analyzed by the short ammonium fluoride method[5] and satisfactory agreement with analyses by other methods obtained.

The shellac has a two-fold function: it causes the precipitated cuprous iodide to flocculate rapidly and settle out as heavy curds, and it also deactivates the surface so that further adsorption is reduced. In the ore analyses referred to above, iron is present as a colloidal complex and may inhibit to some extent the action of the shellac, but in any case the end-point is greatly improved.

(5) Park, *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931)

DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
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A Note on the Calculation of Heat of Reaction from Values of the Equilibrium Constant at Two Temperatures

BY T. B. DOUGLAS AND H. D. CROCKFORD

The relation of the mass action constant to temperature is given by the equation

$$d \ln K = \Delta H \, dT/RT^2 \qquad (1)$$

If ΔH is a linear function of the temperature according to the equation

$$\Delta H = a + bT \qquad (2)$$

elimination of ΔH from (1) and integration lead to the equations

$$R \ln (K_2/K_1) = a[(1/T_1) - (1/T_2)] + b \ln (T_2/T_1) \qquad (3)$$

$$\frac{RT_1T_2 \ln (K_1/K_2)}{T_2 - T_1} = a + b \frac{T_1T_2}{T_2 - T_1} \ln (T_2/T_1) \qquad (4)$$

If now a temperature T_0 is defined by the equation

$$T_0 = \frac{T_1T_2}{T_2 - T_1} \ln (T_2/T_1) \qquad (5)$$

the right-hand member of (4) is ΔH_0, the value of ΔH for the temperature T_0. The resulting equation

$$\Delta H_0 = RT_1T_2 \ln (K_1/K_2)/(T_2 - T_1) \qquad (6)$$

is the same as is usually obtained from (1) by the use of the assumption that ΔH is independent of the temperature.

We have shown therefore that, when ΔH is a linear function of the temperature, (6) can still be used to calculate ΔH from two values of K and the two corresponding temperatures. The calculation does not require knowledge of the constants a and b and the ΔH thus calculated is for one particular temperature T_0, which is calculated by (5) without knowledge of a or b.

The authors recently published a paper[1] on the

(1) Crockford and Douglas, THIS JOURNAL, **56**, 1472 (1934).

ionization constants of certain sulfur derivatives of phenylacetic acid at 0 and 25°. ΔH was calculated by equation (6) for these two temperatures. More exactly the ΔH values obtained are not average but are specifically for 12.1° as determined by substituting 0 and 25° in (5).

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Influence of Thermal Diffusion in Certain Equilibrium Measurements

BY E. D. EASTMAN AND SAMUEL RUBEN

Emmett and Shultz[1] find the Deville method of equilibrium measurement to be subject to large errors attributable to thermal diffusion in the gas phase. They account in this way for discrepancies of long standing in various metal–metal oxide reduction equilibria involving hydrogen and water vapor, and between direct and indirect values of the water gas equilibrium.

This factor was considered by Eastman and Evans[2] in their work by the Deville method in the iron–oxygen–hydrogen system. There were, however, several considerations which led them to believe it might be disregarded. Thus, the tube in which the temperature gradient occurred was of large diameter and was placed horizontally in the hope of securing rapid convection. The speed of attainment of equilibrium was taken as an indication that mixing in the gas phase was in fact rapid, and that in consequence no sort of Soret equilibrium was likely to be important. Moreover, it was believed that had a Soret effect been present, especially if only partially established and varying in completeness with the temperature, it would have been manifested in the plots of log K vs. $1/T$ as a divergence from linearity. In the Fe–FeO systems first investigated no such divergence was present. In the later experiments with FeO–Fe$_3$O$_4$ mixtures (at higher total pressures) there was some divergence which we now think might be ascribed to differing thermal diffusion effects in different parts of the temperature and pressure ranges. In view of these facts it has seemed desirable to look for Soret effects in blank experiments with apparatus duplicating the essential features of that employed by Eastman and Evans.

(1) Emmett and Shultz, THIS JOURNAL, **55**, 1376 (1933).
(2) Eastman and Evans, *ibid.*, **46**, 888 (1924).

In our first experiments a Pirani gage for determination of gas composition by measurement of thermal conduction has been substituted for the water reservoir in an apparatus otherwise similar to that of the previous work. The procedure was then to fill the system to (total) pressures between 2 and 4 cm. with hydrogen and water vapor in about equimolal proportions. After standing until the gases were thoroughly mixed, their composition was determined by the gage. The (empty) equilibrium tube was then heated to about 800° and the temperature held constant for periods of about an hour, the total pressure and gage readings being taken at short intervals. When corrected for the pressure change the readings showed an increase of 10–20% in the mole fraction of water vapor of the gas in the gage. This increase was completed in the few minutes required to secure constancy in temperature of the furnace.

To make sure that the excess water vapor did not result from desorption from the walls of the tube on heating, a second series of experiments has been made. In these, a horizontally placed tube, 2.5 cm. in diameter and 30 cm. long, one end of which was heated to 800° over a distance of 15 cm., was employed. The apparatus was filled while the tube was hot to some 15–20 mm. of water vapor, and hydrogen added until a pressure about double the original was reached. Stopcocks in capillaries leading from the hot end and the cold end of the tube to the thermal conductivity gage were then closed, and the gage and connecting manometer evacuated. Samples of gas from the tube were then introduced into the gage–manometer system, being taken alternately from the hot and cold ends, with evacuation of the gage between samples. The thermal conductivity of the samples showed an accumulation of water vapor in the cold end of the tube, approximately equivalent to that in the experiments first described. Here again the time of establishment of the composition difference was less than that required in the preliminary manipulation.

We agree therefore with the conclusions of Emmett and Shultz. We also agree that thermal diffusion may affect not only the Deville and other static measurements but may be important also in dynamic methods at low rates of flow, as it apparently was in the experiments of Eastman and Robinson[3] in the tin system, and of Chipman and

(3) Eastman and Robinson, THIS JOURNAL, **50**, 1106 (1928).

Fontana[4] with liquid iron. Presumably it would also affect measurements in which a heated filament is employed, such as Langmuir's[5] on the dissociation of water vapor. Unpublished experiments of Sermattei[6] lend some support to this last idea. Sermattei undertook to measure the water gas constant by observing pressure changes produced in various mixtures of the reacting gases, in which the partial pressure of water vapor was fixed by a reservoir of liquid water as in the Deville method, when a platinum wire in the gas phase was glowed at constant temperatures (known from its resistance) between 800 and 1200°. Near 800° the results were in good agreement with the indirect results, but at the higher temperatures tended toward the direct values. We interpret this as due to a differential thermal diffusion, the effect of which was offset to an increasing degree with increasing temperature of the filament by some other factor, perhaps increased convection of the gases.

A few points concerning the probable variation of the effect in systems of different types are perhaps worth noting. Since relative molecular weight largely determines the magnitude of the effect, it will be particularly important in mixtures containing hydrogen but not large in many others. The evidence from the indirect calculations of the water-gas constant, for example, is that carbon monoxide–carbon dioxide mixtures in horizontal tubes and at pressures of the order of an atmosphere are little influenced by it. At low pressures, or in vertical tubes, where the full equilibrium effect may be established, any system in which substances differing significantly in molecular weight are involved may show a considerable effect.

(4) Chipman and Fontana, *ibid.*, **56**, 2011 (1934).

(5) Langmuir, *ibid.*, **28**, 1357 (1906).

(6) Sermattei, Thesis, University of California, 1929.

Theory of the Error of Acid–Base Titration[1]

BY PAUL S. ROLLER[2]

In this note the titer error and electrometric titer deviation in titrating with a weak base is