are connected by a wide tube so that the gas may flow freely from one to the other. On the other hand, where the connecting tube is narrow we no longer get equality of pressure, and apparently this is to be explained by assuming that equilibrium is not obtained because the free movement of the gas is impeded.

Eastman concludes that in perfect solutions in a temperature gradient there is no thermodynamic equilibrium but it is difficult to see why the above condition of equilibrium should not apply in theory to the Soret effect for a solute whose partial molal volume is negligible in dilute solution. Practically, of course, as Eastman indicates, the molecules of the solvent may interfere with the free distribution of the solute molecules. Eastman argues that the heat absorbed by the removal of dn moles of solute by diffusion from a region is zero for dilute solution. Unless this effect is compensated by a transfer of solvent, however, it should be equal to a work term analogous to the pdv term in the case of the perfect gas. This heat effect is easily demonstrated in the case of the perfect gas. It is a reversible effect, of course, and involves no entropy change.

Finally, the difficulty which Eastman discovers in defining osmotic temperature with reference to a semi-permeable membrane might be avoided by considering equilibrium established through the vapor phase, as is customary in defining osmotic pressure. However, if two solutions at different temperatures were in equilibrium through the vapor phase they would almost certainly not be in equilibrium on direct contact. The whole question of equilibrium in non-isothermal systems may probably be summed up by paraphrasing a well known principle; if two phases are not in equilibrium in every way, for example, not at the same temperature, they will never be in equilibrium in more than one way at a time; that is, the condition of equilibrium will depend upon the manner of making contact between the two phases. Thus, if we make contact between two phases which are at different temperatures in two ways, directly and through an intermediate phase we will, in general, get not equilibrium but a cyclic flow of some component which functions continuously as a more or less perfect heat engine. The thermocouple is a familiar example.

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The Thermodynamics of Non-Isothermal Systems.—The comments of Rodebush in the foregoing Note, together with the following, will, I believe, assist those interested in this field to a clearer understanding of certain points which have perhaps not been sufficiently emphasized.

The condition governing equilibrium that was used in my paper is, fundamentally, the first of the two quoted by Rodebush. Some confusion may, however, have been caused by my repeated references to the "system" and the "reservoirs," since the two together constitute the larger *isolated* system (of constant energy) to which the condition for equilibrium was applied. It was, of course, assumed explicitly that effects due to thermal conduction are neglibible compared to the reversible effects, or at least are independent of them. This assumption can scarcely be avoided in any method of treatment based on thermodynamics alone. Aside from this, I see no element of incompleteness in the condition employed.

The application by Rodebush of the alternative condition for equilibrium to the case of a perfect gas in a temperature gradient requires little comment from me. It is readily demonstrated by the method I employed that there is no pressure gradient corresponding to a reversible equilibrium in such systems, in agreement with his result. The small pressure gradients that are actually found at moderate pressures are due, I think, to the imposition of irreversible effects of the same type found at low pressures. With large tubes convection currents are likely to be present, obscuring or destroying the gradient. With very small capillaries it seems possible that surface phenomena (heats of adsorption) may have some effect upon the equilibria.

It is my present belief, in agreement with Rodebush and contrary to the statement in the former paper, that the heat of transfer, and therefore the reversible Soret effect in any imperfect solution, dilute or concentrated, is not zero. This is a point which it has been my intention to discuss in a later paper on the Soret effect. The effect in perfect solutions (defined as those in which Raoult's law holds for both components at all concentrations) I still believe to be zero, since I see no possibility of a heat of transfer in them.

Lastly, the difficulty concerning osmotic temperature may not be avoided by considering equilibrium established through the vapor phase. As Rodebush indicates in the succeeding statements in the last paragraph of his Note, an entirely distinct equilibrium (governed by Equation 13 of the former paper) results in this event. This is an example of an obvious point of difference of non-isothermal from isothermal equilibria. Whereas the latter are independent of the process through which equilibrium is achieved, the former depend entirely upon it. The reason for this is, of course, that by different processes of transfer of the same amount of material different amounts of heat are moved between the lower and higher temperatures. Different changes in state, when this is considered, are therefore brought about in such processes.

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