them against the normal calomel electrodes 3 and 10, which were kept at 25°. The electrodes were connected by means of a glass-tube salt-bridge 30 cm. long and 7 mm. in diameter having cotton plugs in the ends and filled with saturated potassium chloride solution. The average e.m.f. of these cells was 0.0377 volt at 30°, 0.0388 volt at 25° and 0.0398 volt at 20°. This gives as the electrode potential of these saturated calomel electrodes on the hydrogen scale —0.2457 volt at 30°, —0.2446 volt at 25°, and —0.2436 volt at 20°. This gives a temperature coefficient of 0.0002 volt per degree. Fales and Mudge obtained the same value.

Summary

A method of making electrolytic mercurous chloride directly in saturated potassium chloride is outlined.

The advantages of the method are that it gives a dependable quality of calomel mixed with finely divided mercury and it avoids tedious washing and shaking processes and the resultant uncertainties.

The e.m.f. of the cell, Hg + *HgCl*, HgCl in satd. KCl, HgCl in *N* KCl, *HgCl* + Hg is 0.0388 volt at 25°.

The electrode potential of the saturated potassium chloride calomel half-cell is —0.2446 volt at 25° on the hydrogen scale.

The temperature coefficient of the saturated potassium chloride calomel half-cell is 0.0002 volt per degree for the temperature range 20° to 30°.

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EQUILIBRIUM PRESSURES OF INDIVIDUAL GASES IN MIXTURES AND THE MASS-ACTION LAW FOR GASES

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To a surprising degree the ordinary mass-action law, based on the properties of ideal gases, suffices for the treatment of measured gas equilibria. However, the recent work of Larson and Dodge[1] on the Haber equilibrium at high pressures has shown an important deviation from the consequences of the ideal-gas laws, namely, that the equilibrium constant, K_p, at any temperature is found to be a function of the pressure. In the absence of data to the contrary, we must now believe that K_p will vary if the concentrations are varied at constant temperature and pressure —in other words, that K_p is not strictly constant with respect to any change

[1] Larson and Dodge, THIS JOURNAL, **45**, 2918 (1923); also a later paper by Larson, *ibid.*, **46**, 367 (1924).

of condition whatever. Such data can therefore be used, in principle, for testing assumed forms of the mass-action law.

At present we are unable to test without hypothesis even the thermodynamic consistency of data of this type. Existing pressure-volume-temperature data must be supplemented with hypotheses enabling us to pass from the properties of pure gases to those of mixtures. The fugacity rule of Lewis and Randall, which will be discussed below, contains this kind of hypothesis. The correlation of equilibrium data with equations of state is practically the mass-action problem, although the complete solution involves the untangling of implicit functions.

In practise, it is very laborious to carry out the calculations upon data secured for an equilibrium of the above type. The writer has already spent as much time as seems justifiable in view of the circumstances, without arriving at either a satisfactory thermodynamic correlation of the data or any ground for suspecting their accuracy. In the course of the study, however, certain simple considerations have become obvious which seem to merit publication because they are apparently not generally perceived. Furthermore, a simplified experimental attack on the problem has suggested itself, the theory of which presents again obvious, though perhaps novel, aspects.

Because of the various meanings of the term partial pressure, the term equilibrium pressure will be used in the following discussion to denote the pressure of a pure gas which is in equilibrium through a semi-permeable membrane with a system that contains the same gas in mixture with other gases and is at the same temperature. For greater clearness, when necessary, this pressure may be called the equilibrium pressure of the gas in the mixture. This introduces no danger of error, since two systems in equilibrium through semi-permeable membranes with the same pressure of pure gas would be in equilibrium with each other at the given temperature with respect to transfer of the given gas. The term vapor pressure has some advantages over equilibrium pressure, but is readily misunderstood.

For a thermodynamic derivation of a mass-action law a knowledge of the equations of state of the gases involved is not sufficient, even when supplemented with equations applying to the mixtures, but there is also needed some information or hypothesis concerning equilibrium pressures. In this statement, mass-action law means a relation containing concentrations determinable by analysis rather than equilibrium pressures, which would have to be determined by special equilibrium measurements. One of the few treatments of a mass-action law for real gases is that of Washburn.[2] It is worth while to emphasize that the mass-action laws under discussion in that treatment are relations containing "partial pressures" (our equilibrium pressures) rather than concentrations. The fact is not

[2] Washburn, This Journal, 32, 467 (1910), with especial reference to pp. 484–485.

pointed out that these pressures are not calculable from any rigorous equations given.[3]

In order to fill the corresponding gap existing in the fugacity treatment, Lewis and Randall suggested the rule,[4] from a partial analogy with Raoult's law, that the fugacity of a gas in a mixture (that is, the fugacity of the pure gas at the equilibrium pressure) is equal to its mole fraction in the mixture multiplied by its fugacity when pure at the temperature and total pressure of the mixture. That is,

$$f_e = x_1 f_p \tag{1}$$

This rule reduces at large volumes to the following,

$$p_e = x_1 p^* \tag{2}$$

where p^* is used, as by Lewis and Randall, to denote a very small pressure, and p_e denotes the corresponding equilibrium pressure.

Now this latter relation follows directly from our kinetic ideas of very dilute gases and it supplies sufficient information about equilibrium pressures to fill the gap, if we have equations of state, not only for pure gases but also for mixtures.

Let us start with a semi-permeable membrane exposed on one side to a gaseous mixture at a very low pressure p^* and of a mole fraction x_1 with respect to gas No. 1. On the other side is the pure gas 1 at the same temperature, and in equilibrium with the mixture through the membrane. Its pressure will then in general be denoted by p_e, and in this case, by our assumption, Equation 2 will hold.

Now let the pressure be increased on both sides, at constant temperature and constant composition of the mixture, in such a way as to preserve equilibrium. For maintenance of equilibrium the effect of pressure on the chemical potential, μ_1, must be the same on both sides. From the Gibbs equation,

$$\left(\frac{\mathrm{d}\mu_1}{\mathrm{d}p}\right)_{t,n_1,n_2\ldots} = \left(\frac{\mathrm{d}V}{\mathrm{d}n_1}\right)_{t,p,n_2,n_3\ldots} \tag{3}$$

the right-hand member of which reduces in the case of the pure gas to V/n_1, it follows then that

$$\frac{V}{n_1}\,\mathrm{d}p_e = \frac{\partial V}{\partial n_1}\,\mathrm{d}p \tag{4}$$

or, integrating,

$$\int_{p^*x_1}^{p_e} \frac{V}{n_1}\,\mathrm{d}p_e = \int_{p^*}^{p} \frac{\partial V}{\partial n_1}\,\mathrm{d}p \tag{5}$$

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[3] Equations 34 and 35 on p. 484 of Ref. 2, the simple mass-action law in terms of determinable quantities, depend not merely on Boyle's and an extended Avogadro's law but also on the assumption that $p_e = px_1$.

[4] (a) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923,** pp. 226–227; quoted in advance of publication by (b) Bichowsky, THIS JOURNAL, **44,** 116 (1922).

In the upper limits of the integral, p_e is the equilibrium pressure corresponding to the total pressure p of the mixture. If we add and subtract a term before integrating we get

$$\int_{p^*x_1}^{p_e} \frac{V}{n_1}\,\mathrm{d}p_e = \int_{p^*}^{p} \left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p + \int_{p^*}^{p} \frac{V}{n_1}\,\mathrm{d}p \qquad (6)$$

where the last term refers to the pure gas, but the p is the total pressure of the mixture. Again adding and subtracting a term, we have

$$\int_{p^*x_1}^{p_e} \frac{V}{n_1}\,\mathrm{d}p_e + RT\,ln\,p^*x_1 = \int_{p^*}^{p} \left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p + \int_{p^*}^{p} \frac{V}{n_1}\,\mathrm{d}p + RT\,ln\,p^* + RT\,ln\,x_1 \qquad (7)$$

and from the definition of fugacity it follows that

$$RT\,ln\,f_e = \int_{p^*}^{p} \left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p + RT\,ln\,f_p + RT\,ln\,x_1 \qquad (8)$$

This result coincides with the rule only if the integral equals zero. But the rule cannot be restricted to a particular value of the upper limit of the integral, nor to a particular concentration; therefore, the coefficient of dp must be zero for the rule to hold, as otherwise the integral could not be zero for various values of the upper limit. That is, whatever the composition may be, $\frac{\partial V}{\partial n_1} = \frac{V}{n_1}$, which states that the partial molal volume of the gas in the mixture is equal to the molal volume of the pure gas at the same temperature and pressure. In other words, the correctness of the Lewis and Randall rule depends upon the exactness of an analog of Dalton's law, which states that gases do not change in volume when mixed at constant temperature and pressure.

Lewis and Randall state that their generalized Raoult's law (which includes their rule as a special case) implies among other things that the volume and heat content are additive, but they do not indicate whether the exactness of their rule demands additivity of both volume and heat content or only one of these. Having shown above that it is sufficient if the volumes are additive, we may now indicate briefly a proof that if the volumes are additive the reversible heat of mixing will also be zero, so that the heat content will be additive and *vice versa.*

Consider again the system with a semi-permeable membrane discussed above. The system is analogous to a system discussed by Planck[5] consisting of vapor and salt solution and his Equation 176 can be applied to our case. This equation gives on multiplying both sides by ΔV

$$\Delta V \left(\frac{\mathrm{d}p_e}{\mathrm{d}T}\right)_c = \frac{\lambda_c}{T} \qquad (9)$$

Now $\left(\frac{\mathrm{d}p_e}{\mathrm{d}T}\right)_c$ is finite, so that if either ΔV or λ_c is zero, the other must

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[5] Planck, "Treatise on Thermodynamics," translated by Ogg, Longmans, Green and Co., **1903,** p. 197. It is also given, for instance, in MacDougall's "Thermodynamics and Chemistry," John Wiley and Sons, Inc., New York, **1921,** p. 168.

also be zero. The quantity λ_c is the heat absorbed when a small unit of mass is reversibly transferred from pure gas to a large quantity of mixture of composition c and can readily be shown to equal the difference of the partial heat contents per unit of mass.[6] ΔV is the corresponding volume increase.

Of the three propositions—exactness of the Lewis and Randall rule, additivity of volumes, additivity of heat content—proof of any one is sufficient to prove the other two, providing we assume Equation 2 when necessary.

It is known that the rule of additive volumes is not generally exact. To be sure, the large deviations reported by Fuchs[7] were calculated, and not directly observed and are possibly all wrong; at any rate, the writer has confirmed Dalton's law within the experimental error (about 0.2%) in the case of a mixture of oxygen and atmospheric nitrogen at room temperature and one atmosphere. On the other hand, Masson and Dolley[8] have found in careful experiments on binary mixtures of oxygen, argon, and ethylene that the law of additive partial volumes fails worse than Dalton's law itself.

The integral $\left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) dp$ can be evaluated graphically from an assumed equation of state for mixtures, the lower limit being taken as zero, since the area from zero to the pressure p^* is as small as we please to consider it. Van der Waals assumed that the equation of state for a mixture has the same form as for a pure gas, and that the constant b_m for the mixture may be approximately calculated by the rule

$$b_m = b_1x_1 + b_2x_2 + \dots\dots \tag{10}$$

Professor Keyes[9] has reason to believe, from unpublished calculations on the M. I. D. tables[10] for mixing nitrogen and hydrogen and from recent unpublished observations, that this rule may be correct when applied to all the constants[11] of the Keyes equation.

It is to be emphasized that a determination of the mixture equation will bring with it a complete solution of the mass-action law for compressed gases, unless we should be forced to give up the attractive assumption given above in Equation 2. Naturally, such a solution will be too complex mathematically to be of convenient use in the calculation of concentrations, since these enter in a highly implicit manner.

[6] Compare Ref. 4 a, pp. 89–90.

[7] Fuchs, *Z. physik. Chem.*, **92**, 641 (1917).

[8] Masson and Dolley, *Proc. Roy. Soc.*, **103A**, 524 (1923).

[9] F. G. Keyes, private communication.

[10] Munitions Inventions Dept., Ministry of Munitions, Nitrogen Products Committee, *Physical and Chemical Data of Nitrogen Compounds.* From the M. I. D. Research Laboratory, University College, London, **1918**.

[11] Including, of course, the square root of A in $A/(v + l)^2$ which root, as well as all the other constants, is expressed per mole or unit mass.

Using this mode of compounding the constants in the Keyes equation, the writer tried to check the Larson and Dodge data at 400°, after smoothing for temperature, but found that the use of the integrals $\left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p$ did not lead to an improved agreement. So much uncertainty attaches to the values of the constants in the equations for the pure gases, especially ammonia, that no conclusion could be drawn, save that it is unprofitable to apply so complicated a calculation to so complicated an equilibrium in the present state of our knowledge of the constants of the gases. Other hypotheses as to equilibrium pressure were tried—subject to the same uncertainties. One of these hypotheses was that

$$p_e = \int_0^{n_1} \left(\frac{\mathrm{d}p}{\mathrm{d}n_1}\right)_{t,v,n_2,n_3} \mathrm{d}n_1 \qquad (11)$$

where the right-hand side is the analog of the Gibbs partial volume and may well be designated partial pressure. In the integration the composition, temperature and volume are held constant, the number of molecules of all kinds being increased from zero until there are n_1 molecules of gas No. 1, for which gas p_e represents the equilibrium pressure. Applied to perfect gases it coincides with the ordinary ideal-gas partial pressure. It may be integrated in terms of known functions when applied to the van der Waals equation with the above mode of compounding constants. The results differed from the results of the first-mentioned calculations, even when the integration of Equation 11 was carried out graphically using the Keyes equation.

The method of testing the consistency of equilibrium data and equations of state consists in principle in calculating the change of the t-p-thermodynamic potential $U-TS+PV$ for the change of state—pure reactants at arbitrary pressure giving pure resultants at the same pressure and temperature. This change must be independent of the pressure and concentrations in the equilibrium box, which pressure and concentrations are given by the equilibrium data used. This is of course equivalent to calculating fugacities and substituting in the simple mass-action expression, to see whether this is constant. There is naturally no special virtue in fugacity, although it is mathematically very convenient in certain special calculations when $V\mathrm{d}p$ cannot be integrated in terms of known functions from the equation of state used.

Even when checks are obtained in such a calculation, they may be due to compensations, the individual equilibrium pressures or fugacities possibly being greatly in error. In the course of much unreported calculation I have observed such large compensation at work. For a good control a simpler equilibrium must be chosen, so that individual equilibrium pressures can be measured and calculated.

The ideally simple equilibrium system would be hydrogen separated by a palladium membrane from a mixture of hydrogen and inert gas. Since palladium is not rapidly permeated at low temperatures and hydrogen is a relatively perfect gas, especially at high temperatures, this system is not so very promising and apparently has not been carefully studied from this point of view, though Löwenstein[12] has introduced such a membrane into the study of equilibria, assuming ideal-gas relationships. The following method is in principle nearly as simple and is more general in certain respects.

We may use as the equivalent of a semi-permeable membrane a system of mutually insoluble solid phases (n in number) which together with a pure gas phase form a univariant system. At a definite temperature these solid phases will have a definite equilibrium pressure, determinable by experiment. Then an inert gas may be introduced and the equilibrium concentration in the gas phase and total pressure may be measured. From the densities (or eventually also the compressibilities) of the solid phases, we may calculate the equilibrium pressure of the solid phases under the increased external pressure. This result must then be equal to the equilibrium pressure of the active gas in the mixture of known temperature, pressure and composition and can be regarded as the experimentally determined equilibrium pressure of the gas in the mixture.

It is a reasonable expectation that the solid phases will not dissolve enough inert gas to require a correction. Such a solubility would mean that the substitute for a semi-permeable membrane is imperfect. The advantage of choosing a univariant system is that the addition of inert gas will in general change the masses of the solid phases, but in the case of a system which is univariant the equilibrium pressure of the solid phases will be unaffected and therefore no analysis of the solids will be necessary. It is necessary only to ensure that none has entirely disappeared. This may be done by addition of active gas, when the total pressure must be unchanged after re-establishment of equilibrium.

A limitation is imposed on the variety of data which can be obtained in this way from the given solid phases, due to the fact that the total pressure is a function of the composition.

One way of justifying the foregoing theory is by reference to the Gibbs theory. Gibbs always divided the energy, entropy, etc., of a system among the individual phases, in consequence of which any component possessed a potential, a partial volume, etc., in each phase. There is no logical necessity for always doing this. We may better, in a special treatment of univariant systems, divide the energy, entropy, volume, etc., as follows: one portion to the gas phase, the rest to the condensed phases taken collectively. We shall refer to the solid phases, assumed to be mu-

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[12] Löwenstein, *Z. physik. Chem.*, **54**, 715 (1906). In Ramsay's experiments [*Phil. Mag.*, [5] **38**, 206 (1894)] equilibrium was obviously not attained, nor especially sought.

tually insoluble, as the condensate. The condensate has then a potential, a partial molal volume, etc., with respect to a given component and the Gibbs theory applies to these quantities just as to the usual quantities distributed among individual phases, the arguments not being changed. In particular, the change of potential with (total) pressure is measured by the partial volume per unit of mass, but now the partial molal volume of the condensate, unlike that quantity for a pure substance, is physically interpretable, being in fact the algebraic sum of the molal volumes of the solids entering into the reaction in question. Therefore the change of equilibrium pressure of the condensate with external pressure can be calculated from the partial molal volume, as was assumed in the foregoing theory. Since the equilibrium pressure of a condensate is not dependent upon the mass ratios of its constituents, the value of its potential must also be independent.

Experimentation is at present in progress on the determination of the equilibrium pressure of ammonia in mixture with nitrogen, using some of the compounds of metal halides with ammonia as a virtual semi-permeable membrane, in the hope of being able to correlate the results with pressure-volume-temperature data on the gases.

Summary

1. The mass-action law for real gases is briefly discussed. No proposed exact equations permit calculation of equilibrium concentrations from equations of state of pure gases. The upper limits in the integrals of $V\mathrm{d}p$ are still unknown, being called here "equilibrium pressures" (of single gases in mixtures).

2. The rule of Lewis and Randall for calculating the fugacity of a gas in a mixture would suffice, if it were exact. An exact rule is given with an added term containing the integral from zero to the total pressure of $\left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right)\mathrm{d}p$, based on the assumption that at great volumes the equilibrium pressure is equal to the ideal-gas partial pressure.

3. With the aid of this assumption, when necessary, it is shown thermodynamically that all three propositions—exactness of the rule, additivity of volumes and additivity of heat content—follow from any one of the three.

4. Equilibria involving three gaseous species are too complicated to permit a critical test of such rules, owing to compensation of errors. To provide an attack on the simplest case a method of experimentation is outlined for determining equilibrium pressure by means of a virtually semipermeable membrane, consisting of the solids of a univariant system. The thermodynamic discussion involves attributing chemical potentials and partial volumes to the condensed mass of solid phases, which are considered collectively as if they were a single phase in the Gibbs treatment.

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