

Thermodynamic Equilibrium Constant of Isobutane-Isobutylene-Hydrogen System

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Thermodynamic equilibrium constants of the isobutane-isobutylene-hydrogen system were measured at temperatures from 793 to 945K. Equilibrium was established utilizing a commercial grade chromia-alumina catalyst. The equilibrium constants obtained in the present investigation were compared with those computed from the API values. The estimates of ΔH_T° and ΔS_T° were obtained for the above temperature range: $\Delta H_T^\circ = 26.74 \pm 3.11$ Kcal/g-mol and $\Delta S_T^\circ = 29.83 \pm 4.12$ cal/g-mol, K.

Despite the fact that the dehydrogenation and hydrogenation reactions of the C₄ system play a key role in petroleum and petrochemical industries, accurate values of thermodynamic equilibrium constants of the system are surprisingly scarce. The constants may be estimated from the existing thermochemical data (7, 8). However, some discrepancy exists between experimentally obtained and estimated values of the equilibrium constants.

In this investigation it was attempted to measure accurate values of thermodynamic equilibrium constants for the isobutane-isobutylene-hydrogen system at elevated temperatures. Equilibrium was established utilizing a commercial grade chromia-alumina catalyst. The dehydrogenation reaction of isobutane and the hydrogenation reaction of isobutylene on the catalyst at these temperatures were so fast that equilibrium was established readily.

Materials

Matheson CP grade isobutane and isobutylene were used, with a minimum purity of 99%. Electrolytic hydrogen was purchased from Carbide Reduction Inc., Linden, N.J. This gas contained approximately 0.5 volume % oxygen.

The catalyst, 20% chromia (Cr₂O₃) on alumina, is manufactured by the Houdry Process Corp., Philadelphia, Pa., and is designated as Type A50. Typical physical properties are:

| | |
|----------------------------------|-------------------------|
| Surface area | 55 m ² /g |
| Total pore volume | 0.31 cm ³ /g |
| Pellet density | 1.42 g/cm ³ |
| Size | 14-20 mesh |
| Calculated average pore diameter | 225 Å |

Apparatus

A schematic flow diagram of the experimental equipment is shown in Figure 1. The reactor body consisted of 1-in. i.d. Vycor tube of 3-ft length. Six thermocouples inserted into a 1/4-in. thermocouple well running down the center of the catalyst bed, and three others located on the circumference of the bed, measure the complete temperature profile of the catalyst bed of the reactor. The over-all temperature gradient during a run never exceeds 10°C. Ports located immediately before and after the cat-

alyst chamber draw samples of the gases entering and leaving the catalyst chamber and also measure the pressure within the chamber and the pressure drop through the catalyst bed.

Provision is made for introducing into the catalyst chamber, as required, the mixture of isobutane, isobutylene, and hydrogen, nitrogen for purging the reactor system, air for regeneration of the catalyst, and hydrogen for pretreatment of the catalyst. The experimental procedure is described in detail elsewhere (2-4). Each stream is filtered, dried with a column packed with Drierite and Ascarite, and metered by means of calibrated rotameters before entering the reactor. Two preheaters are used to preheat the feed to specified reaction temperature. The heaters are programmed to minimize hydrocarbon decomposition before it enters the reaction zone of the reactor. An electrically heated aluminum-bronze block serves as a heat sink which provides adequate temperature control to the catalyst bed.

Analysis

Analysis of 3-ml normal temperature and pressure (NTP) samples was carried out by gas-liquid chromatography at 25°C using a Model A Varian Aerograph gas chromatograph. A 25-ft. column filled with 20% by weight tributyl phosphate on 40-60-μ Chromosorb B was used with helium as carrier gas flowing at a rate of 50 ml/min. The procedure for analyzing the chromatograms has been presented (2).

Hydrogen in gas samples was determined by a cryogenic technique. The apparatus, as shown in Figure 2, consists of a sample bulb with a finger, a vacuum system, and a mercury manometer. The finger serves for the condensation of hydrocarbons and collection of liquefied material. The inner volumes of the sample bulb and a glass tube which connects the bulb, the manometer, and the vacuum system were accurately determined. A sample bulb containing a mixture of hydrogen and hydrocarbons is connected to the ground glass joint, J1. Stopcocks S2, S3, and S4 are opened and the vacuum pump is turned on. The lower half of the finger attached to the

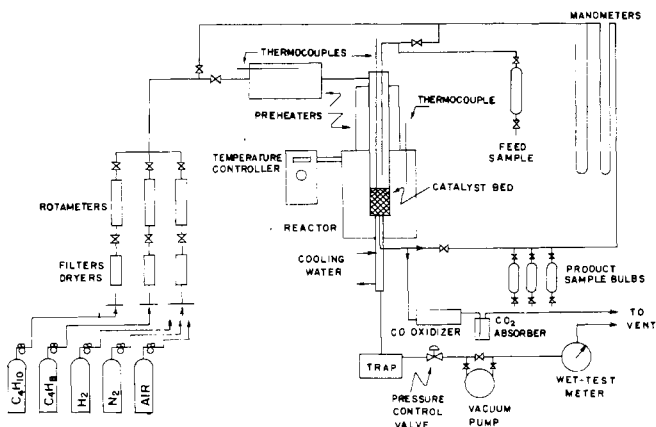


Figure 1. Schematic flow diagram of experimental equipment

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sample bulb is immersed in liquid nitrogen. The pressure of the system is measured by the mercury manometer when full vacuum in the system is attained. Then stopcock S3 is closed to isolate the system from the vacuum pump and stopcock S1 is opened to allow noncondensable gas (hydrogen) in the sample bulb to flow into the system. After the pressure of the system is measured by the mercury manometer, the liquid nitrogen is removed from the finger of the sampling bulb to allow the condensed gases (hydrocarbons) to vaporize. When the entire system including the finger of the sampling bulb returns to room temperature, the pressure of the system is measured. These two pressure measurements along with the measurements of the volume of the system and the room temperature provide the concentration of hydrogen in the sample. The adequacy of this analytical technique was examined by mass spectroscopy. The examination indicated that the hydrogen analysis can be performed within an accuracy of $\pm 0.5\%$. A detailed description of the hydrogen analysis is given elsewhere (4).

Experiments

A standard method of pretreatment was developed to keep the catalyst activity high. The procedure included three steps. First, dry air was passed over the catalyst for 22 hr at a rate of 0.02 ft³/min to regenerate the catalyst to a constant oxidized state. Hydrogen was then passed at a rate of 0.115 ft³/min for 2 hr to reduce the catalyst. The experimental run then followed. The pretreatment runs were conducted at the experimental temperature. All these three steps described above were cyclic and repeated without interruptions.

A mixture of isobutane, isobutylene, and hydrogen was fed into the reactor at a rate of 0.15 g-mol/min at a pressure slightly higher than atmospheric pressure for 10 min. The weight of the catalyst used was about 35 grams. During each run, three samples were collected at 4, 6, and 10 min.

Establishment of Equilibrium Conditions

To test that the equilibrium was virtually established for the dehydrogenation and hydrogenation reactions studied, we used gas feed of two different compositions, which had either substantially higher or lower value of $p_{\text{butylene}} \cdot p_{\text{H}_2} / p_{\text{butane}}$ ratio than predicted values of equilibrium constants (Table I). In this ratio p_i denotes the partial pressure of component i . At the exit of reactor, these two feeds yielded essentially identical gas compositions, on the basis of which the equilibrium constants were computed.

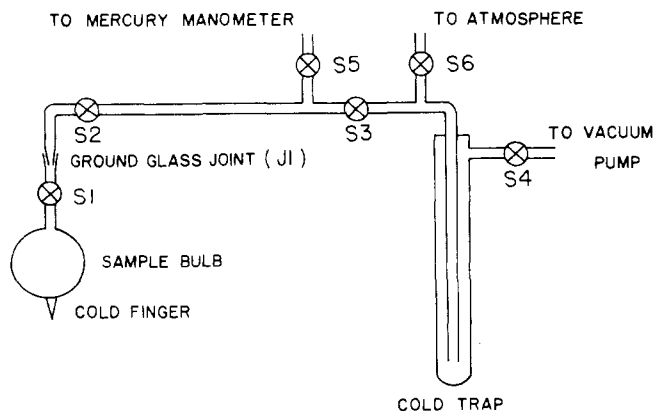


Figure 2. Hydrogen analysis system

Experimental Results and Discussion

Table II shows the equilibrium constants obtained in this investigation. With the thermodynamic equilibrium constants listed in Table II the enthalpy and entropy changes of the constants were calculated. The estimates were $\Delta H_T^\circ = 26.74 \pm 3.11$ kcal/g-mol and $\Delta S_T^\circ = 29.83 \pm 4.12$ cal/g-mol, K, where \pm signs represent 99% confidence limits.

The following relationships may be applicable to estimate the thermodynamic equilibrium constant, K_T , of the isobutane-isobutylene-hydrogen system.

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

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

where

$$\Delta H_{298}^\circ = \Delta H_f^\circ, \text{ products, } 298 - \Delta H_f^\circ, \text{ reactants, } 298$$

$$\Delta S_{298}^\circ = S_{298}^\circ, \text{ products, } 298 - S_{298}^\circ, \text{ reactants, } 298$$

and

$$\Delta C_p^\circ = C_p^\circ, \text{ products} - C_p^\circ, \text{ reactants}$$

$$K_T = \exp(-\Delta H_T^\circ / RT + \Delta S_T^\circ / R) \quad (3)$$

From Equations 1 through 3 it can be seen that ΔH_{298}° , ΔS_{298}° , and the heat capacity values of isobutane, isobutylene, and hydrogen should be supplied for the estimation of thermodynamic equilibrium constant. We employed values listed in the API report (7) and computed the estimates of K_T . The value of ΔH_{298}° can also be ob-

Table I. Compositions of Feed and Product for Isobutane-Isobutylene-Hydrogen System

| Temp, K | Value of ratio, $p_{\text{isobutylene}} \cdot p_{\text{H}_2} / p_{\text{isobutane}}$ | |
|---------|--|---------|
| | Feed | Product |
| 792 | 0.149 | 0.142 |
| 794 | 0.181 | 0.144 |
| 818 | 0.473 | 0.267 |
| 820 | 0.269 | 0.264 |
| 846 | 0.810 | 0.453 |
| 848 | 0.443 | 0.451 |
| 863 | 0.731 | 0.571 |
| 865 | 0.412 | 0.570 |
| 873 | 0.460 | 0.557 |
| 874 | 0.601 | 0.559 |
| 911 | 1.806 | 1.38 |
| 912 | 0.921 | 1.40 |
| 947 | 3.021 | 2.32 |
| 944 | 2.015 | 2.30 |

Table II. Thermodynamic Equilibrium Constants of Isobutane-Isobutylene-Hydrogen System

| Temp, K | Equilibrium constant |
|---------|----------------------|
| 793 | 0.143 |
| 819 | 0.266 |
| 847 | 0.452 |
| 864 | 0.571 |
| 874 | 0.558 |
| 912 | 1.39 |
| 945 | 2.31 |

tained from the heat of hydrogenation of isobutylene. Kistiakowsky et al. (5) and Prosen et al. (6) independently reported the heat of hydrogenation. Their values are in excellent agreement with that of the API table (7). Presumably the API value is based upon the data of Kistiakowsky and Prosen. Figure 2 compares the estimates of thermodynamic equilibrium constants and the constants determined from our experiment. Table III shows the estimates of ΔH_T° and ΔS_T° based on the API values and those obtained from a regression analysis of our experimental values of K_T . Needless to say, ΔH_T° and ΔS_T° are functions of temperature. It was assumed for the estimation that ΔH_T° and ΔS_T° are constant over the temperature range studied. It is apparent from Figure 3 that the equilibrium constants from our study do not agree with those from the API value. Our estimates of ΔH_T° and ΔS_T° also disagree with those based on the values listed in the API table, even though the 99% confidence limits of our estimates of ΔH_T° and ΔS_T° include the estimates from the API value.

As described previously, the API value of $\Delta H_{f,298}^\circ$ seems to be taken from the measurements of heats of hydrogenation by Kistiakowsky and co-workers (5) and of heats of combustion by Prosen and his colleagues (6). The maximum error in $\Delta H_{f,298}^\circ$ would be ± 0.5 kcal/g-mol. The API values of S_{298}° of components involved were calculated mainly from the spectroscopic and molecular data. On the basis of Aston's study (7) a conservative estimate of the error for S_{298}° would be ± 0.5 cal/g-mol, K. Accordingly, the error analysis of ΔH_{298}° and S_{298}° does not seem to explain the difference. It may stem from uncertainty attached to the API heat capacity values.

On the basis of the results it may be concluded that considerable discrepancy exists between our experimental and calculated values of thermodynamic equilibrium constant of the isobutane-isobutylene-hydrogen system. Because of the difference, the use of the API data may produce significant errors in predicting equilibrium concentrations as well as equilibrium constants of the system.

Table III. Estimates of ΔH_T° and ΔS_T°
Temperature range 793 to 945K

| | Source of data | |
|---------------------------------|----------------|--------------------|
| | API | This work |
| ΔH_T° kcal/g-mol | 29.31 | 26.74 ± 3.11^a |
| ΔS_T° cal/g-mol, K | 33.68 | 29.83 ± 4.12^a |

^a \pm signs represent 99% confidence limits.

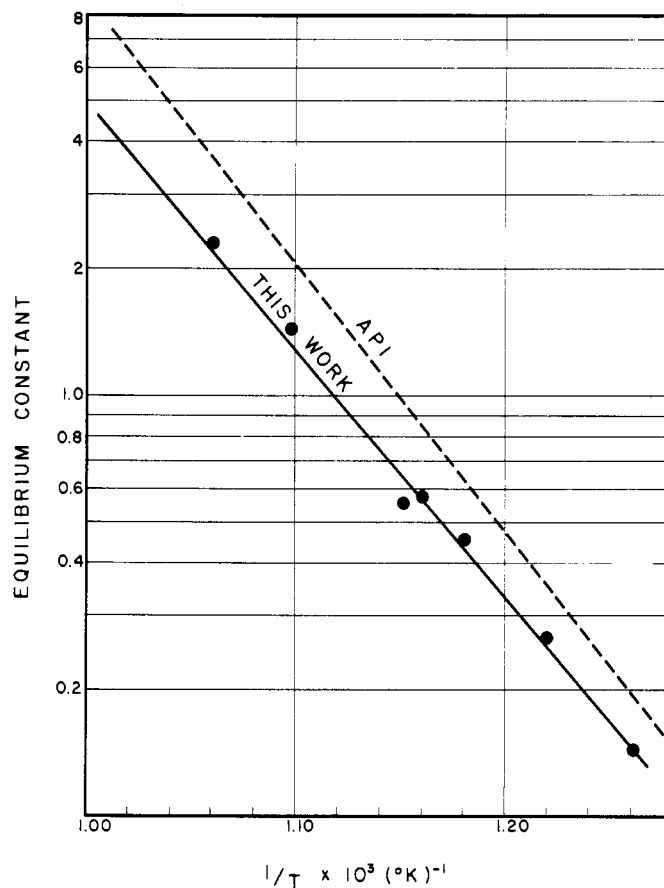


Figure 3. Equilibrium constant and reciprocal of temperature

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Literature Cited

- (1) Aston, J. G., Kennedy, R. M., Schumann, S. C., *J. Amer. Chem. Soc.*, **62**, 2059 (1940).
- (2) Happel, J., Hnatow, M. A., Mezaki, R., *J. Chem. Eng. Data*, **16**, 206 (1971).
- (3) Hnatow, M. A., Ph.D. thesis, Chemical Engineering Department, New York University, Bronx, N.Y., 1970.
- (4) Kamholz, K., Ph.D. thesis, Chemical Engineering Department, New York University, Bronx, N.Y., 1970.
- (5) Kistiakowsky, G. B., Ruhoff, J. R., Smith, H. A., Vaughan, W. E., *J. Amer. Chem. Soc.*, **57**, 876 (1935).
- (6) Prosen, E. J., Maron, F. W., Rossini, F. D., *J. Res. Nat. Bur. Stand.*, **46**, No. 2, 108 (1951).
- (7) Rossini, F. D., Ed., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.
- (8) Stull, D. R., Westrum, E. F., Jr., Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N.Y., 1969.

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