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)

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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 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).

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

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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_3O_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).