\text{CaCl}_2, 3\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH}$: Found, CaCl_2 , 24.9; calc., 25.5%. $\text{CaBr}_2, 3n\text{-C}_3\text{H}_7\cdot\text{OH}$: Found, CaBr_2 , 50.8; calc., 52.6%. $\text{CaBr}_2, 3n\text{-C}_4\text{H}_9\cdot\text{OH}$: Found, CaBr_2 , 45.1; calc., 47.4%. $\text{CaBr}_2, 3n\text{-C}_5\text{H}_{11}\cdot\text{OH}$: Found, CaBr_2 , 41.2; calc., 43.1%. $\text{CaBr}_2, 3\text{iso-C}_5\text{H}_{11}\cdot\text{OH}$: Found, CaBr_2 , 42.6; calc., 43.1%. $\text{CaBr}_2, 3\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH}$: Found, CaBr_2 , 37.9; calc., 38.2%). The dissociation pressures of these compounds (Part I, *loc. cit.*, p. 328) indicate that the alcoholates of calcium bromide are generally more stable than those of calcium chloride, but in contact with the saturated solution the benzyl-alcoholate of calcium bromide breaks down into its components at 32°.

We desire to record our indebtedness to the Chemical Society for a grant which partly defrayed the expenses incurred in this investigation.

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[Received, December 23rd, 1927.]