

acid or one of its homologues are among some of the most interesting compounds of inorganic chemistry for, although basic in composition, they are all crystallized from anhydrous acid.¹

CONCLUSIONS.

The following conclusions seem warranted for the ranges of temperature covered by our experiments:

That the only definite hydrated oxalates are $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ and $\text{BeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

That no acid oxalate of beryllium exists.

That the anhydrous oxalate BeC_2O_4 is difficult, if not impossible to produce, owing to the difficulty of removing the last trace of water without at the same time decomposing the oxalate.

That the so-called basic oxalates of beryllium do not exist as separate and definite chemical compounds but are in reality solid solutions of the oxalate in the hydroxide. They are much more basic in composition when equilibrium with the mother-liquors is reached than when first precipitated.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 10.]

AN ELEMENTARY PROOF OF THE RELATION BETWEEN THE VAPOR PRESSURES AND THE COMPOSITION OF A BINARY MIXTURE.

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Received February 17, 1906.

BOTH partial vapor pressures from a mixture of two liquids are changed by a change in the composition of the mixture, but not independently. As one decreases, the other invariably increases according to the simple law discovered by Duhem,² namely,

$$N \frac{d p}{p} + N' \frac{d p'}{p'} = 0,$$

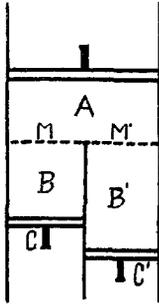
where p and p' are the respective partial vapor pressures from a mixture containing N gram-molecules of the first substance and N' gram-molecules of the second, and dp and dp' are the changes in p and p' accompanying a slight change in composition.

No satisfactory elementary proof of this very important equa-

¹ Urbain and Lacombe: *Compt. rend.* 133, 874; Lacombe: *Ibid.* 134, 772.

² *Compt. rend.* 102, 1449 (1887).

tion has been given. That used by Duhem is rigorous but not elementary, that of Luther¹ is simpler but not entirely rigorous or convincing. I believe that the following proof not only has the advantage of extreme simplicity, but is entirely rigorous and shows clearly the conditions under which the equation is valid.



In the apparatus shown in the figure, A contains a mixture of the substances X and X'. M is a membrane permeable only to the vapor of X, M' a similar membrane permeable only to the vapor of X'. B contains the pure vapor of X, B' the pure vapor of X'.

The partial vapor pressures from a mixture of N gram-molecules of X, and N' gram-molecules of X', will be designated by p and p' respectively, those from a mixture of N gram-molecules of X and $N' - dN'$ gram-molecules of X' by $p + dp$ and $p' + dp'$ (dp being numerically positive, dp' negative).

Let us start with a mixture in A of N gram-molecules of X and N' gram-molecules of X', and with no vapor in B and B', the pistons C and C' being at M and M'. Let us perform the following reversible cycle of *isothermal* operations, *keeping the pressure in A constant*.

(1) Keeping the pressures in B and B' equal to p and p' , respectively, lower the pistons C and C' at such rates that as the mixture in A evaporates, the remainder still has the original composition. Finally, when all the mixture has evaporated there will be N gram-molecules of vapor of X in B, and N' gram-molecules of vapor of X' in B'. The pressures of the two vapors will still be p and p' ; their volumes we will call V and V' .

(2) By simultaneous movements of the pistons C and C' change the vapor pressures in B and B' to $p + dp$ and $p' + dp'$, dp and dp' being defined as above. The corresponding increments of volume we will call dV and dV' . The vapors are now able to exist in equilibrium not with the original mixture, but with a mixture containing X and X' in the proportion of N gram-molecules to $N' - dN'$.

(3) Form a mixture of this composition in A by raising the pistons C and C'. This operation will be just the reverse of (1),

¹ Ostwald's Lehrbuch (2) 2, 639 (2d ed.).

except that the vapors enter the mixture in the constant proportion, not of N to N' , but of N to $N' - dN'$. At the end of this operation all of the vapor of X and all but dN' gram-molecules of X' will have passed into the mixture.

(4) Finally, force into A the remaining dN' of X' , whereby the vapor pressures of the mixture will return to p and p' , and the whole system to its original condition.

During this reversible isothermal cycle the sum of the work done upon the piston in A and the work done upon the pistons C and C' will be zero. Of these the former is itself equal to zero, for the pressure in A remains constant and the original volume is the same as the final volume. Hence, the total work done upon the pistons C and C' must equal zero. Let us find the work done upon these two pistons in each of the four operations described, *assuming that the vapors obey the gas law.*

Operation (1) gives,

$$A_1 = -pV - p'V' = -NRT - N'RT.$$

Operation (2), neglecting differentials of the second order, gives,

$$A_2 = -pdV - p'dV'.$$

From the gas law,

$$-pdV = Vdp = \frac{NRT}{p} dp.$$

Hence,

$$A_2 = \frac{NRT}{p} dp + \frac{N'RT}{p'} dp'.$$

Operation (3) gives

$$A_3 = NRT + (N' - dN')RT.$$

Operation (4), neglecting differentials of the second order, gives

$$A_4 = (dN')RT.$$

We have shown that

$$A_1 + A_2 + A_3 + A_4 = 0.$$

We see by inspection that,

$$A_1 + A_3 + A_4 = 0.$$

Hence,

$$A_2 = 0,$$

and

$$N \frac{dp}{p} + N' \frac{dp'}{p'} = 0.$$

In precisely the same way we can show that for a mixture of more than two constituents,

$$N \frac{dp}{p} + N' \frac{dp'}{p'} + N'' \frac{dp''}{p''} + \dots = 0.$$

These equations are true when both the temperature and the pressure of the mixture are constant, and when the vapors behave like perfect gases. As a matter of fact the latter condition is never exactly fulfilled, and the equations must therefore be regarded only as approximations to the truth. How these approximate equations may be replaced by exact equations of similar form will be shown in another place.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 114.]

THE COMBINATION OF A SOLVENT WITH THE IONS.

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Received March 8, 1906.

I. INTRODUCTION.

THE possibility of the combination of the ions of an electrolyte with the solvent has been suggested by several investigators. Ciamician¹ suggested that the attraction between the solvent and the positive and negative parts of the salt is actually the cause of dissociation. This idea receives support in the fact that the solvents that ionize salts largely are the ones that combine with them to the greatest extent, forming compounds with water of crystallization, alcohol of crystallization, etc.; but the mere fact that such compounds separate out in the solid state is not positive evidence that they exist in the solution.

In this connection it is interesting to note that few of the salts, whose ions are both univalent, separate with water of crystallization, while those with ions of higher valency almost all do. From this we might suspect that univalent ions are less hydrated than bivalent or trivalent ones, and this view is supported by the comparison of the velocities of the ions of different valencies. If we calculate the absolute velocities with which the ions move when subjected to the same force (not the same potential gradient for all

¹ Z. physik. Chem. 6, 403 (1890).