XLII.—*The Dissociation Pressures of Alcoholates. Part I.*

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No account of work on this subject has yet been published, and because of its importance in relation to the affinity of salts for the alcohols and to residual affinity in general, we have undertaken the present investigation.

The methods, which are applicable in the case of hydrates, may be divided into the following classes : (*a*) indirect, (*b*) tensimetric, and (*c*) dynamical, or gas current saturation. In the following, the applicability of each method is discussed.

Among indirect methods are those of Müller-Erzbach (*Ber.*, 1881, **14**, 1093; *Z. physikal. Chem.*, 1888, **2**, 113), Wilson (*J. Amer. Chem. Soc.*, 1921, **43**, 704), Lescœur (*Ann. Chim. Phys.*, 1889, **16**, 378; 1890, **19**, 533), Cumming (J., 1909, **95**, 1772), Linebarger (*Z. physikal. Chem.*, 1894, **13**, 500), Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, **33**, 1309), and Noyes and Westbrook (*ibid.*, 1921, **43**, 726). Müller-Erzbach employed two methods. In the first, he compared the rates of diffusion of aqueous vapour from water and from the hydrate. His second method was to find the dilution of aqueous sulphuric acid solution over which the hydrate neither gained nor lost weight, and, when this was the case, the dissociation pressure was equal to the known aqueous pressure of the acid solution at the temperature of the experiment. Wilson's method is identical in principle with the latter method of Müller-Erzbach. This method might be made applicable to alcoholates if, first, the aqueous sulphuric acid were replaced by an alcoholic solution of a difficultly volatile substance and, secondly, the alcoholic vapour pressures of solutions of various concentrations of this substance in alcohol had been previously determined at various temperatures. The time required for such an investigation might, however, be prohibitive. Both Lescoeur and Cumming determined the dew point of the vapour phase in equilibrium with the pair of hydrates. Their method is directly applicable to the alcoholates, but, where the dissociation pressure is low, suffers from the disadvantage that the steep gradient of temperature in the apparatus introduces a serious source of error. Linebarger found the aqueous vapour pressure of a pair of salt hydrates, at the boiling point of ether, by determining the boiling point of the moist ether in contact and equilibrium with them, and then referring to a table giving the boiling points of various aqueous ether mixtures and their partial aqueous vapour pressures at those temperatures. Foote and Scholes shook a mixture of two hydrates with alcohol, and, after the attainment of equilibrium, determined the water content of the alcoholic layer. The dissociation pressure of the hydrate at the temperature of the experiment is equal to the known partial pressure of a water–alcohol mixture of the same composition as this layer. Noyes and Westbrook have employed a method which in principle is identical with that of Foote and Scholes, the reference liquid used being *iso*amyl alcohol. In the latter three methods, the properties of the reference liquids are so strictly circumscribed that it would be difficult to find a suitable liquid for use in the investigation of the alcoholates. Thus the salt must be insoluble in the reference liquid, the reference liquid must not form stable solid solvates with the salts in the presence of the alcohols, its affinity for the alcohols must be negligible compared with that of the salts for alcohol, and it must be only partly miscible with alcohol.

In order to apply the tensimetric method of Frowein (*Z. physikal. Chem.*, 1887, **1**, 1, 362), a liquid in which the alcohols are insoluble has to be employed in the manometer, and mercury, which is the only practicable liquid, is so dense that accuracy cannot be conveniently attained by its use. Moreover Menzies (*J. Amer. Chem. Soc.*, 1920,

42, 1952) has found that it is extremely difficult to evacuate the tensimeter satisfactorily.

The dynamical method, which is originally due to Tammann (*Ann. Physik*, 1888, **33**, 329), has been elaborated and perfected for the hydrates by Partington (J., 1911, **99**, 466), Baxter and Lansing (*J. Amer. Chem. Soc.*, 1920, **42**, 419), Partington and Huntingford (J., 1923, **123**, 160), Schumb (*J. Amer. Chem. Soc.*, 1923, **45**, 342), and Baxter and Cooper (*ibid.*, 1924, **46**, 923). We have found that this method is eminently suited to the investigation of the dissociation pressures of the alcoholates.

Two objections have been urged against this method, namely, first, that equilibrium is approached only from the side of undersaturation of the air current, and, secondly, that attainment of equilibrium between vapour phase and crystals is so slow that the time allowed in the passage of the air over the solid is insufficient. The first objection is disposed of by the data in Table I, where some experiments are detailed in which the equilibrium was approached both from undersaturation and from supersaturation, with results which within experimental error are identical. The second objection can be met only by ensuring that the rate of passage of air employed in the experiments is sufficiently slow, and by demonstrating that the same value is obtained for the dissociation pressures when a considerably slower rate is employed. The necessary slowness of the current depends, among other things, on the nature of the solvent, the salt, the temperature, and the dimensions of the saturator used. In our experiments the passage of 100 c.c. per hour gave the same result as that obtained with 500 c.c. per hour, and these were the extreme rates used. Furthermore, the fact that in our experiments air which was initially supersaturated with alcohol vapour gave the same result as air which was initially dry proves that the air leaving the saturator was adequately saturated with alcohol vapour and that a true state of equilibrium was attained.

EXPERIMENTAL.

The method adopted in the present work consisted in drawing a measured volume of dry air, free from carbon dioxide, through an intimate mixture of the pair of alcoholates, and finding the weight of alcohol vapour taken up by the air, either by collecting the alcohol in weighed **U**-tubes containing phosphorus pentoxide, or by determining the loss of weight of the mixture. The air, which was drawn through the mixture of alcoholates by means of an aspirator, was purified by passage in succession through concentrated sulphuric acid, a large calcium chloride tower, a **U**-tube filled with broken sticks of potassium hydroxide, and finally a 210 cm. train of freshly prepared phosphorus pentoxide powder mixed with glass wool. The purified air passed into the saturator, which was similar in form to that used by Partington (J., 1911, **99**, 468, Fig. 1A), except that our **U**-tubes were sealed off instead of being closed with paraffined corks. The saturator was filled to the level of the side tube with a mixture of the pair of alcoholates under investigation. The diameter of the column of mixture was 2 cm. and its mean length 42 cm. The saturator was immersed in a thermostat with only the side tubes emergent. A differential mercury manometer attached to the exit side tube served to give the difference in pressure between the external atmosphere and the mixture of air and alcohol vapour as it left the saturator, and consequently the sum of the partial pressures of the alcohol and air could be found. The saturated air afterwards passed into a **U**-tube filled with phosphorus pentoxide mixed with glass wool, whereby it was deprived of its alcohol. All connexions in this part of the apparatus were made with tightly fitting rubber tubing, inside which the ends of the glass tubes were brought into contact with each other. The air next passed into a **U**-tube filled with calcium chloride, which served as a trap to prevent back-diffusion of moisture from the aspirator in which the air was finally collected. At the beginning of the experiment the aspirator was filled to the top with water, which had been allowed to come to room temperature before the air current was started. The air inlet tube reached practically to the bottom of the water in the aspirator, and the air acquired the temperature of the aspirator during its passage downwards through the inlet tube and upwards through the water to the top of the aspirator, where it collected. The volume of air passed over the alcoholates was found by weighing the water expelled from the aspirator. The temperature of the room was maintained constant. An open-limb differential mercury manometer served to give the difference in pressure between the air collected inside the aspirator and the external atmosphere.

Care was taken that the dry air always entered the saturator at the same end in order that the air leaving the saturator should always come into contact with a mixture of both solid phases. Similar care was taken with the phosphorus pentoxide tube in order to retain all traces of alcohol. Atmospheric moisture was rigorously excluded in the preparation of the alcoholates, and in their transfer to the saturator, which had been previously thoroughly dried by a current of hot air.

The alcoholic dissociation pressure, p, of the pair of alcoholates under investigation at the temperature of the thermostat is given in mm. of mercury by the equation $p/p' = v/(V + v)$, where v and V are the respective volumes of alcohol vapour and dry air in the mixture leaving the saturator at the temperature of the experiment and under the pressure p', which is the sum of the partial pressures of the alcohol vapour and air as they leave the saturator, expressed in mm. of mercury. Since we are dealing with a ratio of volumes, the ratio of the pressures is unaltered if we substitute the values of the volumes at *N.T.P.*, which can be determined as follows :

$$v = \frac{22410m}{M}; \quad V = \frac{273{\cdot}1(P-f)W}{(273{\cdot}1+t)760d},$$

wherein m is the mass of alcohol in grams lost from the saturator and M is the molecular weight of the alcohol, P is the final pressure of the air inside the aspirator, f is the aqueous vapour pressure at the temperature, $t°$, of the aspirator, both pressures being expressed in mm. of mercury, W is the mass in grams in a vacuum of the water expelled from the latter, and d its density.

Thus $$p = \frac{22410 \times 760(273{\cdot}1+t)p'md}{273{\cdot}1 \times WM(P-f) + 22410 \times 760(273{\cdot}1+t)md}.$$

P is determined by taking the barometer reading at the end of the experiment and subtracting therefrom the reading of the aspirator manometer.

The sum of the partial pressures, p', is equal to the average barometric pressure during the run minus the average value of the readings of the mercury manometer attached to the exit tube of the saturator.

The mass, m, of the alcohol lost by the saturator was found either by the increase in weight of the phosphorus pentoxide tube or by the decrease in weight of the saturator, or by both means. In these weighings suitable counterpoises were employed. Both methods agreed, as is shown in the tables.

In a typical experiment the results obtained were as follows : $CaBr_2,3n\text{-}C_3H_7{\cdot}OH - CaBr_2$ at 60°. P 766·7; p' 764·7; t 17·7°; f 15·0; d 0·99868; W 4281; M 60·06; m by loss in weight of saturator 0·2200; m by gain in weight of phosphorus pentoxide tube 0·2193; giving p by loss in weight of saturator 15·447, and by gain in weight of phosphorus pentoxide tube 15·398, in both cases in mm. of mercury.

The losses in weight of the saturators recorded in the present experiments were between 0·0148 and 0·6271 g., whilst the volumes of air employed fell between 356·4 and 14155 c.c.

In order to eliminate initial disturbances due to liquid alcohol adhering to the crystalline alcoholates each new charge in the saturator was aged by drawing through it a small volume of dry air before the readings were begun.

The present method is applicable only where the dissociation pressure is lower than the vapour pressure of the pure alcohol at room temperature, since, if the former is greater than the latter, condensation will occur in the side tubes which emerge from the thermostat.

Results.

In Table I, $p_s^{t°}$ denotes the values of p at $t°$ determined from supersaturation, and $p_u^{t°}$ those determined from undersaturation, by the gain in weight of the P_2O_5 tube, and $p_l^{t°}$ and $p_g^{t°}$ denote the values of p determined from the loss in weight of the saturator and the gain in weight of the P_2O_5 tube, respectively.

TABLE I.

$CaBr_2,4CH_3\cdot OH$–$CaBr_2,3CH_3\cdot OH$.

$p_s^{20°}$ 19·99, 19·57, 19·78, 19·82, 19·88.
$p_u^{20°}$ 19·90, 19·90, 19·98, 19·94, 19·92.

$p_s^{30°}$ 40·70, 40·46, 40·58, 40·54, 40·60.
$p_u^{30°}$ 40·42, 40·28, 40·30, 40·28, 40·30.

$CaCl_2,4CH_3\cdot OH$–$CaCl_2,3CH_3\cdot OH$.

$p_l^{15°}$ 49·90, 49·70, 49·40, 49·60, 50·10, 49·84; mean 49·76.
$p_g^{15°}$ 48·90, 48·99, 48·92, 49·20, 49·09, 48·84; mean 48·84.

$p_l^{20°}$ 70·08, 70·14, 70·06, 70·15, 69·89, 70·00; mean 70·05.
$p_g^{20°}$ 69·80, 69·72, 69·69, 69·73, 69·73, 69·53; mean 69·70.

$p_l^{30°}$ 99·7, 100·5, 99·6, 99·2, 99·5, 99·8; mean 99·7.
$p_g^{30°}$ 98·8, 99·1, 98·6, 98·9, 99·0, 98·9; mean 98·9.

$CaBr_2,4CH_3\cdot OH$–$CaBr_2,3CH_3\cdot OH$.

$p_l^{15°}$ 13·55, 13·54, 13·62, 13·58, 13·72; mean 13·60.
$p_g^{15°}$ 13·52, 13·58, 13·59, 13·52, 13·60; mean 13·56.

$p_l^{20°}$ 19·91, 19·92, 19·96, 20·00, 19·93, 20·06; mean 19·96.
$p_g^{20°}$ 19·90, 19·90, 19·98, 19·94, 19·92, 20·02; mean 19·94.

$p_l^{30°}$ 40·45, 40·47, 40·30, 40·43, 40·28, 40·41, 40·36; mean 40·45.
$p_g^{30°}$ 40·42, 40·28, 40·30, 40·28, 40·30, 40·34; mean 40·32.

$p_l^{40°}$ 75·77, 75·80, 74·95, 75·87, 75·85, 75·54, 75·90; mean 75·67.
$p_g^{40°}$ 75·85, 75·50, 75·19, 75·58, 75·01, 75·49, 74·98; mean 75·37.

$CaCl_2,3C_2H_5\cdot OH$–$CaCl_2$.

$p_l^{30°}$ 7·81, 7·53, 8·00, 7·57, 7·72, 7·78; mean 7·74.
$p_l^{40°}$ 17·57, 17·67, 17·57, 17·83, 18·12, 18·28, 17·67, 17·79; mean 17·81.
$p_l^{50°}$ 48·56, 48·89, 48·58, 48·55, 49·40, 49·66, 49·20, 49·01; mean 48·98.

$CaBr_2,3C_2H_5\cdot OH$–$CaBr_2,C_2H_5\cdot OH$.

$p_l^{20°}$ 3·89, 3·70, 3·74, 3·92, 3·72, 3·83, 3·73, 3·77; mean 3·79.
$p_l^{30°}$ 9·45, 8·82, 9·06, 9·31, 9·49, 9·40, 9·25, 9·29; mean 9·32.
$p_l^{40°}$ 20·68, 20·18, 20·71, 20·76, 20·40, 20·76, 20·25, 20·95; mean 20·59.
$p_l^{50°}$ 41·48, 41·31, 41·65, 40·20, 41·81, 42·10, 42·00, 41·90; mean 41·55.
$p_l^{60°}$ 73·83, 72·88, 74·50, 73·04, 72·70, 73·40, 72·56, 73·02; mean 73·24.

TABLE I (*continued*).

$CaCl_2,3n\text{-}C_3H_7\cdot OH\text{-}CaCl_2$.

$p_l^{30^\circ}$ 6·41, 6·50, 6·40, 6·44, 6·43, 6·46, 6·45, 6·42, 6·42, 6·45; mean 6·43.

$p_g^{30^\circ}$ 6·40, 6·47, 6·40, 6·39, 6·38, 6·39, 6·42, 6·38, 6·40, 6·40; mean 6·40.

$p_l^{40^\circ}$ 16·45, 16·32, 16·16, 16·38, 16·38, 16·28, 16·40, 16·37, 16·38, 16·43; mean 16·36.

$p_g^{40^\circ}$ 16·27, 16·18, 16·14, 16·26, 16·31, 16·23, 16·32, 16·28, 16·20, 16·31; mean 16·25.

$p_l^{50^\circ}$ 34·10, 34·12, 34·43, 34·30, 34·23, 34·11, 34·24, 34·14, 34·10, 34·37; mean 34·21.

$p_g^{50^\circ}$ 34·02, 33·90, 34·34, 34·10, 34·01, 34·00, 34·08, 34·03, 34·03, 34·22; mean 34·17.

$CaBr_2,3n\text{-}C_3H_7\cdot OH\text{-}CaBr_2$.

$p_l^{30^\circ}$ 1·70, 1·72, 1·73, 1·67, 1·71, 1·78, 1·70, 1·72, 1·72; mean 1·72.

$p_g^{30^\circ}$ 1·70, 1·70, 1·67, 1·67, 1·67, 1·73, 1·69, 1·68, 1·71; mean 1·69.

$p_l^{40^\circ}$ 3·73, 3·72, 3·77, 3·77, 3·76, 3·73, 3·76, 3·73, 3·72, 3·74; mean 3·74.

$p_g^{40^\circ}$ 3·69, 3·66, 3·70, 3·67, 3·71, 3·66, 3·70, 3·66, 3·71, 3·68; mean 3·68.

$p_l^{50^\circ}$ 7·61, 7·67, 7·65, 7·64, 7·66, 7·66, 7·69, 7·68, 7·67, 7·64; mean 7·66.

$p_g^{50^\circ}$ 7·47, 7·55, 7·53, 7·55, 7·59, 7·57, 7·62, 7·58, 7·59, 7·55; mean 7·57.

$p_l^{60^\circ}$ 15·59, 15·44, 15·63, 15·68, 15·54, 15·45, 15·63, 15·56, 15·50, 15·53; mean 15·56.

$p_g^{60^\circ}$ 15·43, 15·18, 15·44, 15·50, 15·50, 15·40, 15·48, 15·42, 15·43, 15·48; mean 15·43.

$CaCl_2,3n\text{-}C_4H_9\cdot OH\text{-}CaCl_2$.

$p_l^{30^\circ}$ 1·44, 1·42, 1·48, 1·49, 1·48, 1·46, 1·49, 1·47, 1·47, 1·47; mean 1·47.

$p_g^{30^\circ}$ 1·44, 1·43, 1·47, 1·44, 1·43, 1·44, 1·47, 1·43, 1·43, 1·44; mean 1·44.

$p_l^{40^\circ}$ 3·96, 3·64, 3·72, 3·66, 3·68, 3·70, 3·72, 3·75, 3·70, 3·70; mean 3·72.

$p_g^{40^\circ}$ 3·94, 3·61, 3·68, 3·63, 3·64, 3·68, 3·69, 3·71, 3·70, 3·64; mean 3·69.

$p_l^{50^\circ}$ 9·22, 9·18, 9·11, 9·10, 9·20, 9·16, 9·23, 9·15, 9·21, 9·21; mean 9·18.

$p_g^{50^\circ}$ 9·08, 9·09, 9·10, 9·06, 9·13, 9·08, 9·21, 9·03, 9·08, 9·18; mean 9·09.

$p_l^{60^\circ}$ 13·43, 13·52, 13·82, 13·50, 13·48, 13·55, 13·50, 13·49, 13·56, 13·42; mean 13·53.

$p_g^{60^\circ}$ 13·26, 13·32, 13·61, 13·41, 13·39, 13·52, 13·31, 13·27, 13·40, 13·33; mean 13·38.

$CaBr_2,3n\text{-}C_4H_9\cdot OH\text{-}CaBr_2$.

$p_l^{30^\circ}$ 1·56, 1·54, 1·59, 1·53, 1·59, 1·54, 1·60, 1·54, 1·56, 1·53; mean 1·56.

$p_g^{30^\circ}$ 1·55, 1·52, 1·58, 1·53, 1·55, 1·53, 1·57, 1·54, 1·53, 1·52; mean 1·53.

$p_l^{40^\circ}$ 2·84, 2·80, 2·81, 2·78, 2·85, 2·80, 2·81, 2·85, 2·83, 2·82; mean 2·82.

$p_g^{40^\circ}$ 2·81, 2·81, 2·79, 2·77, 2·84, 2·79, 2·81, 2·84, 2·82, 2·80; mean 2·81.

$p_l^{50^\circ}$ 5·08, 5·04, 5·07, 5·09, 5·05, 5·00, 5·08, 5·08, 4·99, 5·10; mean 5·06.

$p_g^{50^\circ}$ 5·06, 5·01, 5·06, 5·08, 5·03, 5·00, 5·04, 5·04, 4·98, 5·05; mean 5·04.

$p_l^{60^\circ}$ 9·38, 9·58, 9·36, 9·42, 9·48, 9·54, 9·57, 9·41, 9·45, 9·40; mean 9·46.

$p_g^{60^\circ}$ 9·38, 9·48, 9·34, 9·36, 9·43, 9·49, 9·55, 9·41, 9·40, 9·35; mean 9·42.

Table II summarises the preceding results and gives the dissociation pressures in mm. of mercury at the various temperatures.

TABLE II.

Temp.	$CaCl_2$ 4—3 $CH_3\cdot OH$.	$CaBr_2$ 4—3 $CH_3\cdot OH$.	$CaCl_2$ 3—0 $C_2H_5\cdot OH$.	$CaBr_2$ 3—1 $C_2H_5\cdot OH$.	$CaCl_2$ 3—0 $n\text{-}C_3H_7\cdot OH$.	$CaBr_2$ 3—0 $n\text{-}C_3H_7\cdot OH$.	$CaCl_2$ 3—0 $n\text{-}C_4H_9\cdot OH$.	$CaBr_2$ 3—0 $n\text{-}C_4H_9\cdot OH$.
15°	49·30	13·58	—	—	—	—	—	—
20	69·88	19·95	—	3·79	—	—	—	—
30	99·3	40·39	7·74	9·32	6·42	1·71	1·45	1·55
40	—	75·52	17·81	20·59	16·31	3·71	3·70	2·82
50	—	—	48·98	41·55	34·19	7·62	9·14	5·05
60	—	—	—	73·24	—	15·50	13·45	9·44

Determinations of the dissociation pressures of other alcoholates are now in progress, and it is hoped to make the results obtained and the comparison of the affinities of the alcohols for salts the subjects of a further communication.

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