Reliability of the Heat Data as a Factor in Calculating Equilibria Involving Methanol[1]

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A RECENT note on the methanol equilibrium contains the statement (*3*) that if the heat of combustion of methanol as determined by Richards and Davis (*12*) were assumed to be only 0.75 per cent low, the free-energy change for the methanol reaction

$$CO + 2H_2 = CH_3OH\ (g.) \qquad (1)$$

as calculated from low-temperature heat data by use of the third law of thermodynamics, would be in agreement with the free-energy equation based upon the equilibrium measurements of Smith and Branting (*13*).

We feel obliged, however, to present a reconsideration of this question as follows. First, for Reaction 1 we have

$$\Delta H = \Delta H_0 - 19.54T + 0.01586T^2 \qquad (2)$$

$$\Delta F = \Delta H_0 + 19.54T\ln T - 0.01586T^2 + IT \qquad (3)$$

using the high-temperature specific heat data from Kelley's paper (*6*). Substituting the value of ΔH from (2) in the equation

$$\Delta F = \Delta H - T\Delta S \qquad (4)$$

we have

$$\Delta F = \Delta H_0 - 19.54T + 0.01586T^2 - T\Delta S \qquad (5)$$

Subtracting (5) from (3) we obtain

$$O = 19.54T\ln T + 19.54T - 0.03172T^2 + IT + T\Delta S \qquad (6)$$

Substituting Kelley's (*6*) value for ΔS_{298} we obtain $I = -69.40$ from (6) without the use of any heat of reaction data. If we now use $\Delta F_{577} = 8597$ as determined at 577° K. by Smith and Branting directly from K_p for Reaction 1, we obtain $\Delta H_0 = -17{,}810$ or, from (2), $\Delta H_{298} = -22{,}225$. Thus, these are the ΔH values which would be required to make the equilibrium data of Smith and Branting agree with the third law calculations of Kelley. The value of ΔH_{298} which depends upon Richards and Davis's value for the heat of combustion of methanol is $-25{,}150$ according to Kelley (*6*). Thus the heat of combustion of methanol (if the specific-heat data involved are assumed to be correct) would need to be 2925 calories low in order for Kelley's entropy determination to be in agreement with Smith and Branting's equilibrium data. Dodge states that an error of about 1300 calories will bring the third law value into agreement with Smith and Branting's equation. However, it is not permissable to retain the original equation deduced by Smith and Branting if the heat-of-reaction data used therein are not accepted.

We do not believe that Richards and Davis's value for the molal heat of combustion of methanol is in error by 3000 calories, in spite of the fact that the Richards and Davis data on methanol are said to be not so reliable as their other data. From Kharasch's (*7*) consideration of the data on heats of combustion of organic compounds, we notice that his method of calculating heats of combustion gives 169,300 calories for CH_3OH (l.) as compared with 170,760 calories determined by Richards and Davis. In cases where the experimental values are reliable the agreement with the calculated values is very good. Furthermore, when comparing the calculated values for ethyl, *n*-propyl, *n*-butyl, and isobutyl alcohols with the corresponding values determined by Richards and Davis, we find increasingly good agreement as we go to the less volatile alcohols. The calculated value for methanol, however, is lower than the Richards and Davis value. These considerations would certainly indicate that the Richards and Davis value is not anything like 3000 calories too low. Verkade and Coops (*14*), who have done much valuable work on heats of combustion of organic compounds, state that the Richards and Davis value for methanol is not in error by more than 0.2 per cent. It can thus be said with a fair degree of certainty that there is not enough error in the accepted value for the heat of combustion of methanol to introduce appreciable error in the thermodynamic calculations.

Although the high temperature heat-capacity data for methanol were determined by the velocity of sound method and may thus be subject to appreciable uncertainty, no reasonable assumption of error in these data will bridge the discrepancy between the third law data and the equilibrium measurements. For example, if one assumes the heat capacity of CH_3OH (g.) to be 8 calories instead of 10.6 calories at 298° K. and 15.5 calories instead of 20 calories at 600° K., using Kelley's heat and entropy data for 298° K., it is found that the resulting difference in the free-energy change calculated for the methanol reaction at 600° K. is only 340 calories. Likewise assuming 8 calories at 298° K. and 20 calories at 600° K., the difference is only 360 calories.

There still seems to be a slight uncertainty as to correcting the entropy values of hydrogen and the more complicated hydrogen compounds for the fact that hydrogen exists in the symmetric and anti-symmetric states. In the paper by Kelley (*6*) (received for publication October 24, 1928) the entropy of H_2 at 298° K. is taken as 31.25. In a later paper by Parks, Kelley, and Huffman (*11*) (received for publication December 10, 1928) this value is apparently taken as 29.6. Evidently, however, the value 31.25 is considered the better at the present time.

In this connection, it may be of interest to check these third law entropy values for H_2, using the third law entropy value for H_2O (l.) at 298° K., against the very reliable high temperature heat and equilibrium data on the reaction

$$H_2 + 0.5\ O_2 = H_2O\ (l.) \qquad (7)$$

Giauque and Johnston (*5*) give S_{298} for 0.5 O_2 as 24.5. Latimer and Greensfelder (*9*) give S_{298} for H_2O (l.) as 15.92. Eastman (*4*) gives the heat of formation of H_2O (l.) at 298° K. as $-68{,}320$ calories and the free energy as $-56{,}530$. Using Equation 4 we find $\Delta F_{298} = -56{,}451$, when S_{298} for H_2 is taken as 31.25, and $-56{,}942$ when S_{298} for H_2 is taken as 29.6. Evidently the value $S_{298} = 31.25$ agrees much better with the accurate high temperature heat and equilibrium data when no correction is made for any "spin effect" in the H_2O entropy. It seems unlikely that any further spin effect corrections will be found necessary which will appreciably change the entropy values now accepted.

We now have equilibrium measurements (or estimates based upon practical operation of the methanol process) for Reaction 1 by Brown and Galloway (*2*), by Smith and Branting (*13*), by Audibert and Raineau (*1*), by Newitt, Byrne, and Strong (*10*), and by Lacy, Dunning, and Storch (*8*). All of these

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measurements agree as to order of magnitude, but the third law data are considerably different.

We are not now in a position to say just what is the cause of the discrepancy. However, it is hoped that work which is now going on in this laboratory may throw some light on the question.

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Viscosity of Pectin Sols

II—Effects of Citric Acid and Various Sugars[1]

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This paper represents the continuation of a previous study on the viscosity of sols containing pectin, citric acid, and sucrose. In the present work the effect of citric acid and sucrose, fructose, dextrose, and lactose on the viscosity of these sols has been studied.

Citric acid decreased the viscosity of unheated pectin sols and that of pectin-sugar sols.

Sucrose, dextrose, fructose, or lactose may be used to produce pectin-acid-sugar jellies. Under the same conditions the addition of sucrose caused greater increase in the viscosity of pectin sols than the addition of dextrose, fructose, or lactose. Pectin-acid-sugar jellies containing sucrose were firmer in appearance and more stable than those containing dextrose, fructose, or lactose. Crystalline formation appeared at a lower hydrogen-ion concentration in sucrose jellies than in dextrose or lactose jellies. Under the same conditions no crystalline formation was found in the fructose jellies.

The pH range for jelly formation determined either before or after the addition of sugar is approximately the same.

The mechanism for the gelation of pectin-acid-sugar jellies may depend chiefly upon the specific effect of the acid on the fibrils of pectin.

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SOME data were presented by the writer (5) in 1926 on the relative viscosity of pectin sols containing pectin, citric acid, and sucrose. These determinations were made with the Stormer viscometer, which employs a rotating cylinder for the measurement of the resistance of the sols to the torque produced by a definite weight. The data showed that variations in the concentration of the hydrogen ion, pectin, and sucrose were all effective in governing the rate of change of the viscosity of sols containing pectin, citric acid, and sucrose. The viscosity measurements were made during the cooling of the pectin-acid-sugar sols from 103° to 60° C. However, in order to find out the specific effect of each of these substances, it seemed desirable to measure the viscosity of very dilute as well as concentrated sols of pectin with each of these variables, separately and together, using the rate of flow method by means of an Ostwald viscometer.

In the present investigation the study of the specific effect of citric acid, sucrose, fructose, dextrose, and lactose upon the viscosity of pectin sols and their ability to aid gelation was made upon sols which were not heated. In this way it is assumed that the maximum viscosity values will be obtained.

Preparation of Pectin Sols

The pectin used was precipitated by ethyl alcohol from distilled-water extracts of pectin obtained from the inner white rind of orange peel (5). This powdered pectin, which had passed through a 100-mesh sieve, was sprinkled on the surface of freshly prepared distilled water, which was then covered with a rubber dam and kept at 20° C. without stirring for about 3 hours until the pectin was completely dissolved. These precautions were taken since it had been found that stirring or storage at high or very low temperatures decreased the viscosity of pectin sols considerably. Chart I shows the decrease in viscosity of pectin sols that had been stored in the ice box. Pitman and Cruess (6) have recently shown the effect of microörganisms on the viscosity of pectin sols. When the pectin was completely dissolved, the citric acid or sugar was added to the pectin sol.

Measurement of Relative Viscosity

An Ostwald viscometer calibrated with purified mercury and standardized with distilled water was used for the measurement of the viscosity of the sols. The passage of water through this viscometer took 63.3 seconds at 20° C. The viscosity ratio is obtained by dividing the time of outflow of the sol by the time of outflow of water (3). The hydrogen-ion concentration was determined potentiometrically with a Hildebrand type of electrode and a Leeds and Northrup potentiometer.

Effect of Citric Acid

Determinations were made on the viscosity of the pectin sols containing varying amounts of citric acid with and without the addition of sugar. In all cases recrystallized citric and recrystallized sucrose were used. Citric acid solution was used in some cases, and in others citric acid crystals.

Table I and Chart II show that citric acid decreases the viscosity of pectin sols. The decrease was quite great when small amounts of citric acid were added, but not so noticeable with larger amounts of the acid. Practically the same results were obtained with the solution and with the crystals. For instance, when 0.1 cc. of $3N$ citric acid solution was added to 10 cc. of 0.1 per cent pectin sol having a viscosity of 1.84, the viscosity ratio dropped to 1.65. When 1.0 cc. of the same

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