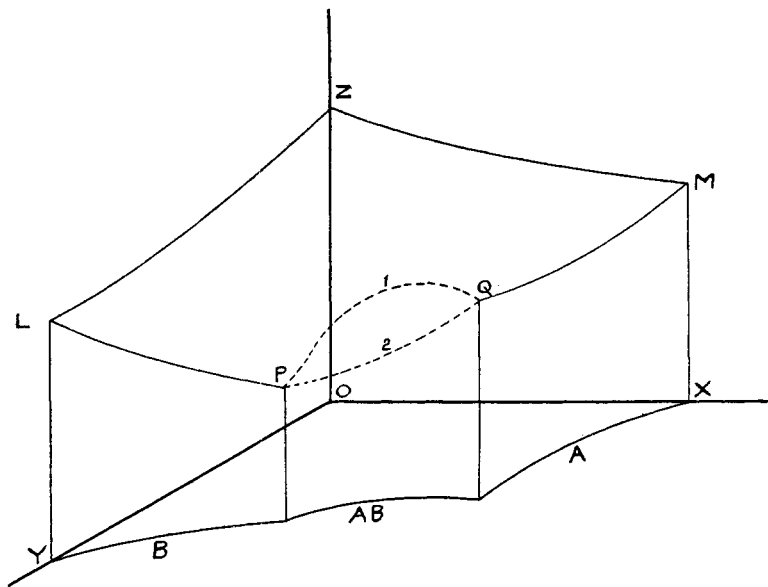


# THE ISOTHERMAL PRESSURE-SURFACE IN THE CASE OF TWO SINGLE SALTS AND ONE DOUBLE SALT

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The phenomena which occur on isothermal variation of the system whose components are water, A, B, where A and B are two single salts with a common ion, have been already investigated, and the discussion of the phenomena from the point of view of the solubility relations has been given by van't Hoff<sup>1</sup> and by Bancroft<sup>2</sup> in easily accessible form. It may nevertheless be of some interest to reconsider the phenomena purely from the point of view of the pressure relations.



In the figure the concentration with respect to A is meas-

<sup>1</sup> Vorlesungen über Bildung und Spaltung von Doppelsalzen, Leipzig, 1897.

<sup>2</sup> The Phase Rule, Ithaca, N. Y., 1897.

ured along OX, and with respect to B along OY. Vapour-pressures are measured along OZ. The curves in the  $xy$ -plane represent the usual typical solubility relations for the double salt AB and the two single salts A, B. OZ represents the vapour-pressure of pure water at the temperature in question, and the curves ZL, ZM are the vapour-pressure curves for pure solutions of B and A respectively, while the curves LP, PQ, QM are the saturation pressure-curves for B, AB and A respectively, that is to say, they give the pressures of solutions which are in equilibrium with B, AB, and A respectively. The general trend of the curves ZL, ZM, LP, and QM is evident from the law of lowering of vapour-pressure with increasing concentration and from the theorem that the vapour-pressure of a saturated solution is in general lowered by saturation with respect to a new substance.

One of the most important isothermal variations is the removal of water by evaporation. We shall consider in this case the motion of the point which represents at any given moment the vapour-pressure of the solution. For unsaturated solutions, i. e. for points lying on the pressure-surface, since the relative amounts of A and B cannot change, the motion is along a curve determined by the intersection of the pressure-surface with a vertical plane through OZ and the starting-point. On reaching a saturation-curve, the corresponding salt begins to precipitate and the motion now possesses only one degree of freedom, i. e. along the border curve. The direction is determined by the fact that the pressure cannot rise on isothermal evaporation of a system in equilibrium. On arriving at the point of intersection of two saturation pressure-curves, the next substance begins to precipitate. We have now two cases to consider, according as the curves in the neighborhood of the point of intersection lie entirely above or partly above and below this point. Supposing the curve PQ to have the form (2), then the former case occurs at P and the latter at Q. It is evident that on reaching such a point as P it cannot be passed, as any such motion would involve an increase of vapour-pressure. Hence

the solution must dry up completely at P leaving a mixture of B and AB. A point of this sort has been termed an *end-point of crystallization*.<sup>1</sup>

Consider now the point Q. On arriving at Q, AB begins to precipitate. If we imagine any solid A present removed, the motion will be, from what has been said, along PQ in the direction Q2P. The solution does not therefore deposit A on further evaporation, and if the solid A be replaced the only effect will be to detain the point at Q until all the solid A has disappeared, after which the point will proceed down Q2P. It is evident that none of the saturation-curves LP, PQ, QM can possess a minimum, for this would involve the stoppage of the tracing-point on isothermal evaporation at these minima, which leads to obvious absurdities. The curve PQ may however under certain conditions possess a maximum point as in P1Q. Let us consider what the existence of such a maximum would involve. It could evidently be reached by isothermal evaporation only from the pressure-surface. Since on reaching points on PQ infinitely near it either to the right or left, the subsequent motion would be either towards P or Q, it is clear that on arriving exactly at the maximum point on PQ the tracing-point would remain stationary here on further isothermal evaporation, and the solution would evaporate down to pure double salt. This shows then that the curve PQ possesses a maximum for temperatures outside the *transformation-interval* of the double salt and in the region of complete stability in contact with water. The maximum on PQ corresponds in fact to a pure saturated solution of double salt, and the straight line  $\frac{x}{y} = \frac{a}{b}$  in the  $xy$ -plane (where  $\frac{a}{b}$  = ratio of components A,B in AB) cuts the solubility curve for AB in a point vertically under this maximum point. For temperatures within the transformation-interval the curve PQ will possess the form P2Q. If we imagine supersaturation with respect to one of the single salts

<sup>1</sup> Van 't Hoff und Meyerhoffer, Untersuchungen über die Bildungsverhältnisse der Oceanischen Salzablagerungen, (V). Sitzungsber. Akad. Wiss. Berlin, XLVI, 1897.

to occur, we may suppose  $P_2Q$  continued, and since in this case also the point corresponding to saturation with respect to pure double salt will be a maximum-point, it follows that if as in the figure the pressure at  $Q$  exceed that at  $P$ , then the line  $\frac{x}{y} = \frac{a}{b}$  cuts the solubility curve for  $A$ . It likewise follows in this case that at the temperatures separating the region of complete stability and the transformation-interval, the curve  $PQ$  will touch a horizontal plane through  $Q$ .

With respect to the surface  $ZLPQM$  all that can be said is that for temperatures in the region of complete stability of the double salt it would appear to possess a saddle-shaped form.

The foregoing considerations show that the phenomena of isothermal evaporation are rendered immediately evident by means of the vapour-pressure surface, and can be fairly well considered by means of it alone.