



Experimental researches on the tension of the vapour of solutions

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WHY IRON RAILS WHICH ARE IN USE DO NOT RUST SO RAPIDLY AS UNUSED ONES. BY W. SPRING.

The fact that iron rails on those sections of a road which are much travelled over do not rust so rapidly as in those places which are not travelled over, or, which are kept in store, has been variously explained but not in a satisfactory manner. According to the author they rust in consequence of atmospheric moisture just like other iron. Whenever a train passes over them the rust previously formed combines under the joint influence of the pressure and friction to form magnetic oxide of iron; according to the author this protects the iron in consequence of the electrical polarity which it imparts by making it passive, and thereby preserves the rail from further destruction. In confirmation of this explanation the author pressed ferric hydrate between iron plates under a pressure of 1000 to 1200 atmospheres. If the ferric hydrate was dry there was no reaction; but if the hydrate was moistened with a few drops of water, then, near the iron, it became black and adhered to the metal; the surface of the plates was visibly attacked, and quantitative analysis showed the presence of magnetic oxide. The author holds that this is the process which naturally takes place. On the surface of the rails, where the wheels pass, he has found magnetic oxide mixed with varying quantities of ferric oxide, and a small quantity of pure iron.—*Bull. de l'Acad. Roy. de Belge*, xvi., p. 47, 1888; *Beiblätter der Physik*, vol. xiii. p. 122.

EXPERIMENTAL RESEARCHES ON THE TENSION OF THE VAPOUR OF SOLUTIONS. BY F. M. RAOULT.

The object of the present research is to investigate how far the tension of volatile liquids varies when different solids are dissolved in them. The quantities to be determined are the tensions of the vapour f of a pure volatile solvent, and then f' , that of the same solvent containing in solution a known weight of the solid, the temperature remaining constant.

Two methods were used—a statical and a dynamical one. The statical is essentially that of Dalton, and consists in measuring the depression produced in barometric columns, when equal volumes of the pure solvent and of the solution are severally introduced. This method, the details of which are described, gives the most accurate results.

The dynamic method is easily applied when the law is known according to which the vapour-tension of the pure solvent varies with the temperature. It is sufficient then to boil successively the solvent and the solution in the same reflux apparatus, and to note exactly their boiling-points under the atmospheric pressure. In these conditions the vapour-tension of the boiling solution is given

by the barometer, that of the pure solvent by a table prepared in advance.

It follows, from the researches of Von Babo, Wüllner, and others, that the ratio $\frac{f-f'}{f}$ between the vapour-tension of a salt in aqueous solution and the tension f of pure water is sensibly independent of the temperature; the exceptions to this rule are probably due to an incipient dissociation of the salts dissolved.

The author has investigated whether this holds also for other solvents, and has found that it does with sufficient nearness.

The experiments of Von Babo and of Wüllner have shown that if a number N of molecules of a salt be dissolved in 100 grammes of water, the vapour-tension undergoes a diminution which, for the same temperature, is proportional to the number of molecules dissolved. This is expressed by the formula

$$\frac{f-f'}{fN} = K,$$

where K is a constant depending on the nature of the salt.

This law only holds if the solutions are very dilute; for stronger solutions the formula should be replaced by the following one:

$$\frac{f-f'}{fN'} = K;$$

where N' is the number of molecules of the fixed substance contained in 100 molecules of the *mixture*. The value of N' is given by the formula

$$N' = \frac{100N}{100+N}.$$

The ratio $\frac{f-f'}{fN'}$ being what is called the *relative diminution of vapour-tension* of the substance in question, the latter formula may be thus expressed in ordinary language. *For all solutions of the same kind the relative diminution of vapour-tension is proportional to the number of molecules of the solid dissolved in 100 molecules of the mixture.*

The author cites a series of experiments made with benzoate of ethyl, dissolved in ether in proportions varying from 9 to 97 per cent., the results of which closely agree with those calculated by the modified formula.

The author further found that there is a relation between the lowering of the freezing-point and the diminution of the vapour-tension of the same solution. *For dilute aqueous solutions of the same nature and the same concentration, the number which expresses the relative ension of the vapour is always near the $\frac{1}{100}$ part of that which expresses the lowering of the freezing-point.*

This holds also for other solvents than water; thus, with benzene the ratio appears to be about 63.

It thus appears from these researches that:—

1. Any solid which dissolves in a volatile liquid diminishes the vapour-tension of this liquid.

2. In all volatile solvents the molecular diminution of the vapour-tension due to different compounds in solution approaches two mean values, which vary with the nature of the solvent, and one of which, called *the normal*, is twice that of the other: it is that which is most frequently produced.

As determined from a large number of solvents, values are given for this constant which amount to 0.0104.

Hence it may be said that even 1 molecule of a solid dissolved in 100 molecules of any volatile solvent diminish the vapour-tension of the liquid by an almost constant fraction of its value, and near to 0.0104.

The formula
$$\frac{f-f'}{fN} = 0.0104$$

may be utilized to determine the molecular weight of solid or volatile bodies. If P is the weight of a substance dissolved in 100 grammes of a volatile liquid, M' the molecular weight of the solvent, and M that of the body dissolved, we have

$$N = \frac{PM'}{M}, \text{ from which } \frac{M}{M'} = 0.0104 \times \frac{fP}{f-f'}.$$

It is thus possible to calculate M when M' is known, and conversely.

This method of determining molecular weights is more difficult to carry out, and is less exact than the *cryoscopic method*, which depends on the freezing-point of solutions; but it may be of great service in many cases.—*Journal de Physique*, [2] vol. viii. p. 1.

ON CHEMICAL ACTION BETWEEN BODIES IN THE SOLID STATE.

BY W. SPRING.

The author mixed copper filings with perfectly dry pulverulent mercuric chloride, and kept the mixture in closed glass tubes which he shook from time to time. A very slow decomposition of the two bodies set in, with the formation of cuprous and mercurous chlorides. In like manner there was a decomposition of dry potassic nitrate with powdered sodic acetate freed from water of crystallization; for, after standing for four months in the drying-vessel, the mass was deliquescent in the air, from which the presence of potassic acetate may be inferred, since the original salts are not deliquescent. This reaction takes place much more rapidly at a high temperature; for although the melting-point of the two salts is above 300°, the mixture in question fused in a water-bath in three hours to a white mass, which was also seen to be deliquescent in air.—*Bull. de l'Acad. Roy. de Belge*, vol. xvi. p. 43, 1888; *Beiblätter der Physik*, vol. xiii. p. 123.