

ART. XLII.—*Chemical Action between Solids* ;* by WILLIAM HALLOCK.

IN a note on a new method of forming alloys published some time ago,† I suggested some additional experiments which I intended to make, and I now give the results thus far obtained. Unfortunately other work prevents my continuing the investigation at present.

Inasmuch as the method and principle‡ seemed well established where metals were used to produce alloys, an attempt was made to include some chemical reactions in the list. The most natural cases were the freezing mixtures where solid reagents are used. In order to surely have both constituents in a decidedly solid state the experiments were performed in a vessel cooled to a temperature of minus 10° or 12° C., care being always taken to leave the reagents in the vessel long enough for them to assume a temperature decidedly below zero Centigrade. Under these conditions a crystal of rock salt (NaCl) and a piece of clean dry ice were gently brought in contact, lying side by side on a watch glass. Of course the result was a solution of salt, but odd as this experiment may be, it appears here in a new connection, as an example of the union of two solids below the melting point of either, but above that of the product. The piece of ice was frozen to the glass and during the operation the crystal was drawn several millimeters across the glass, doubtless by capillarity, as the solution ran out at the bottom of the surface of contact as fast as it formed, the attraction being sufficient to move a crystal several grams in weight.

Similar experiments were performed with sodium and potas-

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† W. Hallock, *Zeitschr. f. Phys. Chem.*, ii, 6, 1888. *Science*, xi, 265, 1888.

‡ O. Lehmann Wiedemann *Ann.*, xxiv, p. 5, 1885, suggested the theoretical possibility of producing an alloy in this way. I had overlooked his paper until recently. Mr. Lehmann, however, evidently did not consider it possible to fulfill the necessary conditions and did not try the experiment.

sium nitrate, potassium, calcium and ammonium chloride and sodium and potassium hydrate, with a similar result in all cases. These are all well known results, but wherein do they differ from the new method of forming alloys? This question suggests another. Are the metals combining to form an alloy in the new way a freezing mixture? A thorough investigation of this question would require more complicated experiments than I had time to perform. One test, however, is very simple, that with potassium and sodium.

Into a small porcelain crucible weighing 15 grams and containing about an equal weight of petroleum were placed pieces of the two metals, about 3 grams of each. One junction of a thermo-element was forced into the piece of potassium and gave its temperature accurately. After the whole had assumed the room temperature, clean faces of the two metals were brought in contact, the liquefaction began and *the temperature immediately fell*. It required about two hours to complete the liquefaction and about one and a half hours to attain the minimum of temperature. No precautions were taken to prevent the calorimeter taking up heat from its surroundings, and no doubt it absorbed considerable in the long time, and yet the maximum fall in temperature amounted to 2.4° C., very large considering the small weight of the reagents compared with the calorimeter. Thus it appears that sodium and potassium are, under such circumstances, a "freezing mixture," and analogy at least would lead one to believe that other alloys also absorb heat in their formation; but future experiment must decide the point.

In the cool vessel above described a piece of sodium or potassium was placed upon a piece of dry ice, almost instantly the reaction commenced and proceeded vigorously. It is, however, scarcely safe to consider this a case of chemical action between solids, because the reaction is probably as follows: the vapor from the ice attacks the metal forming the hydrate which unites with other ice forming a solution, which is then further acted upon by the metal, and in the whole process heat is generated sufficient to raise the temperature of the reagents very considerably. Perhaps in the other freezing mixtures, ice and salt, etc., it is the vapor of the water or ice which initiates the reaction.

In view of these and other considerations, the idea is evident that perhaps many substances have a slight vapor tension at temperatures considerably below their melting points, and are surrounded by a thin atmosphere of their own vapor over their clean surfaces, and it is only necessary to bring two such atmospheres to interpenetration in order to initiate the reaction which

will then continue, provided the product (liquid or gas) escapes easily and does not clog the operation. In very many cases substances are found to give off a vapor below their melting point, and it is natural to suppose that there is a film of that vapor over the surface of the body, as there is a layer of saturated air over water. The mechanical theory of the composition of matter lends plausibility to the above suggestion. If these considerations are correct they foretell the regelation of substances like camphor and ice, without any pressure whatever. That loose pieces of camphor will become welded together by simple contact is well known. The operation appears to me thus: In an irregular mass of camphor in an atmosphere of camphor vapor, there is a constant interchange of state for the molecules at the surfaces of the solid, molecules previously solid are getting too far off and becoming gas, and molecules previously gas are beating upon the solid and staying there, thus the state of equilibrium is when, as a whole, there are as many molecules which fly off and become gas as fly on and become solid. On a projecting point of the solid the chances are in favor of more flying off than on, in a reëntrant angle the reverse is true. Theoretically, then, the piece ought ultimately to become a sphere, not only by the rounding down of the corners, but by the building up of the flat or reëntrant sides. That the corners do round off all know. If this is all true we only need to bring the two pieces together and consider them as one and the crack between them as a reëntrant angle, and the union is brought about as above indicated. If in the above the word liquid be substituted for vapor or gas, the explanation will apply to the regelation of ice in water at 0°C .

We may go even further and predict a uniting without actual contact and this prediction has been experimentally demonstrated in the case of ice and water. A large rough block of ice (about 15 lbs.) was sawed nearly in two, the slit washed out and all the fine pieces removed. In this way it was possible to hold two plane surfaces of ice parallel and near each other (1 to 2^{mm}) without danger of actual contact. Into the outer edge of the saw-cut a cotton wick was pressed, thus isolating the space between the faces from the outside and preventing any currents from circulating through the crack. The whole block was then placed in water at zero and enclosed in non-conducting cases and left for 25 to 30 hours. This experiment was tried three times and each time a freezing across the space had taken place. The whole space was not filled, but in numerous places notably along just inside the wicking and up from the bottom of the cut. No doubt the regelation would have gone further if the experiment could have been continued longer. The melting of

the whole block puts an end to each experiment. As these experiments were performed in summer there is scarcely a possibility that the ice was colder than 0° C.

Inasmuch as there seems to be an increasing inclination to regard solutions and alloys as chemical compounds it seems justified to speak of the action according to the alloy law as chemical. On the other hand there are some cases which at first appear as chemical action between solids which upon closer investigation can be explained on a simpler assumption.

For example, Mr. W. Spring* in a recent paper on this subject cites three particular cases as being chemical action between solids, the union of copper and sulphur, the reaction between copper and mercuric chloride, and between potassium nitrate and sodium acetate.

The formation of the sulphide of copper, and other sulphides, was accomplished by Mr. Spring by compression of the elements. But it is not even necessary that the sulphur and copper be in contact. I have made the sulphide at ordinary temperatures with the two an inch apart and a wad of cotton in the tube between them. It is simply the *vapor* of sulphur which attacks the copper. That sulphur gives off a perceptible vapor at ordinary temperatures, especially in *vacuo*, is a fact any one can easily demonstrate. The case of the copper and mercuric chloride is precisely the same. The *vapor* of the chloride will go through a whole tube past cotton wads and attack the copper (or color potassic iodide). Hence we can scarcely assert that these reactions are between *solid* bodies. The reaction between potassium nitrate and sodium acetate is equally unconvincing. Mr. Spring expected an interchange of bases and acids and left the mixture of the dry fine powders four months in a desiccator to give time for the exchange. On removing them from the desiccator a deliquescence was noticeable and he therefore concludes that the interchange had taken place, since the original salts do not easily deliquesce; but the product of the reaction (potassium acetate) does. It appears to me thus: the moment the powders were brought to the air, the water vapor enters the operation and we have, potassium nitrate, water vapor, and sodium acetate, and the result of their mutual interaction is a solution of potassium acetate and sodium nitrate. In fact if the dry powdered salts are stirred together, in a very few moments deliquescence begins, showing that whatever the reaction it goes on at once, and is a matter of moments and not of months. Thus even this experiment in its present form does not convince us that a chemical exchange took place *before* the water vapor entered the reaction.†

* W. Spring, Zeitschr. für phys. Chemie, ii, p. 536, 1888.

† See note on p. 406.

The question of chemical action between solids is by no means new but is being constantly extended. I may say I believe chemical action may take place wherever the product or products are liquid or gaseous even though the reagents are solid, with perhaps the added condition that one or both the reagents be soluble in the liquid produced. If this be true my new method of forming alloys is but a special case of the above general principle.*

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