approximately 5×10^{-10} torr. The other limitation was that the vacuum chamber had to be at a low enough temperature so that the vapor pressure in the chamber was much less than the corresponding sublimation rates being measured. In the case of Xe, a chamber wall temperature near 50K limited the measurements to above 10^{-8} torr.

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Thermodynamic Equilibrium Constant of Ethyl Alcohol-Acetaldehyde-Hydrogen System

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Thermodynamic equilibrium constants of the ethyl alcohol-acetaldehyde-hydrogen system were determined experimentally at temperatures from 456 to 540K. Equilibrium was established utilizing a commercially available cupric oxide-chromia catalyst. The equilibrium constants obtained in the present investigation were compared with those of published literature and with estimates obtained from thermochemical data. The values of $\Delta H_T°$ and $\Delta S_T°$ were estimated for the above temperature range: $\Delta H_T° = 17.09 \pm 0.71$ kcal mol^{-1} and $\Delta S_T° = 28.02 \pm 1.01$ cal mol^{-1} K^{-1}.

Accurate values of thermodynamic equilibrium constants are vitally needed for rate modeling near chemical equilibrium as well as for the determination of equilibrium concentrations. The equilibrium constants of the ethyl alcohol-acetaldehyde-hydrogen system have been experimentally determined by a few investigators (5, 9, 11). But some discrepancy exists among the constants so far reported.

In this investigation an attempt was made to obtain accurate values of thermodynamic equilibrium constants for the ethyl alcohol-acetaldehyde-hydrogen system at temperatures between 456 and 540K. The constants so obtained were compared to the literature values and those estimated from existing thermochemical data (10). Thermodynamic equilibrium was established utilizing a commercially available copper-chromia catalyst. The dehydrogenation reaction of ethyl alcohol and the hydrogenation reaction of acetaldehyde on the catalyst were quite fast at these temperatures so that thermodynamic equilibrium was attained rather easily.

Materials

Pure ethyl alcohol was supplied by U.S. Industrial Chemicals Co., New York, N.Y. Kodak CP grade acetaldehyde was used, with a minimum purity of 99%. Elec-

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trolytic hydrogen gas was purchased from Carbide Reduction Inc., Linden, N.J. This cylinder gas contained approximately 0.5 vol % oxygen. Hydrogen was purified before being transferred to a reactor. Hydrogen passed through a Matheson deoxo gas purifier, which catalytically converted oxygen contaminated to water.

A commercial cupric oxide-chromia catalyst, Harshaw Cu-1407 T-⅛, was used as supplied by the Harshaw Chemical Co., Cleveland, Ohio. It consisted of 37 wt % of CuO, 52 wt % of Cr_2O_3, and 11 wt % of binder. Typical physical properties are:

Size, ⅛ in. diam, ⅛ in. long (extruded)
Pellet density, 1.65 g cm^{-3}
Surface area, 17.9 m^2 g^{-1}

This catalyst was crushed and screened to $-8 + 14$ mesh.

Apparatus

A schematic flow diagram of the experimental equipment is shown in Figure 1. The reactor body consisted of a 1-in. i.d. Pyrex tube of 3-ft length, which provided for a catalyst chamber 1 in. in diameter by 1 in. long. Three thermocouples inserted into a ¼-in. thermocouple well measured, respectively, the top, middle, and bottom sections of the catalyst bed of the reactor. An electrically heated aluminum-bronze block served as a heat sink which provided an adequate temperature control to the catalyst bed. During a run the overall temperature gradient in the catalyst bed never exceeded 2°C.

The feed to the reactor contained ethyl alcohol, acetaldehyde, and hydrogen. A mixture of ethyl alcohol and acetaldehyde was transferred to the reactor with a mini pump. The flow rate of the mixture was measured from the volume change in the liquid reservoir. The hydrogen flow rate was controlled with a precision needle valve and was metered with a rotameter.

Analysis

Analysis of 20-ml gas samples collected at 120°C and 1 atm was performed by a gas-liquid chromatograph by

using a Model A 350 Varian Aerograph gas chromatograph. A 2-m column filled with Carbowax 1540 on Teflon was used to analyze the gas samples. The column temperature was maintained at 40°C. A mixture of helium and hydrogen (helium 91.5 vol % and hydrogen 8.5%) was used as a carrier gas flowing at a rate of 100 cc min^{-1}. The mixture was purchased from Carbide Reduction Inc. A Leeds and Northrup recorder (0 ∼ 50-mV range) was employed for recording the gas chromatograms. In the above operating conditions of the gas chromatograph, hydrogen, ethyl alcohol, and acetaldehyde peaks were sufficiently separated to allow quantitative analyses of these components.

Experiments

A standard method of pretreatment was developed to maintain the activity of catalyst at a high level. The procedure consisted of three steps. First, air was passed through the catalyst bed for 2 hr at a rate of 0.09 g-mol hr^{-1} to regenerate the catalyst to a constant oxidized state. Nitrogen was then introduced at a rate of 0.5 g-mol hr^{-1} for about 10 min to remove all the air in the reactor. Finally, hydrogen was passed at a rate of 0.09 g-mol hr^{-1} for 15 ∼ 20 hr. The experimental run then followed. The pretreatment of catalyst was performed at the experimental temperature. The experimental run and the pretreatment of catalyst were conducted in a cyclic manner and repeated without interruptions.

A mixture of ethyl alcohol and acetaldehyde was transferred to the reactor at a rate between 25 and 100 cc hr^{-1}. The hydrogen gas rate ranged from 0.1 to 0.7 g-mol hr^{-1}. The weight of the catalyst used was about 7.5 grams. The experiments were conducted essentially at atmospheric pressure. The pressure drop across the catalyst bed never exceeded 10 mm Hg.

Establishment of Equilibrium Conditions

To ensure that the equilibrium conditions were reached for the dehydrogenation and hydrogenation reactions, we used gas feed of two different compositions; one had a value of $p_{acetaldehyde} \cdot p_{hydrogen}/p_{ethyl\ alcohol}$ ratio substantially higher than that predicted from existing literature data, and the other had a value of that ratio noticeably lower than the predicted value. In this ratio, p_i denotes the partial pressure of component i in the gas feed. When these two feeds provided virtually the same gas compositions at the exit of the reactor, we assumed that the equilibrium condition was attained and computed the equilibrium constants on the basis of the compositions. Table I shows the compositions of various feeds and those measured at the exit of reactor.

Results and Discussion

Table II shows the thermodynamic equilibrium constants obtained in the present investigation. Figure 2 compares our data with those experimentally determined by various investigators (5, 9, 11). With the exception of the low-temperature data of Rideal (9), the existing equilibrium data are in disagreement with our values. In the study of Franckaerts and Froment (5), no detailed description was given for the experimental procedure and the analytical method. Rideal (9) determined the equilibrium concentrations of ethyl alcohol, acetaldehyde, and hydrogen from the pressure measurement of the static system. In this method, as Rideal stated, the occurrence of side reactions gave a substantial uncertainty to equilibrium concentrations. Suitable corrections were not made to Rideal's data, even though the side reactions did take place. Regarding the study of Yada and Mihara (11), they used a flow-type reactor to attain equilibrium
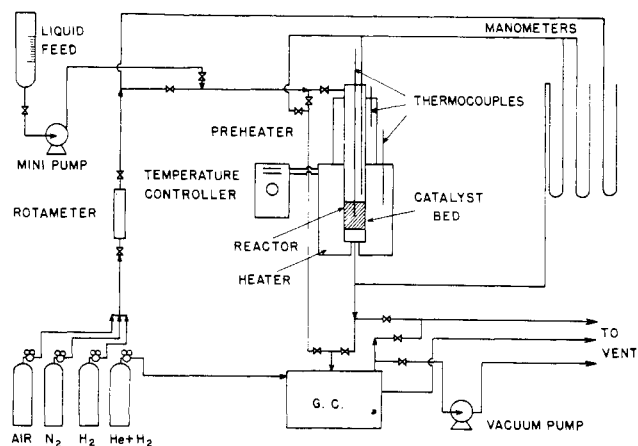

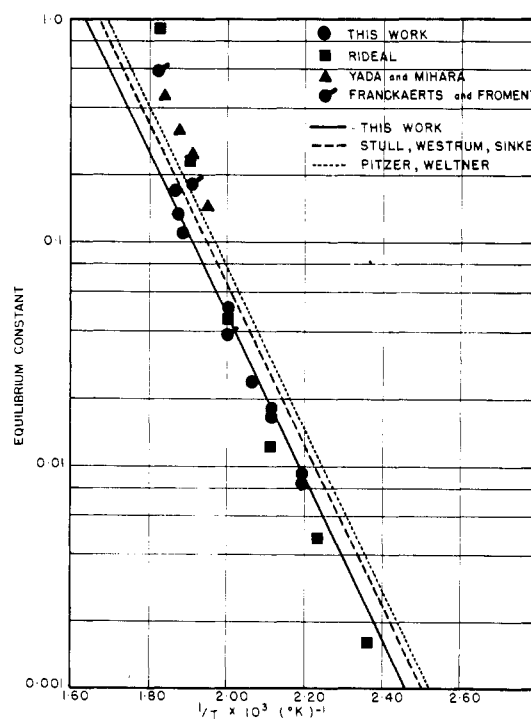**Figure 1.** Schematic flow diagram of experimental apparatus

Figure 2. Equilibrium constant and reciprocal of temperature

Table I. Composition of Feed and Product for Ethyl Alcohol–Aldehyde–Hydrogen System

	Value of ratio, $p_{acetaldehyde} \cdot$ $p_{hydrogen}/p_{ethyl\ alcohol}$	
Temp, K	Feed	Product
456	0.00534	0.00841
457	0.0221	0.00923
458	0.0133	0.00967
473	0.00559	0.0166
474	0.0237	0.0169
475	0.0189	0.0185
530	0.00821	0.107
533	0.115	0.130
533	0.135	0.136

p_i is the partial pressure of i-component, atm

Table II. Thermodynamic Equilibrium Constants of Ethyl Alcohol–Acetaldehyde–Hydrogen System

Temp, K	Equil constant, atm
456	0.00841
457	0.00923
458	0.00967
473	0.0166
474	0.0169
475	0.0185
481	0.0234
501	0.0458
530	0.107
533	0.135
540	0.176

Table III. Estimates of $\Delta H_T°$ and $\Delta S_T°$ Temperature Range 456–540K

Source of data	$\Delta H_T°$, kcal mol^{-1}	$\Delta S_T°$, cal mol^{-1} K^{-1}
This work	17.09 ± 0.71[a]	28.02 ± 1.01[a]
Stull et al. (10)	17.03 ± 0.55	28.60 ± 0.73
Pitzer and Weltner (8)	17.01 ± 0.43	28.64 ± 0.65

[a] ± signs represent approximate 99% confidence limits of estimates.

Table IV. Entropy of Ethyl Alcohol

	$S_{298,16}°$, cal mol^{-1} K^{-1}
Brickwedde et al. (2)	66.45
Barrow (1)	67.58
Green (exptl) (6)	67.58 ± 0.3
Green (estd) (6)	67.54

conditions. However, they failed to make experiments to confirm that the equilibrium conditions were actually attained. These would explain the differences observed among the equilibrium data of the present study and those of previous studies.

The thermodynamic equilibrium constant, K_T, can be estimated from the following relationships:

$$\Delta H_T° = \Delta H_{298}° + \int_{298}^{T} (\Delta C_p°)dT \qquad (1)$$

$$\Delta S_T° = \Delta S_{298}° + \int_{298}^{T} (\Delta C_p°/T)dT \qquad (2)$$

where

$\Delta H_{298}° = \Delta H_f°$, products, 298 $-$ $\Delta H_f°$, reactants, 298

$\Delta S_{298}° = S°$, products, 298 $-$ $S°$, reactants, 298

and

$\Delta C_p° = C_p°$, products $-$ $C_p°$, reactants

$$\ln K_T = -\Delta H_T°/RT + \Delta S_T°/R \qquad (3)$$

For an estimation of K_T, we used the values of $\Delta H_{f,298}°$, $S_{298}°$, and the heat capacity data which were compiled by Stull et al. (10). The estimates of K_T thus obtained are presented by the broken line of Figure 2. For the purpose of comparison, Figure 2 also shows a regression line (the solid line) determined on the basis of our experimentally obtained equilibrium constants together with the values of equilibrium constants which Pitzer and Weltner (8) estimated by using their molecular data (the dotted line). We note that these three lines dis-

agree, but that the lines are virtually in parallel with each other. Thus, we computed the values of $\Delta H_T°$ and $\Delta S_T°$ for the three sets of data through a regression analysis. For the analysis, it was assumed that $\Delta H_T°$ and $\Delta S_T°$ were constant over the temperature range studied. Table III summarizes the results of computation, indicating that the values of $\Delta H_T°$ are in excellent agreement. Strictly speaking, our experimental equilibrium data should be corrected when they are compared with the calculated values based on the properties of ideal gas. For the experimental conditions employed in the present investigation (1 atm, 456 $\sim$ 540K), the departure of each gas from ideal behavior is insignificant.

Perhaps uncertainty attached to the $S_{298}°$ value of ethyl alcohol, acetaldehyde, or hydrogen attributes to the difference among the estimates of $\Delta S_T°$. A calculation indicates that our equilibrium constants would have coincided with the estimates based upon Stull's data if $\Delta S_{298}°$ were 26.30 instead of 26.82 cal mol^{-1} K^{-1}. Because of its simple molecular structure, the $S_{298}°$ value of hydrogen seems to be quite accurate. Regarding the standard entropy of ethyl alcohol, Green (6) compared the existing data. Table IV was abstracted from Green's work. We note that the entropy value recommended by Stull et al. is taken from Green's estimate. Table IV shows that error attached to Green's experimental data was ±0.3 cal mol^{-1} K^{-1}. Even with the application of the maximum error, the difference encountered in $\Delta S_{298}°$ does not seem to be reconciled. With respect to the standard entropy of aldehyde, Stull et al. listed $S_{298}°$ (g) = 63.15 cal mol^{-1} K^{-1}, which is based upon the molecular data gathered by Pitzer and Weltner (8). The data of Pitzer and Weltner were revised by Lin and Kilb (7) and Fateley and Miller (4). However, Evans and Bernstein (3) found that the revisions result in a negligible effect on the calculated thermodynamic values. Accordingly, errors involved in the $S_{298}°$ values of ethyl alcohol and acetaldehyde cannot satisfactorily explain the difference between our equilibrium constants and the estimates from Stull's data.

Accurate equilibrium constants were experimentally obtained for the ethyl alcohol–acetaldehyde–hydrogen system at temperatures between 456 and 540K. The constants were compared with those estimated from existing thermochemical data and with those published in the literature. The comparison indicated that the most recent literature values of equilibrium constants disagreed with our values. Our equilibrium constants agreed most closely with those estimated from the thermochemical data compiled by Stull and et al. However, a consistent difference still exists between our data and the estimates from Stull's data. Because of the difference, the standard entropy values of ethyl alcohol or acetaldehyde which are reported in the literature should be reexamined. The determination of equilibrium constants would provide accurate estimates of $\Delta H_{f,298}°$ and $S_{298}°$, when precise $C_p°$ functions are available.

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