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THERMODYNAMICS OF NON-ISOTHERMAL SYSTEMS

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An isolated system obviously cannot be said to have reached equilibrium until the temperature is the same in all its parts. It is, however, ideally possible to establish non-isothermal equilibrium of a constrained sort in any material system by the use of a series of heat reservoirs differing infinitesimally in temperature. By contact with the appropriate reservoirs, any desired gradient or difference in temperature may be induced and maintained within the system. If, under these circumstances, the substances constituting the system are able to move independently from one region of temperature to another, they will in general do so until a condition of equilibrium, accompanied by no further net transfer of material, is reached. The elucidation by thermodynamic methods of the equilibrium conditions in a number of typical systems of this kind is the purpose of this investigation.

In carrying out this purpose it is necessary to recognize at once an important limitation. Attainment of equilibrium in transfer of material does not necessarily imply thermal equilibrium with respect to the same process. In illustration, the transpiration of a gas through perforations in a wall between a hot and a cold region may be considered. When the mean free path of the molecules is sufficiently large they will pass back and forth through the wall without undergoing collision in the orifices. When the number of molecules passing in each direction is the same, equilibrium is established. When this condition is fulfilled, a pressure difference on the two sides of the dividing wall is found to exist. But in this state of balance the molecules passing from the hot to the cold compartment in any given time transfer larger amounts of heat than those passing in the same time in the reverse direction. The equilibrium, therefore, is incomplete. It follows that it cannot be exactly treated thermodynamically (though it obviously may be by the kinetic theory). The distinguishing feature of the system in this illustration is that the mechanism of conduction of heat is identical with and inseparable from that of transfer of material between regions. In gases at higher pressures and in liquids and solids the two mechanisms are less closely interlocked. In such cases it is possible to distinguish in thought between the irreversible processes of heat conduction and those that are reversible from a thermal as well as a material viewpoint. It must be said, however, that even when the direct transfer of material by the conductive process is greatly reduced, the influence of the irreversible effects upon the distribution of the substances in any real system cannot be considered to be wholly eliminated. It is, therefore, only to systems in which these effects are of known magnitude or negligibly small that the treatment in this paper is intended to apply.

The method of investigating equilibria that will be employed is the standard one based upon the first and second laws. In accordance with the latter principle, any substance in one region is in equilibrium with the same substance in another region of the system if no net change in entropy results from a virtual transfer of the substance between the regions. Complete equilibrium is established if this is true for every substance present. Calling the entropy of the reservoirs S_R and of the system S_S, and considering separately the changes in these values, it is clear that for every virtual transfer under equilibrium conditions

$$\delta S_R + \delta S_S = 0 \tag{1}$$

Evaluation of δS_R and δS_S in Equation 1, in the course of which the first law is used, leads to expressions exhibiting the equilibrium conditions, as illustrated in the examples which follow.

Homogeneous Systems

Thermal Endosmosis.—Consider two chambers, infinite in size, containing the same pure substance maintained at constant pressures P and $P + \mathrm{d}P$ and temperatures T and $T + \mathrm{d}T$, respectively, there being a non-conducting wall between them which is permeable to the substance enclosed. If under equilibrium conditions in this system one mole of the substance is transferred from the colder to the warmer compartment, two transfers of heat occur which may be considered separately. The first of these is the loss by the reservoirs to the system of a quantity of heat equal to the difference, $\mathrm{d}H$, in molal heat content of the substance in the two compartments. The second effect arises from the fact that in general a heat effect attends the solution of the substance in the membrane at one temperature and its withdrawal at another, the result of which is a transfer of heat between the reservoirs of different temperatures. The heat so transferred is equal to the heat absorbed when one mole of the substance dissolves in a large amount of the material of the saturated membrane. This quantity is the relative molal heat content[1] of the substance in the membrane with respect to its pure state. It will be designated $\overline{L}_M$. The two heat transfers together produce an entropy change in the reservoirs which is

$$\delta S_R = -\mathrm{d}H/T - \overline{L}_M\mathrm{d}T/T^2 = -\ [(\partial H/\partial P)_T\mathrm{d}P + (\partial H/\partial T)_P\mathrm{d}T]/T - \overline{L}_M\mathrm{d}T/T^2$$

The entropy change of the system itself in this process is the difference in molal entropy, S, of the substance in the two compartments. We have, therefore, $\delta S_S = \mathrm{d}S = (\partial S/\partial T)_P\mathrm{d}T + (\partial S/\partial P)_T\mathrm{d}P$. These expressions,

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[1] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 88.

substituted in (1) give, as a general condition for equilibrium in systems of this type,

$$dP/dT = -\bar{L}_M/T(\partial F/\partial P)_T \tag{2}$$

In this equation F represents the molal free energy of the substance. For perfect gases Equation 2 reduces to

$$d\,ln\,P/dT = -\bar{L}_M/RT^2 \tag{3}$$

For liquids (2) becomes

$$dP/dT = -\bar{L}_M/VT \tag{4}$$

where V represents molal volume of the liquid. It will be observed as an important characteristic of these systems that, unlike those usually isothermal, the equilibrium in them is determined by the properties of the membrane as well as of the substances considered.

In general $\bar{L}_M$ is a function of temperature. This does not affect Equations 2, 3 or 4 directly, since the entropy effects (in the reservoirs) arising from the variation of the heat of solution in a differential temperature interval are of the second order. In the integration of these equations, however, the change in $\bar{L}$ with temperature may, if it is important, be taken into account in the usual way by means of terms involving specific heats.

It will be noted, further, that the above equations neglect entirely the irreversible effects. With the assumption of non-conducting membranes which was made this is doubtless quite justifiable. It appears permissible to neglect these effects in most actual cases also. Many of the real membranes which might be used are very poor conductors, and in those which are not, the process of conduction probably has little connection with the motion through them of the dissolved substances.

In systems in which heat is evolved when the substance dissolves in the saturated membrane, it follows from (3) and (4) that if the pressure is initially the same on the two sides of the wall, the material must flow from the colder to the warmer compartment. This qualitative effect was found in experiments with various gases and liquids by Lippmann[2] who gave the name thermal endosmosis to the phenomenon. From his results it appears that $\bar{L}_M$ is negative in every system studied by him. Equilibrium data sufficient to permit any conclusion more general than this were, however, not published.

Osmotic Temperature.—The idea that the decrease in activity of a solvent caused by the presence of a solute might be compensated by an increase in temperature as well as by an increase in pressure (as in the usual osmotic equilibrium) has often been discussed.[3] The temperature difference necessary to maintain equilibrium of the solvent in a solution with that in a more dilute solution (or the pure solvent) at a lower temperature has

[2] Lippmann, *Compt. rend.*, **145**, 104, 105 (1907).

[3] For example, Kohnstamm, *Proc. Akad. Wetenschappen Amsterdam*, **13**, 778 (1911).

been called the "osmotic temperature." This conception may be investigated by the methods employed above.

Imagine the compartments of the preceding section to be filled with a solution of two components, A and B, to one of which (A) the dividing membrane is permeable. Imagine the pressure to be maintained the same and constant in each compartment and a temperature difference $\mathrm{d}T$ to be established. Consider the transfer, under equilibrium conditions, of one mole of A through the membrane from the colder to the warmer compartment. The heat absorbed by the system from the reservoirs in this process is the difference in partial molal heat content, $\overline{H}_{\mathrm{A}}$, of substance A in the two compartments. This difference, $\mathrm{d}\overline{H}_{\mathrm{A}}$, arises from the temperature difference and from any difference in the mole fraction, N_{A}, which may exist at equilibrium. The heat transferred from the colder to the warmer reservoir is now $\overline{H}_{\mathrm{M}}-\overline{H}_{\mathrm{A}}$, where $\overline{H}_{\mathrm{M}}$ represents the partial molal heat content of A in the membrane in equilibrium with the solution. The entropy change of the reservoirs is, therefore,

$$\begin{aligned}\delta S_{\mathrm{R}} &= -\mathrm{d}\overline{H}_{\mathrm{A}}/T + (\overline{H}_{\mathrm{A}} - \overline{H}_{\mathrm{M}})\mathrm{d}T/T^2 \\ &= -(1/T)[(\partial\overline{H}_{\mathrm{A}}/\partial T)_{P,N}\mathrm{d}T + (\partial\overline{H}_{\mathrm{A}}/\partial N_{\mathrm{A}})_{P,T}\mathrm{d}N_{\mathrm{A}}] + (\overline{H}_{\mathrm{A}} - \overline{H}_{\mathrm{M}})\mathrm{d}T/T^2\end{aligned}$$

The entropy change of the system is the difference in partial molal entropy, $\overline{S}_{\mathrm{A}}$, of A in the two states. That is,

$$\delta S_{\mathrm{S}} = \mathrm{d}\overline{S}_{\mathrm{A}} = (\partial\overline{S}_{\mathrm{A}}/\partial T)_{P,N}\mathrm{d}T + (\partial\overline{S}_{\mathrm{A}}/\partial N_{\mathrm{A}})_{P,T}\mathrm{d}N_{\mathrm{A}}$$

The insertion of these values of δS_{R} and δS_{S} in (1) leads to the equation

$$\mathrm{d}N_{\mathrm{A}}/\mathrm{d}T = (\overline{H}_{\mathrm{A}} - \overline{H}_{\mathrm{M}})/T(\partial\overline{F}_{\mathrm{A}}/\partial N_{\mathrm{A}})_{P,T} \qquad (5)$$

in which $\overline{F}_{\mathrm{A}}$ represents the partial molal free energy of A. For a perfect solution $(\partial\overline{F}_{\mathrm{A}}/\partial N_{\mathrm{A}}) = RT/N_{\mathrm{A}}$ and there results

$$\mathrm{d}\ ln\ N_{\mathrm{A}}/\mathrm{d}T = (\overline{H}_{\mathrm{A}} - \overline{H}_{\mathrm{M}})/RT^2 \qquad (6)$$

A significant feature of the conception under discussion appears from the foregoing development. The osmotic temperature of a component of any solution depends upon the specific properties of the membrane employed. Furthermore, resort to ideal membranes showing no heat effects fails to generalize the concept, for it then appears that, in perfect solutions, equilibrium can result only when there is no difference in composition of the solution in the two compartments. The conception, therefore, has no general meaning or application in thermodynamics.

The Soret Effect: Thermal Diffusion.—A solution in which there is a gradient in temperature shows a gradient in composition also. This phenomenon was first experimentally studied in certain aqueous solutions by Soret.[4] In gaseous solutions its existence was predicted from kinetic theory by Enskog[5] and by Chapman,[6] and experimentally verified by Chap-

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[4] Soret, *Ann. chim. phys.*, [5] **22**, 293 (1881).

[5] Enskog, *Physik. Z.*, **12**, 538 (1911); *Ann. Physik*, **38**, 750 (1912).

[6] Chapman, *Proc. Roy. Soc.*, (London), **93A**, 1 (1916); *Phil. Mag.*, **34**, 146 (1917); **38**, 182 (1919).

man and Dootson,[7] Ibbs,[8] and Elliott and Masson, who refer to it as thermal diffusion. Its thermodynamic investigation will now be undertaken.

Consider the transfer (spontaneously occurring under conditions very close to equilibrium) of a mole of component A of a binary solution between regions of differential temperature difference in an infinitely large tube. The withdrawal of A from the solution at T produces an infinitesimal change in concentration. In the general case this change in concentration may be assumed to give rise to a corresponding change in the intensity of intermolecular forces. The adjustments occasioned by the change in forces, extending throughout the infinite quantity of solution, may result in a finite heat effect. Assuming, therefore, a quantity of heat $\overline{Q}_{\mathrm{A}}$ to be absorbed from the reservoir at T, and given out at $T + \mathrm{d}T$, where the reverse changes must occur, the change in entropy in the reservoirs from this cause is $\overline{Q}_{\mathrm{A}}\mathrm{d}T/T^2$. In addition there is the exchange of entropy between the reservoirs and system of $\mathrm{d}\overline{H}_{\mathrm{A}}/T$. The total change in entropy of the reservoirs is then

$$\begin{aligned}\delta S_{\mathrm{R}} &= -\mathrm{d}\overline{H}_{\mathrm{A}}/T - \overline{Q}_{\mathrm{A}}\mathrm{d}T/T^2 \\ &= -(1/T)[(\partial\overline{H}_{\mathrm{A}}/\partial T)_{P,N}\mathrm{d}T + (\partial\overline{H}_{\mathrm{A}}/\partial N_{\mathrm{A}})_{P,T}\mathrm{d}N_{\mathrm{A}}] - \overline{Q}_{\mathrm{A}}\mathrm{d}T/T^2\end{aligned}$$

The entropy change of the system remains

$$\delta S_{\mathrm{S}} = \mathrm{d}\overline{S}_{\mathrm{A}} = (\partial\overline{S}_{\mathrm{A}}/\partial T)_{P,N}\mathrm{d}T + (\partial\overline{S}_{\mathrm{A}}/\partial N_{\mathrm{A}})_{P,T}\mathrm{d}N_{\mathrm{A}}$$

Substituted in (1) these reduce to

$$(\partial\overline{F}_{\mathrm{A}}/\partial N_{\mathrm{A}})_{P,T}\mathrm{d}N_{\mathrm{A}} = -\overline{Q}_{\mathrm{A}}\mathrm{d}T/T \tag{7}$$

As ordinarily carried out experiments on the Soret effect include a volume constraint requiring $\overline{V}_{\mathrm{A}}/\overline{V}_{\mathrm{B}}$ moles of B to be transferred in reverse direction to the transfer of the mole of A. It may be shown, however, that the equations with the constraint introduced ultimately reduce to (7) which remains, therefore, the final equilibrium condition.

The quantity $\overline{Q}_{\mathrm{A}}$ in Equation 7 has never been determined experimentally. It cannot be obtained from the usual heats of dilution or relative molal heat contents because these are all dependent upon some arbitrary reference state. A few facts concerning it may, however, be stated. In solutions whose internal dynamic conditions are independent of concentration, that is, in perfect solutions and dilute solutions, $\overline{Q}_{\mathrm{A}}$ is zero. In such solutions the Soret effect, as governed by Equation 7, is therefore zero. In non-ideal solutions $\overline{Q}_{\mathrm{A}}$ must reach a maximum at some finite concentration, at which point the first member of (7) must also have a maximum. Except for abnormal variations in $(\partial\overline{F}_{\mathrm{A}}/\partial N_{\mathrm{A}})$, the Soret differences in concentration themselves should be greatest at this point.

The actual systems in which the Soret effect occurs perhaps depart more widely from the ideal than do many of the others considered here.

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[7] Chapman and Dootson, *Phil. Mag.*, **33**, 248 (1917).

[8] Ibbs, *Proc. Roy. Soc.*, (London), **99A**, 385 (1921). Elliott and Masson, *ibid.*, **108A**, 378 (1925).

It is probable, therefore, that the irreversible aspects are not without appreciable influence upon the phenomenon. In the case of pure gases at low pressures discussed in the introduction, the pressure effect was ascribed entirely to irreversible processes. In gaseous solutions at ordinary pressures, very distinct Soret concentration gradients are found experimentally. As these solutions are as nearly perfect as may ordinarily be obtained, and since the effect is qualitatively predictable merely from the relative molecular weights, it follows that irreversible processes are in large part responsible here also. Liquid solutions present a more difficult problem. It seems likely that in them irreversible effects may be less important. Some indication as to whether this is true may perhaps be obtained by study of nearly perfect solutions of constituents of large difference in molecular weight. Until more definite information is available it appears desirable to consider all actual Soret effects as composed of a reversible and an irreversible part, either of which may be negligible in specific instances.

In the derivation above, the pressure was assumed to be constant throughout the tube. In many instances this condition is, no doubt, fulfilled closely. In dilute gases it is not, and even at ordinary pressures a finite, but small, pressure gradient must remain. In the later work of this paper, the concentration and pressure changes are conveniently replaced by the corresponding free energy changes. In accordance with these and the above ideas, therefore, Equation 7 may be generalized to define a reversible Soret coefficient, k_r, as follows.

$$k_r = [(\partial \bar{F}_A/\partial N_A)_{P,T} dN_A + (\partial \bar{F}_A/\partial P)_{N,T} dP]/dT = d\bar{F}_A/dT = -\bar{Q}_A/T \qquad (8a)$$

The irreversible coefficient, k_i, may be evaluated in terms of the changes $(dN_A)_i$, $(dP)_i$ and $(d\bar{F}_A)_i$ produced by irreversible processes and will be written

$$k_i = [(\partial \bar{F}_A/dN_A)_{P,T}(dN_A)_i + (\partial \bar{F}_A/\partial P)_{N,T}(dP)_i]/dT = (d\bar{F}_A)_i/dT \qquad (8b)$$

The Soret coefficient that will be employed in all of the following work will be designated s and is

$$s = k_r + k_i \qquad (9)$$

The coefficients involved in Equation 9 are of course functions of T, N and P, although in many applications they may be considered constant without large error. It is also understood that at present they are determinable only empirically.

Heterogeneous Systems

Systems of Two Components.—The treatment of the numerous systems of this class which may occur will be illustrated by a typical example. Consider liquid solutions of two volatile components A and B at different temperatures in equilibrium through a connecting vapor phase, in which the temperature gradient lies. The transfer of a mole of either substance is now accompanied by the transfer of a quantity of heat equal to its heat of vaporization from the solution, $\Delta\overline{H}$, between the reservoirs, in addition to the exchange of an infinitesimal quantity of heat between reservoirs and system. Considering both components and using the known relations between the differential coefficients, there results as the equation governing equilibrium

$$[(1/1 - N_{\mathrm{A}})](\partial\overline{F}_{\mathrm{A}}/\partial N_{\mathrm{A}})_{P,T}\mathrm{d}N_{\mathrm{A}} = (\Delta\overline{H}_{\mathrm{B}} - \Delta\overline{H}_{\mathrm{A}})\mathrm{d}T/T \qquad (10)$$

If the solution is perfect, Equation 10 becomes

$$\mathrm{d}N_{\mathrm{A}}/N_{\mathrm{A}}(1 - N_{\mathrm{A}}) = (\Delta\overline{H}_{\mathrm{B}} - \Delta\overline{H}_{\mathrm{A}})\mathrm{d}T/RT^2 \qquad (11)$$

In perfect solutions the heats of vaporization are functions of temperature only and, since they vary little with the temperature, Equation 11 may be integrated considering them constant and equal to the heat absorbed, ΔH, in vaporization of the pure liquids. The result is

$$ln[Na_{\mathrm{A}_2}(1 - N_{\mathrm{A}_1})/N_{\mathrm{A}_1}(1 - N_{\mathrm{A}_2})] = (1/T_1 - 1/T_2)(\Delta H_{\mathrm{B}} - \Delta H_{\mathrm{A}})/R \qquad (12)$$

Equilibrium may exist only in systems that satisfy Equation 12. It may be noted that some systems originally not in equilibrium would attain the equilibrium state by distillation, but that this need not be true for all systems. In some cases it would appear that distillation might continue until the exhaustion of the high temperature container without approach to the equilibrium compositions.

If only one of the components is appreciably volatile, the usual development gives, if A is the volatile component in a perfect solution,

$$\mathrm{d}\ ln\ N_{\mathrm{A}}/\mathrm{d}T = -\Delta\overline{H}_{\mathrm{A}}/RT^2 \qquad (13)$$

Distillation in this case will always result in equilibrium, regardless of the initial compositions of the solutions.

In the above discussions the Soret effect in the vapor is assumed to be negligible. When it is not negligible the equation of condition with respect to equilibrium of component A takes the form $(\partial\overline{F}_{\mathrm{A}}/\partial N_{\mathrm{A}})\mathrm{d}N_{\mathrm{A}} = -\Delta\overline{H}_{\mathrm{A}}\mathrm{d}T/T + s_{\mathrm{A}}\mathrm{d}T$. In this equation s_{A} is the Soret coefficient of A in the gas phase in equilibrium at temperature T with liquid of mole fraction N_{A}. If the cold compartment is always considered to contain liquid of mole fraction N_{A_1} at temperature T_1, s_{A} is nearly independent of the variation of N_{A} in the hot bulb. Combination of the above expression with the corresponding one for component B and integration on the assumption of perfect solutions give as the corrected form of (12)

$$ln\,[N_{\mathrm{A}_2}(1 - N_{\mathrm{A}_1})/N_{\mathrm{A}_1}(1 - N_{\mathrm{A}_2})] = (1/T_1 - 1/T_2)(\Delta H_{\mathrm{B}} - \Delta H_{\mathrm{A}})/R + [s_{\mathrm{A}}\ ln\ (T_2/T_1)]/R\ (1 - N_{\mathrm{A}_1}) \qquad (14)$$

The Thermocouple.—A thermocouple consisting of metals M_1 and M_2 with junctions at T and $T + \mathrm{d}T$, as in Fig. 1, may be regarded as a two-phase system of the three components M_1^+, M_2^+ and E^-. The electrons, E^-, are mobile, while the ions of the metals do not move appreciably under an electric force. If a mole of electrons, in an infinitely large couple, be transferred under equilibrium conditions through the path *a b c d*, the entropy changes may be analyzed as in the preceding sections. Calling the partial molal heat content of electrons[9] in the two metals $\overline{H}_E'$ and $\overline{H}_E''$, respectively, the heat absorbed at the junction *b* and given out at *c* is $\overline{H}_E' - \overline{H}_E''$, or $\Delta\overline{H}_E$. The heat exchange between system and reservoir is $\mathrm{d}\overline{H}_E'$. We write, therefore,

$$\delta S_R = \Delta\overline{H}_E \mathrm{d}T/T^2 - \mathrm{d}\overline{H}_E'/T$$

and

$$\delta S_S = \mathrm{d}\overline{S}_E'.$$

Noting that $\mathrm{d}\overline{H}_E'$ and $\mathrm{d}\overline{S}_E'$ depend only upon the difference in "mole fraction of electrons," N_E', in the regions *a* and *d*, we obtain by substituting in (1)

$$(\partial\overline{F}_E'/\partial N_E')_T \mathrm{d}N_E' = \Delta\overline{H}_E \mathrm{d}T/T \qquad (15)$$

The coefficient in the first member of Equation 15 cannot be evaluated at present. The equations, therefore, cannot be used to study the composition difference in M_1 at *a* and *d*. The first member of the equation is equal, however, simply to $\mathrm{d}\overline{F}_E'$, and this in turn to the work which could be obtained on transfer of a mole of electrons directly between *d* and *a*. It is the e.m.f., $\mathrm{d}E$, of the couple. The heat effect at *b* corresponds to equilibrium conditions and is equal to $T\Delta\overline{S}_E$. We obtain, therefore,

$$\mathrm{d}E/\mathrm{d}T = \Delta\overline{H}_E/T = \Delta\overline{S}_E \qquad (16)$$

Equation 16 is the same as that which results from the treatment of the thermocouple as a heat engine, as in the work of Kelvin. It is to be noted that the heat and entropy terms in it refer to transfer of electrons between metals in contact equilibrium and, therefore, charged with respect to each other. They are not the same as, although they may be nearly equal to, the similar changes involving the "neutral" metals (consisting of equivalent quantities of ions and electrons).

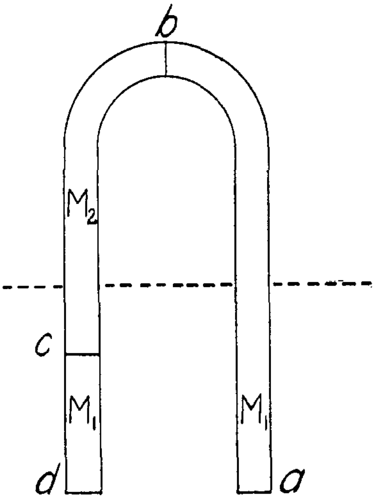

Fig. 1.—Diagram of a thermocouple.

The thermo-electric power, $\mathrm{d}E/\mathrm{d}T$, of the differential couple considered above changes with temperature, due not only to the temperature change as such, but in part to the shifting equilibrium compositions (charges) of the metals. The specific-heat term involved in equations governing this effect refers, therefore, to the difference in specific heats of the electrons in the two metals under conditions of contact equilibrium. Representing this as $\Delta\overline{C}_E$, we then have

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[9] The character of the partial molal quantities relating to the electron is discussed in a previous paper, This Journal, **48**, 552 (1926).

$$\mathrm{d}(\Delta\bar{S}_{\mathrm{E}})/\mathrm{d}T = \Delta\bar{C}_{\mathrm{E}}/T$$

Integration and combination with (16) lead to

$$(\mathrm{d}E/\mathrm{d}T)_{T_2} = (\Delta\bar{S}_{\mathrm{E}})_{T_1} + \int_{T_1}^{T_2} \Delta\bar{C}_{\mathrm{E}}\mathrm{d}\ ln\ T \tag{17}$$

This equation is also familiar in form.

The development leading to Equations 16 and 17 neglects entirely the Soret phenomenon. The Soret effect, no doubt, exists in metals, as previously pointed out.[9] The experiments[10] which support this idea are of dates very early in the history of thermo-electricity and are, perhaps, of doubtful value. Nevertheless, if the electrons play the important part in thermal conduction which is usually assigned to them, a considerable Soret effect, in the sense defined in Equation 8b alone, may reasonably be expected. As affecting Equation 16 it is clear that the effect in the two metals is likely to be partly compensating. The difference ($s_{\mathrm{E}}'' - s_{\mathrm{E}}' = \Delta s_{\mathrm{E}}$) of the coefficient in the two metals may often be negligible as compared with the thermo-electric power that is due to the Peltier heat. Since so little is known concerning this point, it appears desirable to recognize, as in the following equation, the possibility that the effect is appreciable.

$$\mathrm{d}E/\mathrm{d}T = \Delta\bar{S}_{\mathrm{E}} - \Delta s_{\mathrm{E}} \tag{18}$$

The irreversible process affects the validity of Equation 17 relating to a differential couple, in that Δs_{E}, plus its change with temperature (presumably negligible), must be added. Equations 16, 17 and 18 give the values of $\mathrm{d}E/\mathrm{d}T$ for thermocouples with differential temperature differences at the particular temperatures indicated. An equation of the form of (17) also applies to any couple in which T_1 is the fixed temperature of one junction and T_2 the variable temperature of the other. In such systems, however, there is a gradient in charge along the wires caused by the Soret phenomenon, and it is necessary to use the difference, $\Delta\sigma$, in the reversible Thomson effects, in place of $\Delta\bar{C}_{\mathrm{E}}$ in the equation. This point has been discussed in the former paper.[9]

The following statements summarize separately the irreversible effects which may surely be said to be present, though their magnitudes are unknown and no doubt often small. In the differential couple the thermal conduction simply impresses an extra e.m.f. upon that due to the reversible transfer of heat, without affecting the latter. The change with temperature of $\mathrm{d}E/\mathrm{d}T$ for a differential couple is irregular only in so far as the Soret coefficients are affected. In the non-differential couples the irreversible process impresses a composition (or charge) gradient upon the system which has an effect upon the reversible heat transfer, just as a similar gradient produced by application of pressure would have.

Non-electric Thermocouples.—If the metals M_1 and M_2 of Fig. 1

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[10] Lardner and Walker, "Electricity and Magnetism," Longmans, London, **1844**, vol. II, p. 533.

be replaced by any two solutions having a common solute dispersed in immiscible solvents, a system entirely analogous in kind to the thermocouple, although of quite a different type, is obtained. Some of the points of interest concerning thermocouples would appear to be more susceptible of study in these than in the electric couples since the coefficient $(\partial \bar{F}/\partial N)$ might be known in many instances. Preliminary experiments performed in this Laboratory by M. J. Pollissar with this end in view were rendered invalid by a rather obvious and practically important difference of the solutions employed as compared with metals. The solvent molecules in ordinary solution have far higher diffusion rates than the atoms of solid metals. By a relatively rapid process of "distillation" at the hot boundary, the system continues to change toward one in which there is but a single boundary. This difficulty might be overcome by means of membranes permeable only to the solute placed at the boundaries *b* and *c*. No systematic search for such membranes has yet been made. Thermocouples of this kind are, therefore, most useful at present as conceptions in which is offered a complete analogy with the electric couples, involving quantities which seem more familiar than those pertaining to electrons.

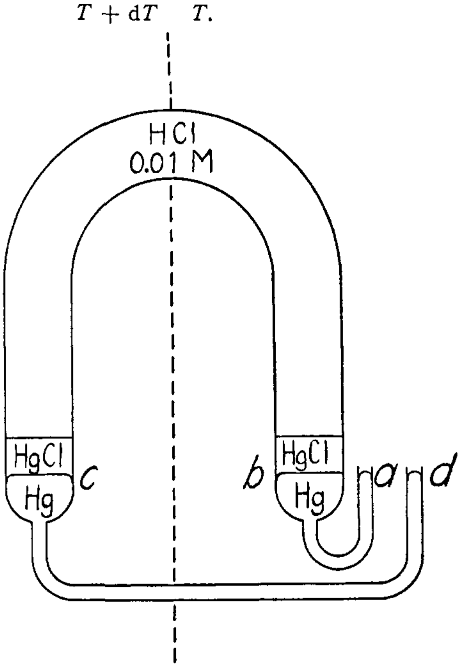

Fig. 2.—Diagram of a thermocell.

Thermocells.—Gockel,[11] Coggeshall[12] and Richards[13] have measured e.m.f.'s in a number of cells similar to that shown in Fig. 2. Systems of this type transform thermal into electrical energy, and in other fundamental aspects are similar to thermocouples and for many purposes are more conveniently classed with them than with cells. The treatment outlined in the preceding is readily applicable to these "thermocells."

At equilibrium, electrons will be at different concentrations (but the same temperature) in the metal at *a* and at *d* in Fig. 2. When a mole of

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[11] Gockel, *Wied. Ann.*, **24**, 618 (1885).

[12] Coggeshall, *Z. physik. Chem.*, **17**, 62 (1895).

[13] Richards, *ibid.*, **24**, 39 (1897).

electrons is used up from the mercury in *ab* and produced at *c* by the reversible electrode processes and then transferred to *d*, certain entropy changes occur. If these are formulated in the usual way, it is found that only two factors are of final significance, that is, are not eliminated in combining δS_R and δS_S in Equation 1. These two factors are the difference, $d\bar{F}_E$, between the partial molal free energies of electrons in the metal at *d* and at *a*, and the heat absorbed in the electrode reaction at *c*. The equation for the latter reaction in the example given may be written

$$\text{Cl}^- \ (0.01\ M\ \text{HCl}) + \text{Hg} = \text{HgCl} + \text{E}^- \ (\text{Hg}) \qquad \text{(I)}$$

Since the reaction occurs under equilibrium conditions, the heat effect in it is equal to $T\Delta S_I$, where ΔS_I is the increase in entropy of the system accompanying Reaction I. The relation involving these quantities which is finally obtained is

$$d\bar{F}_E/dT = dE/dT = \Delta S_I \qquad (19)$$

In this equation it will be observed that the sign of the electromotive force is given as positive if the positive current is from the warm to the cold electrode through the cell. The Soret effect is assumed to be negligible in this development.

The heat effect in Reaction I is no doubt directly determinable experimentally (though under irreversible conditions, so that only approximate identity with $T\Delta S_I$ might be claimed) by methods devised for the study of Peltier heats. It may obviously be obtained approximately from e.m.f. measurements with the aid of (19). By using the known entropies of calomel and mercury and neglecting that of the electrons in mercury, the partial molal entropy of chloride ion might, therefore, be calculated. Moreover, if one entropy change like ΔS_I is known, together with those of the complete reactions in a series of (isothermal) cells having some electrodes in common, the entropy changes of all the other half reactions will be known. For example, combining Reaction I with the following,

$$\text{HgCl} + \tfrac{1}{2}\text{H}_2 = \text{Hg} + \text{H}^+ \ (0.01\ M\ \text{HCl}) + \text{Cl}^- \ (0.01\ M\ \text{HCl}) \qquad \text{(II)}$$

$$\tfrac{1}{2}\text{H}_2 = \text{H}^+ \ (0.01\ M\ \text{HCl}) + \text{E}^- \ (\text{Pt}) \qquad \text{(III)}$$

$$\text{E}^- \ (\text{Pt}) = \text{E}^- \ (\text{Hg}) \qquad \text{(IV)}$$

it is found that

$$\Delta S_{III} = \Delta S_I + \Delta S_{II} - \Delta S_{IV} \qquad (20)$$

The term ΔS_{IV} of (20) may be neglected or determined experimentally, resulting in a value for ΔS of the half reaction represented by (III).

Summary

The first and second laws are applied to the deduction of the equilibrium conditions in a number of interesting non-isothermal systems. The equilibrium pressures in systems exhibiting thermal endosmosis are shown to depend upon the heat of solution of the substance in the dividing membrane. The conception of osmotic temperature is lacking in significance because it depends upon the properties of the membrane as well as of the solution. The Soret effect, or thermal diffusion, in perfect solutions is considered to be entirely the result of irreversible processes and not to represent a thermodynamic equilibrium. In imperfect solutions it consists in part of a reversible effect, equations for which are derived. The compositions of solutions at different temperatures connected with each other through a vapor phase are discussed as examples of heterogeneous non-isothermal equilibria. The equations of the thermocouple are deduced. The precise significance of the quantities in the thermo-electric equations is stated, and the way in which the reversible and irreversible Soret effects may be expected to influence the phenomena is indicated. Non-electric thermocouples furnishing interesting analogies to the electric, are considered. Finally, certain thermocells, consisting of similar electrodes at different temperatures, are discussed.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF WASHINGTON AND LEE UNIVERSITY]

FLUOREMETRY. II.[1] THE RELATION BETWEEN FLUORESCENCE AND HYDROGEN-ION CONCENTRATION[2]

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While chemical literature abounds with references to the fact that acid or alkali must be added in order to develop maximum fluorescence in solutions of many different substances,[3] little or no attention seems to have been paid to the optimum hydrogen-ion concentration.[4] Having observed that for certain substances there appeared to be a characteristic and rather narrow range of hydrogen-ion concentration within which the change in intensity of fluorescence is most marked, this effect has been investigated with the results here reported.

Comparisons of the relative intensities of fluorescence were made by the method previously described by one of us,[1] which should be consulted for details.[5] Aqueous solutions of colorless substances were uniformly

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[1] Desha, THIS JOURNAL, **42**, 1350 (1920).

[2] Presented in substance before the Organic Section of the American Chemical Society at the Baltimore Meeting, April 10, 1925.

[3] Among others: (a) Lepine, *Ann. Phys.*, [IX] **4**, 208 (1915). (b) Kauffmann, *Ann.*, **344**, 30 (1906). (c) Winther, *Z. Elektrochem.*, **19**, 389 (1913). (d) Stark and Lipp, *Z. physik. Chem.*, **86**, 36 (1913). (e) Nichols and Merritt, "Studies in Luminescence," Publication No. 152, Carnegie Institution of Washington, **1912.**

[4] Aside from the articles of Ley and his co-workers (Ref. 17) the closest approach to a quantitative statement we have been able to find is that of Mecklenburg and Valentiner [*Physik. Z.*, **15**, 267 (1914); *C. A.*, **8**, 1695 (1914)].

[5] In order to avoid a misunderstanding as to the nature of the measurements re-