Procedure

The nickelous hydroxide is employed in the form of a suspension in water, 0.0050 g. in 1 cc., prepared by precipitation from a soluble nickelous salt with excess of sodium hydroxide. The precipitate must be washed free from all the excess of sodium hydroxide; it is then stirred with distilled water. This mixture will keep indefinitely. The mixture is well shaken and then added in excess to the hypochlorite solution. This is heated, just under its boiling point, for about ten minutes, and then filtered. While filtering, a portion of the filtrate can be tested for unconverted hypochlorite by adding a few drops of the nickelous hydroxide suspension to it and heating for one minute. A darkening of the precipitate indicates the presence of hypochlorites. Should this occur, the entire filtrate must be retreated with nickelous hydroxide. The filtrate is now ready for titration with hydrochloric acid.

The error of the determination was found to be ± 0.06 cc. when the alkali was sodium hydroxide in a 1 N solution. For determining calcium hydroxide it was found that this method could not be used, since the calcium hydroxide was partially removed from the solution by adsorption into the gelatinous nickel hydroxide.

The simplicity and accuracy of this method are of practical interest and value, and commend themselves to all analysts.

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The Thermodynamics of Non-Isothermal Systems.—In a recent article Eastman[1] has discussed the application of thermodynamics to non-isothermal systems and especially to the Soret effect, in an interesting manner. It will be difficult to add anything of practical significance to Eastman's paper since his conclusion that in general these effects can only be determined empirically is undoubtedly correct. It seems necessary, however, to urge a different viewpoint from that of his paper in certain particulars. In the first place, his statement of the condition for equilibrium $\Sigma\delta S = 0$ is incomplete. Gibbs[2] has stated the conditions for equilibrium upon which the laws of thermodynamics are based in two ways which are equivalent: (a) in an *isolated system* at constant energy the entropy shall be a maximum, or (b) in an *isolated system* at constant entropy the energy shall be a minimum.

These conditions are stated mathematically as $(\delta S)_E \leqq 0$, $(\delta E)_S \geqq 0$.

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[1] Eastman, This Journal, **48,** 1482 (1926).

[2] Gibbs, "Scientific Papers," Longmans, Green and Co., New York, **1906,** vol. 1, p. 56.

Now it is obviously impossible to maintain a thermal gradient in an isolated system. If, however, we supply heat at a constant rate to one part of a system and withdraw heat at the same rate from another part, we establish a thermal gradient under conditions in which the energy, so far as heat flow is concerned, is constant and the system may be designated as quasi-isolated. With these assumptions we may attempt to apply the conditions for equilibrium with the understanding that any deductions must be verified experimentally.

It seems worth while to consider the application of the complete conditions for equilibrium to a very simple quasi-isolated system. Let us consider two containers at temperatures T_1 and T_2, respectively, connected by a pipe of sufficient size, along which is the stationary temperature gradient from T_2 to T_1. A quantity of perfect gas is introduced into the system. Let us calculate the condition for equilibrium.

By means of an auxilary cylinder and piston we can remove dn moles of gas from one container, transfer it slowly through the thermal gradient, and introduce it into the other container, the whole process being reversible; hence $\Sigma\delta S = 0$. We may then apply the second form of the Gibbs condition for equilibrium $(\delta E)_S \geqq 0$. However, we cannot draw inferences as to the behavior of a system by imagining the reversible transfer of material from one part to another by an auxiliary apparatus unless a corresponding reversible process can take place spontaneously in the system itself. Such a reversible transfer can only take place in the system in question when the pressure is sensibly constant throughout. The work of transfer under these circumstances is readily calculated. If we draw dn moles of gas from the container at the temperature T_1 the work done is $p\text{d}v$, where $\text{d}v = \text{d}nRT/p$; hence, the work is $\text{d}nRT$. In carrying the dn moles through the temperature gradient a further expansion gives $\text{d}nR(T_2-T_1)$ as the work done and on introducing the gas into the container at T_2 the work $-\text{d}nRT_2$ is done. The total work is thus seen to be zero and hence by the first law $\delta E = 0$. It remains to show that E is a minimum for this condition. If we assume constant pressure through the system as an initial condition, then an appreciable difference in pressure can only come about by a flow of gas from the lower to the higher pressure. Now if zero work is required to move dn moles of gas from one container to another at constant pressure, then work must be done on the gas in order to transfer dn moles from a lower to a higher pressure regardless of whether the higher pressure is at the higher or the lower temperature. (This can be demonstrated rigorously by considering the work of transfer, using the auxiliary cylinder and piston.) If work is done on the gas then the energy is increased; hence, the energy must have been at a minimum and the condition $(\delta E)_S \geqq 0$ is satisfied. This result is confirmed by experiment at high pressures when two containers at different temperatures 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,