

A NOTE ON THE EXPERIMENT OF THE CRYOPHORUS

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The familiar experiment of Wollaston's cryophorus rests on the principle of Watt,¹ according to which water distils from a place of higher temperature to one of lower temperature. As ordinarily carried out with an apparatus consisting of two bulbs containing water, one of which stands in a freezing mixture, the other in the air, the water in both bulbs finally freezes; distillation will then cease when the temperature becomes the same in both bulbs.

The following question leads to some rather amusing considerations: What will be the final conditions of equilibrium if ice does not form in the outer bulb, and there results merely a state of supercooling?

The rules that will govern all possibilities for a true equilibrium starting with ice in one bulb, water in the other, are quite simple.

I. No equilibrium is possible with a difference of vapor pressure, for water then passes from one bulb to the other.

II. No equilibrium is possible with a difference of temperature, for heat then passes from one bulb to the other.

Hence since water and ice of the same temperature and under ordinary pressure, have the same vapor pressure only at 0°C , it follows that if ice remains in one bulb, water in the other, the final temperature must be 0° . Or, for all possible cases, either

- (a) the temperature of both bulbs rises to 0° , or
- (b) only one phase survives.

Let us assume both bulbs cooled to -10° . Then the following ways in which the apparatus may be arranged will include all that offer any interest, and essentially all that are possible:

- (1) The whole apparatus is adiabatically enclosed.

¹ Van Deventer : Physical Chemistry, Chap. IV.

(2) The ice bulb (A) is maintained at a fixed temperature below 0° , the water bulb (B) is adiabatically enclosed.

(3) The water bulb is maintained at a fixed temperature below 0° , the ice bulb is adiabatically enclosed.

(4) Both bulbs are maintained at fixed temperatures.

(1) Under arrangement (1) we have ice in A, water in B, both at -10° . By rule I, equilibrium is impossible under these conditions. Distillation takes place from B to A. This causes a difference of temperature and brings rule II into operation. Hence there will be a continuous transference of vapor from B to A, and of heat from A to B. But since the vaporization in B absorbs only the latent heat of vaporization, whereas the condensation in A liberates both latent heat of vaporization and latent heat of fusion, there will be a continuous gain in free heat, and consequently a rise of temperature in both bulbs. The distillation will cease when both water and ice have risen to 0° . Thus the end state will be: water at 0° in B; ice at 0° in A.

If the quantity of water in B was originally small, it may all distil over before this end state has been reached, in which case only the ice phase survives, and its final temperature may be anywhere between -10° and 0° .

In case (1) then, the process goes on as if the two phases were mixed after the supercooling had been brought about. In other words it is a relieving of the state of supercooling without contact between the solid and liquid phases; and further it is an autodistillation process from the point of view of the water, since the heat required for vaporization comes from the condensation of the vapor already formed; or in other words, the warmer ice is heated at the expense of the colder water—the heat being transferred as latent heat of vaporization—and free heat then passes back from the ice to the water; and finally, distillation here goes on from a place of lower temperature to one of higher temperature.

(2) If the ice bulb is maintained at a fixed temperature, say -10° , and the water bulb adiabatically enclosed, the water in B will immediately fall below -10° on account of distilla-

tion, and we shall have the same state of affairs as in (1)—vapor passing from B to A, heat passing from A to B. The temperature of B can never rise to that of A because any approach to that point causes the distillation process to go on more rapidly but the transfer of heat from A to take place more slowly. Conversely, the temperature of the water can never fall to the point where its vapor pressure is equal to that of the ice, for any fall of temperature causes a decrease in the distillation from B to A and an increase in the heat transfer from A to B.

Since no change of temperature is possible in A, the liquid must eventually all distil over from B, and in the end state will be found as ice in A, at the temperature of the bath. This end state is independent of the original quantities of water in the two bulbs.

(3) If B is maintained at -10° , A being adiabatically enclosed, the process will go on again as described under (2), but the variation of temperature will now take place in the ice bulb. The initial temperatures being the same, distillation will be immediately set up from the water to the ice, and this will cause a rise of temperature in the ice. This rise can never bring the ice up to the point where its vapor pressure is equal to that of the water in B because of the continual loss of heat from A to B. Hence all the water will distil from B to A, and in the final state there will only be ice in A at the temperature of the bath about B.

These two cases are on the whole almost identical with the first.

(4) If both bulbs are maintained at fixed temperatures, then whether these be the same or different, the water will finally all be found in that bulb where the vapor pressure is lowest, and in the phase that was originally there.

In the special case where the bulbs are maintained at temperatures such that their vapor pressures are exactly equal, no change will take place, if we assume the baths to be ideally efficient, and indefinitely renewed. But there will be no true equilibrium here, for heat will always pass from the

warmer to the colder bulb, and there be taken care of by the bath.

Thus the resulting end states are all such as we should obtain if the two phases were placed in contact, though most of the above arrangements would then be experimentally impossible.

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