Adsorption of Solvent Vapour by the Solute Crystal.

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(Received April 13th, 1937.)

Lumping of Powder of the Soluble Substance. Lumping of the powder of cane sugar or common salt in the wet air is usually attributed to deliquescence, but this explanation is not necessarily correct. When the dry powder of pure substances (the humidity of the vapour from the saturated aqueous solution being h_s) containing no deliquescent impurities is exposed to the air of the humidity h, lumping is observed even when h is less than h_s in a few minutes and sometimes even in under one minute, if h is larger than about two-third of h_s in the cases of fairly soluble salts.

Table.

Powder (magnitude)	h_s %	h %	of air bubbled through H_2SO_4 or the saturated solution of	Lumping of powder
NaCl	76.0 (25°)	0 (25°)	conc. H_2SO_4	not observed (−)
(0.1−0.3 mm.)		36.9 ,,	50 % ,,	− ?
		46.2 ,,	45 % ,,	+
KBr	84 (20°)	55.5 (20°)	$Ca(NO_3)_2 \cdot 4H_2O$	a little
(0.1−0.3 mm.)		63.4 ,,	NH_4NO_3	+
		77.9 ,,	NaCl	strongly +
		79.4 ,,	NH_4Cl	strongly +
		81.0 ,,	$(NH_4)_2SO_4$	strongly +
Tartaric acid	86 (26.18°)	0 (25°)	conc. H_2SO_4	−
(0.1−1 mm.)		62.1 ,,	NH_4NO_3	?
		76.0 ,,	NaCl	+
		79.5 ,,	NH_4Cl	strongly +
Cane sugar	81.2−79.5(2) (25°)	76.0 ,,	NaCl	+
(0.2−0.8 mm.)				

As the lump maintains its form on quiet heating, this phenomenon is not due to the cohesion of condensed water. The regional formation of

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(1) NaCl was heated for several hours at 400°.

(2) This value is between that of ammonium sulphate and ammonium chloride and determined by observing deliquescence putting in one vessel.

the saturated solution and recrystallization of particles through this liquid layer is probable, as h_s is depressed due to the incomplete surface structure of the powder, but this not considered the most important cause, for lumping is also observed when h is less than h_s in the case of the following samples of which surface structure is fairly normal:

(1) powder of sodium chloride is put in the saturated solution for hours, filtered, washed with alcohol, and dried without touching each other. After putting in the air of $h = 60\%$ for several hours water adsorbed is driven away by heating quietly.

(2) powder of sodium chloride or potassium bromide, which had undergone the repeated adsorption and desorption of water vapour and is supposed to have lost the abnormally active part at the crystal surface by recrystallization if the liquid layer is formed.

(3) powder of these salts heated for hours at 200–400° where the motion of ions is violent enough to rearrange the irregular surface.(3)

Adsorption of the Solvent Vapour on the Solute Crystal. After repeated adsorption and desorption of water vapour, powder of potassium bromide (0.1–0.3 mm., 47.7816 g.) is put in an evacuated small desiccator with the saturated solution of a salt of which h_s is known and weighed after two hours (20.8°).

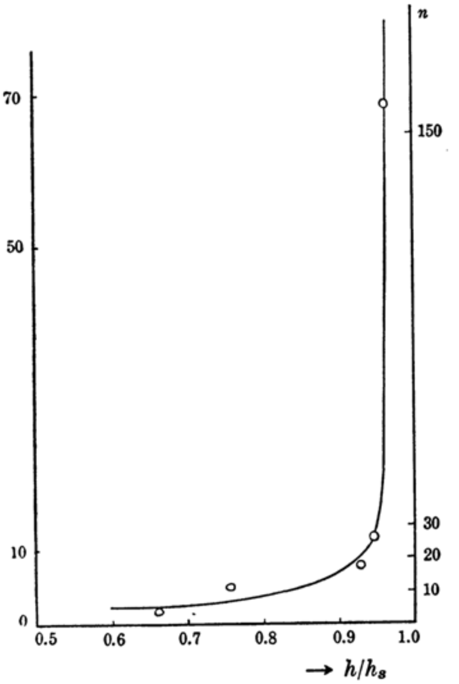

Fig. 1. Water Adsorbed by 47.7816 g. n-Molecular Layer of KBr Powder at 20.8°.

The dimension of each particle of a part of the well mixed sample is measured under the microscope and the surface area (0.563 cm.^{2}

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(3) According to Tammann, *Z. anorg. Chem.*, **126** (1923), 119, powders of various substances lump even at temperatures considerably lower than the melting point (NaCl 260°, cane sugar 69° ..), and this is attributed to the recrystalization due to the increased vibration of ions or molecules in the crystal. As our results were obtained at common temperature, they can not be explained in this way.

for 340 particles) and weight (density = 2.756, volume = 1.40×10^{-3}c.c., ∴3.85×10^{-3}g.) are computed as the rectangular parallelopiped and the total area is 7.0×10^{3}cm.^{2}(4) The thickness of the adsorption layer is calculated assuming the real surface area is twice the geometrically determined value and is shown in Fig. 1. (monomolecular layer corresponds 3.1×10^{-8}g. H_2O/cm.^{2}) Only little is known about the adsorption of the solvent vapour on the solute crystal. Durau(5) studied the adsorption of water vapour by sodium chloride powder by measuring the pressure and obtained the analogous curve with that in Fig. 1, but he described that this method does not give exact results for soluble solids.

Electric Conductance and Electrolysis in the Adsorbed Layer. A crystal of potassium bromide is heated to 400–500° and is cooled in the apparatus shown in Fig. 2 in the current of dry air, then the surface con-

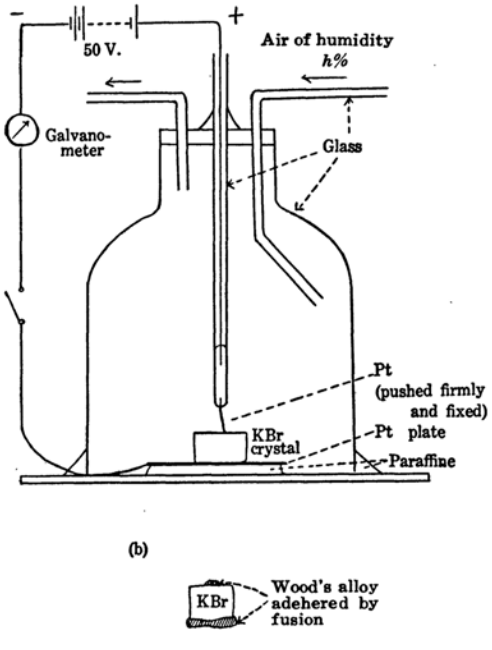

Fig. 2.

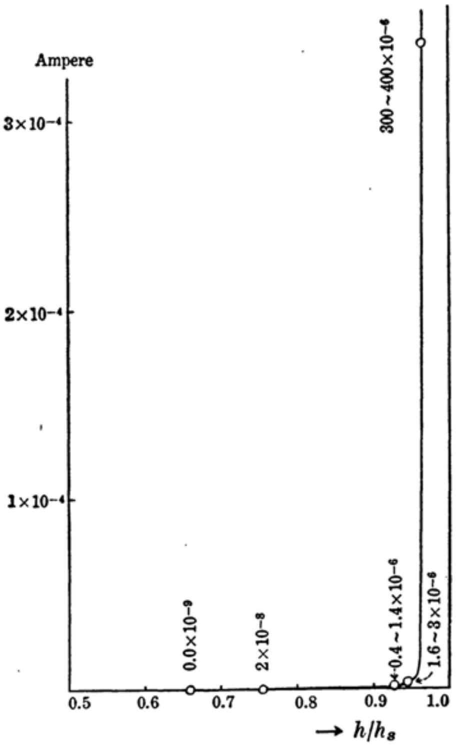

Fig. 3. The Current which flows through the Surface of KBr Crystal.

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(4) This value may be more exact than that calculated from the real weight and calculated area of a small part of the sample.

(5) Durau, *Ann. Physik*, (4), **87** (1928), 307.

ductivity is measured passing the air of known humidity, when the circuit is closed only for a short time to avoid the polarization as far as possible.(6) (Fig. 3). In the dry air the conductance and consequently electrolysis are not observed at common temperature, while in the air of $h/h_s = 79.4/84$ alkali is detected at the cathode after a few hours.

Discussion of the Results. That potassium bromide or sugar is soluble in water means that it is more stable for ions or molecules at the crystal surface to exist hydrated by water molecules or in the dissolved state apart from the crystal. When water vapour is adsorbed at the surface of these crystals, it is easily supposed that this layer shows the affinity as the solvent to the ions (or molecules) at the surface though the properties of the adsorbed water under the influence of the surface field are somewhat different from those of the ordinary water.

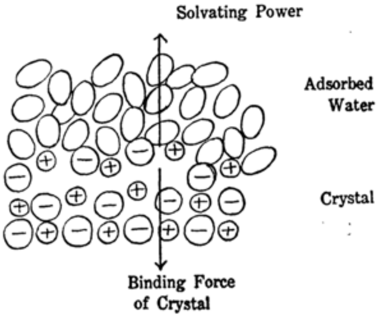

Fig. 4.

Fig. 5.

When the adsorbed quantity is little, complete hydration of ions (or molecules) is impossible as shown in Fig. 4 and so ions can not be separated from the crystal (accordingly no conductance in the case of electrolytes) though the binding force of the crystal may be weakened. When the adsorbed layer is thicker, comparatively perfect hydration being possible, some of ions (or molecules) can be dissolved in this (Fig. 5), and consequently conductance or electrolysis is observed in the case of electrolytes. As the ions are negatively adsorbed at the surface of the aqueous solution, it may be also true in the adsorbed layer

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(6) Values of the same order were obtained when the sample shown in (b) was used

and so surface conductance is not observed until the layer has a certain thickness. This "solution" has the vapour tension lower than that of the usual saturated solution by the influence of the surface field of the crystal. This field may be more far-reaching than in the case of insoluble adsorbent as the surface of the solute is disturbed and becomes mobile when the solvent is adsorbed.

When the humidity of the atmosphere h becomes h_s, the adsorbed layer is thick enough and so the surface of which is not influenced by the crystal field and has the same vapour tension with that of the usual saturated solution. This vapour tension being independent of the thickness, the layer can become infinitely thick and deliquescence takes place. Accordingly adsorption of the solvent vapour and dissolution are continuous processes in the case of the soluble adsorbent.

The range of mobility of the surface ions (or molecules) is broadened by such an adsorption and rearrangement of the crystal surface takes place through this adsorbed layer so that the surface energy or area of the crystals may be decreased, and this results in the lumping of the powder. (Fig. 6. a→b).

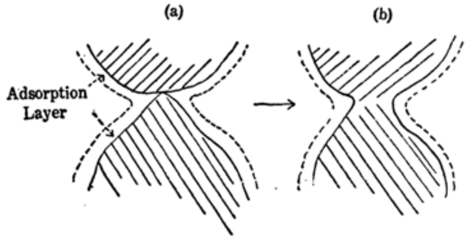

Fig. 6.

Therefore lumping by humidity is not remarkable when the solubility is not large (sodium bicarbonate, potassium chlorate etc.) and is not observed in the case of insoluble substances (calcium phosphate, calcium carbonate etc.). The analogous phenomena can be observed for other solvent. For instance, sulphur particles which are large enough not to lump by sublimation lump in carbon disulphide vapour of which tension is lower than that of the saturated solution. A sample of sodium chloride sealed in a glass tube with water vapour lumped at 29° but not at 36°. This is easily explained as the result of the decrease of adsorption with rising temperature.

Humidity and Reaction between Solids. As the reaction between solid substances takes place at the contact point at the temperature where sublimation is negligible, the reaction velocity is increased when the surface ions (or molecules) become mobile and so the contact area is increased by the adsorption of the solvent vapour as shown above. Reactions which occur only in the solution may be also accelerated in this layer. (Fig. 7 and 6 a.) For examples, at common temperature tartaric

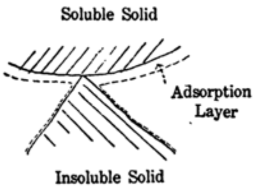

Fig. 7.

acid ($h_s = 86\%$) does not react with calcium carbonate in the desiccator but evolves carbon dioxide in the air of $h = 76\%$. The fact that this mixture lumps when the chemical change occurs shows that these phenomena have a common cause, mobility of tartaric acid molecule at the surface. On mixing calcium hydroxide and ammonium sulphate ($h_s = 81.2\%$) no change is observed in the air of $h = 63.0\%$, but when $h = 76.0\%$ ammonia smells strongly after a few hours, while the mixture of calcium hydroxide and magnesium ammonium phosphate, the latter being insoluble in water and so the surface mobility not increased by adsorption, does not evolve ammonia even when $h = 100\%$. The reaction between sodium chloride and sodium bisulphate is also greatly accelerated by the trace of water.(7) Balarev(8) studied many solid reactions at high temperature and found that a small quantity of water depresses the reaction temperature greatly and he attributed this to the relaxing of the binding of the surface molecules due to the adsorption, but he did not noticed the relation between this and the solubility. Though at high temperature adsorbed quantity is very little, the accelerating power is reported to be strong and may perhaps be catalytic, while at common temperature water seems to act as solvent.

Soluble and Insoluble Adsorbent. In the case of insoluble adsorbent which has been studied exclusively, the range of the surface force is very limited, and so monomolecular layer is formed when the adsorption takes place at low pressure. Though the multimolecular layer is formed when the pressure is higher, adsorbed molecules except in the first layer is held by the cohesion force among them. In the case of soluble adsorbent the range of force is broadened by the mobility of the surface ions (or molecules) due to the adsorption of solvent vapour, and this force, with the cohesion force among the adsorbed molecules, takes part in the formation of the multimolecular layer.

The authors express their thanks to Mr. S. Arakawa, Mr. H. Wakesima, and Mr. K. Yamazi for the kind helps.

Summary.

1) When some quantity of the solvent vapour is adsorbed by the solute crystal, a sort of solution is formed in the adsorbed layer.

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(7) Isikawa, Masuda and Takai, *Bull. Inst. Phys. Chem. Research* (Tokyo), **14** (1935), 833.
(8) Balarev, many papers in *Z. anorg. Chem.*, (1924–1925).

2) Lumping of the powder, surface conductivity of the crystal, and the increase of the velocity of reactions between solids are explained as the result of the mobility of ions (or molecules) in this layer at the crystal surface.

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