various screening constants are self-consistent. Excellent agreement with experiment is found also for the normal alkaline-earth oxides, sulfides selenides and tellurides with the sodium chloride structure, and for the normal alkaline-earth halides, alkali oxides and sulfides and quadrivalent oxides with the fluorite and rutile structures.

In lithium chloride, bromide and iodide, magnesium sulfide and selenide and strontium chloride the inter-atomic distances depend on the anion radius alone, for the anions are in mutual contact; the observed anion-anion distances agree satisfactorily with the calculated radii. In lithium fluoride, sodium chloride, bromide and iodide and magnesium oxide the observed anion-cation distances are larger than those calculated because of double repulsion; the anions are approaching mutual contact, and the repulsive forces between them as well as those between anion and cation are operative.

In crystals containing eighteen-shell cations and not easily deformable anions (F^-), the agreement between the calculated and observed radii is good; for deformable anions ($O^=$, Cl^-, Br^-, I^-), the observed inter-atomic distances are shorter than those calculated.

The theoretical result is derived that ionic compounds MX_2 will crystallize with the fluorite structure if the radius ratio R_M/R_X is greater than 0.65, and with the rutile (or anatase) structure if it is less. This result is experimentally substantiated.

It is also shown that theoretically a binary compound should have the sphalerite or wurzite structure instead of the sodium chloride structure if the radius ratio is less than 0.33. The oxide, sulfide, selenide and telluride of beryllium conform to this requirement, and are to be considered as ionic crystals. It is found, however, that such "tetrahedral" crystals are particularly apt to show deformation, and it is suggested that this is a tendency of the anion to share an electron pair with each cation.

A brief discussion of crystals containing complex ions is given.

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NOTES

Colloidal Phenomena in Dye Solutions.—A remarkable instance of colloidal behavior was observed during a recent investigation of concentration effects. If an aqueous solution of rosaniline hydrochloride is treated with phenol an addition product, $C_{20}H_{20}N_3Cl.2C_6H_5OH$, is formed which does not differ very greatly from the dye itself in general properties and behavior. If rosaniline base is fused with phenol, however, rosaniline phenolate, $C_{20}H_{20}N_3.C_6H_5O$, is obtained. This phenolate is only slightly soluble in water and its aqueous solutions are extremely colloidal. If a dilute, aqueous solution is diluted with an equal volume of water the resulting solution would be expected to show only half the original color. In point of fact such dilution actually increases the color in a material degree owing to the dissociation of solute molecules which accompanies the dilution. The effect of similar dilution with alcohol is even more marked. The color differences of such solutions become greatly accentuated on standing. The color of the undiluted aqueous solution decreases at a relatively rapid rate, owing to further progressive association of solute molecules. The corresponding alteration in the dilute aqueous solution is much less and the dilute alcoholic solution gives but little indication of physical instability. The phenomenon appears suitable for classroom demonstration.

Table I gives the spectrophotometric measurements obtained in such tests. The values recorded are the extinction coefficients measured at the absorption maxima of the respective solutions in a 1cm. layer. In the aqueous solutions the maximum absorption was found at 542 mμ and in the aqueous alcoholic solution at 548 mμ. The original aqueous solution was prepared by saturating distilled water with phenolate at room temperature.

TABLE I

EXTINCTION COEFFICIENTS AT ABSORPTION MAXIMA

	Original aqueous soln.	Original soln. diluted with an equal volume of water	Original soln. diluted with an equal volume of alcohol
Immediate absorption	0.54	0.69	0.88
After 1 day	.34	.63	.875
After 6 days	.16	.41	.85

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Determination of Excess of Alkali in Hypochlorite Solutions.—The procedure is based upon the removal of the hypochlorite by means of a reducing agent, giving removable and non-interfering compounds. The hypochlorites are removed as indicated in the equation $2Ni(OH)_2 + NaOCl + H_2O = NaCl + 2Ni(OH)_3$. The change in condition from nickelous to nickelic is indicated by the change in color from light green to black. Inasmuch as both nickel hydroxides are insoluble in water, they can be completely removed before titrating.

Ferrous, manganous and cobaltous hydroxides react in like manner. Nickelous hydroxide, however, was found to be best for the purpose, due to its stability and insolubility.

The presence of ammonium salts vitiates this method.

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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 $p\mathrm{d}v$, where $\mathrm{d}v = \mathrm{d}nRT/p$; hence, the work is $\mathrm{d}nRT$. In carrying the dn moles through the temperature gradient a further expansion gives $\mathrm{d}nR(T_2-T_1)$ as the work done and on introducing the gas into the container at T_2 the work $-\mathrm{d}nRT_2$ 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, 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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