# Yu. M. Bakshi, A. I. Gel'bshtein, and M. I. Temkin

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## Abstract

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## PHYSICAL CHEMISTRY

Yu. M. Bakshi, A. I. Gel' bshtein, and M. I. Temkin

# ADDITIONAL DATA ON THE EQUILIBRIUM OF ETHYL ALCOHOL SYNTHESIS

*(Presented by Academician S. S. Medvedev, 30 XII 1959)*

Previously published data ($^1$) on the equilibrium

$$C_2H_4(g) + H_2O(g) = C_2H_5OH(g) \tag{1}$$

at pressures up to 81 atm show a linear dependence of $\log K_P$ on the total pressure $P$. This dependence, at a constant ratio $N_{H_2O}/N_{C_2H_4}$, corresponds to the equation of state of a gas mixture with the second virial coefficient. The values of $\log K_f$, obtained by linear extrapolation of $\log K_P$ to $P = 0$, were represented by the equation ($^1$)

$$\log K_f = \frac{2093}{T} - 6.304. \tag{2}$$

Additional measurements, the results of which are reported here, make it possible to judge the dependence of the ratio $\log K_\gamma / P$ on the composition of the mixture and to refine the dependence of this ratio on temperature ($K_\gamma = \gamma_{C_2H_5OH}/\gamma_{C_2H_4}\gamma_{H_2O}$, where $\gamma_{C_2H_5OH}$ is the activity coefficient of $C_2H_5OH$, etc.). The measurement procedure did not differ from that described in ($^1$). Gas-mixture compositions at which condensation was excluded were used. The results are presented in Table 1, where values of $K_P$ calculated with the aid of equation (2) are also given, taking, according to ($^1$), $\log K_\gamma / P = 14.2 \cdot 10^{-4}$ for 286°, and $K_\gamma = 1$ for 332°. As is seen from Table 1, the values

**Table 1**

| $T_{working}$, °C | Pressure, atm | Volume rate with respect to $C_2H_4$, $h^{-1}$* | $N_{H_2O}/N_{C_2H_4}$ | Initial mixture composition, mole fraction: $C_2H_4$ | Initial mixture composition, mole fraction: $H_2O$ | Initial mixture composition, mole fraction: $C_2H_5OH$ | Exit mixture composition, mole fraction: $C_2H_4$ | Exit mixture composition, mole fraction: $H_2O$ | Exit mixture composition, mole fraction: $C_2H_5OH$ | $K_P \cdot 10^3$, $atm^{-1}$ | $K_P \cdot 10^3$ by eq. (2), $atm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 286 | 36 | 3160 (40) | 0.16 | 0.863 | 0.137 | – | 0.840 | 0.146 | 0.0102 | 2.32 | 2.34 at $N_{H_2O}/N_{C_2H_4} = 0.51$ |
| 286 | 36 | 3160 (40) | 0.16 | 0.848 | 0.139 | 0.0124 | 0.838 | 0.146 | 0.0104 | 2.36 | 2.34 at $N_{H_2O}/N_{C_2H_4} = 0.51$ |
| 286 | 71 | 577 (40) | 1.3 | 0.450 | 0.650 | – | 0.434 | 0.526 | 0.0345 | 2.13 | 2.08 at $N_{H_2O}/N_{C_2H_4} = 0.51$ |
| 286 | 71 | 577 (40) | 1.3 | 0.464 | 0.521 | 0.0154 | 0.463 | 0.496 | 0.0351 | 2.16 | 2.08 at $N_{H_2O}/N_{C_2H_4} = 0.51$ |
| 332 | 41 | 1300 (12) | 0.35 | 0.739 | 0.261 | – | 0.735 | 0.250 | 0.0110 | 1.46 | 1.43 at $N_{H_2O}/N_{C_2H_4} = 1.8$ |
| 332 | 41 | 2180 (40) | 0.35 | 0.730 | 0.256 | 0.0149 | 0.728 | 0.258 | 0.0108 | 1.40 | 1.43 at $N_{H_2O}/N_{C_2H_4} = 1.8$ |
| 332 | 51 | 1310 (12) | 0.66 | 0.601 | 0.399 | – | 0.590 | 0.388 | 0.0164 | 1.41 | 1.43 at $N_{H_2O}/N_{C_2H_4} = 1.8$ |
| 332 | 61 | 1270 (12) | 0.96 | 0.511 | 0.489 | – | 0.497 | 0.477 | 0.0200 | 1.38 | 1.43 at $N_{H_2O}/N_{C_2H_4} = 1.8$ |

| $T_{working}$, °C | Pressure, atm | Volume rate with respect to $C_2H_4$, $h^{-1}$* | $N_{H_2O}/N_{C_2H_4}$ | Initial mixture composition, mole fraction: $C_2H_4$ | Initial mixture composition, mole fraction: $H_2O$ | Initial mixture composition, mole fraction: $C_2H_5OH$ | Exit mixture composition, mole fraction: $C_2H_4$ | Exit mixture composition, mole fraction: $H_2O$ | Exit mixture composition, mole fraction: $C_2H_5OH$ | $K_P \cdot 10^3$, $atm^{-1}$ | $K_P \cdot 10^3$ by eq. (2), $atm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 332 | 71 | 1260 (12) | 1.2 | 0.445 | 0.555 | – | 0.411 | 0.561 | 0.0224 | 1.37 | 1.43 at $N_{H_2O}/N_{C_2H_4} = 1.8$ |
| 332 | 81 | 1200 (12) | 1.5 | 0.400 | 0.600 | – | 0.363 | 0.606 | 0.0255 | 1.43 | 1.43 at $N_{H_2O}/N_{C_2H_4} = 1.8$ |
| 332 | 81 | 466 (40) | 1.5 | 0.373 | 0.593 | 0.0347 | 0.370 | 0.600 | 0.0255 | 1.42 | 1.43 at $N_{H_2O}/N_{C_2H_4} = 1.8$ |

* The content of $H_3PO_4$ in percent by weight of the catalyst is indicated in parentheses.

of $K_P$ at a given $P$, within the accuracy of the measurements, do not depend on the composition of the gas mixture. In addition, it is seen from the table that at 332° $K_P$

does not depend on $P$, i.e., this temperature is close to the "Guldberg-Waage temperature" (1). At lower temperatures $K_\gamma > 1$*. The table does not include data on the ether content, since equilibrium with respect to the ether-formation reaction was not reached.

As was shown (1),

$$\frac{\ln K_\gamma}{P} = \frac{2\sum_i \nu_i B_i - B\sum_i \nu_i}{RT}. \tag{3}$$

The dependence of the quantities $B_i$ and $B$ on $T$ can be represented by series of the form $a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} + \cdots$. Assuming that two terms of the series are sufficient, we arrive at a temperature dependence of $\log K_\gamma/P$ of the form

$$\frac{\log K_\gamma}{P} = \frac{A_0}{T} + \frac{A_1}{T^2}. \tag{4}$$

The experimental data correspond to the values $A_0 = -10.47$; $A_1 = 6.37 \cdot 10^3$. Equation (2), on the basis of the equality $K_P = K_f/K_\gamma$, gives

$$\log K_P = \frac{2093}{T} - 6.304 + \left(\frac{10.47}{T} - \frac{6.37 \cdot 10^3}{T^2}\right) P. \tag{5}$$

Equation (5) describes the dependence of $K_P$ on $T$ and $P$ and takes into account the independence of $K_P$ from the composition of the mixture. In Table 2 the values of $K_P$ according to equation (5)

Table 2

| Temp., °C | Pressure, atm* | $K_P \cdot 10^3$, exptl., atm$^{-1}$ | $K_P \cdot 10^3$ according to eq. (5), atm$^{-1}$ | Temp., °C | Pressure, atm | $K_P \cdot 10^3$, exptl., atm$^{-1}$ | $K_P \cdot 10^3$ according to eq. (5), atm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 258 | 41 | 3.30 | 3.31 | 318 | 41 | 1.65 | 1.64 |
| 258 | 81 | 2.52 | 2.54 | 318 | 81 | 1.63 | 1.57 |
| 286 | 41 | 2.30 | 2.35 | 345 | 41 | 1.18 | 1.24 |
| 286 | 51 | 2.25 | 2.26 | 345 | 81 | 1.17 | 1.27 |
| 286 | 71 | 2.08 | 2.10 | 365 | 41 | 0.94 | 1.02 |
| 286 | 81 | 2.03 | 2.02 | | | | |

*Note. In communication (1) an inaccuracy was introduced in specifying the unit of pressure. The pressures were measured in technical atmospheres (kg/cm$^2$).

are compared with the experimental values of $K_P$ obtained earlier (1). Tables 3 and 4 contain the equilibrium degrees of conversion of ethylene $\alpha$, calculated according to equation (5) under the assumption that only reaction (1) proceeds.

Table 3

Equilibrium degrees of conversion of ethylene to alcohol, $\alpha \cdot 10^2$, at $N_{H_2O}/N_{C_2H_4} = 1$

| Temp., °C | $P = 1$ atm | $P = 20$ atm | $P = 40$ atm | $P = 60$ atm | $P = 80$ atm | $P = 100$ atm |
|---|---|---|---|---|---|---|
| 250 | 0.253 | 4.14 | 6.85 | 8.64 | 9.78 | 10.5 |
| 270 | 0.184 | 3.16 | 5.40 | 7.11 | 8.40 | 9.35 |
| 290 | 0.130 | 2.36 | 4.28 | 5.85 | 7.15 | 8.24 |

| Temp., °C | $P = 1$ atm | $P = 20$ atm | $P = 40$ atm | $P = 60$ atm | $P = 80$ atm | $P = 100$ atm |
|---|---|---|---|---|---|---|
| 310 | 0.0985 | 1.86 | 3.50 | 4.95 | 6.27 | 7.40 |
| 330 | 0.0746 | 1.45 | 2.83 | 4.15 | 5.40 | 6.74 |

Table 4

Equilibrium degrees of conversion of ethylene to alcohol, $\alpha \cdot 10^2$, at 290°

| $N_{H_2O}/N_{C_2H_4}$ in the initial mixture | $P = 1$ atm | $P = 20$ atm | $P = 40$ atm | $P = 60$ atm | $P = 80$ atm | $P = 100$ atm |
|---|---|---|---|---|---|---|
| 0.4 | 0.0740 | 1.33 | 2.43 | 3.31 | 4.05 | 4.65 |
| 0.6 | 0.0972 | 1.75 | 3.20 | 4.37 | 5.34 | 6.25 |
| 0.8 | 0.115 | 2.09 | 3.79 | 5.20 | 6.36 | 7.29 |
| 1.0 | 0.130 | 2.36 | 4.28 | 5.85 | 7.15 | 8.24 |
| 2.0 | 0.173 | 3.14 | 5.68 | 7.78 | 9.51 | 10.9 |

For calculating $\alpha$ it is convenient to use the series

$$\alpha = \frac{n}{1+n}\frac{K_N}{1+K_N} + \frac{n^2}{(1+n)^3}\left(\frac{K_N}{1+K_N}\right)^2 + 2\frac{n^3}{(1+n)^5}\left(\frac{K_N}{1+K_N}\right)^3 + \cdots, \qquad (6)$$

where $n$ is the number of moles of $H_2O$ per 1 mole of $C_2H_4$ in the initial mixture, $K_N = PK_P$. The equilibrium gas mixture at $N_{H_2O}/N_{C_2H_4} = 1$, 250°, and 100 atm (and also, possibly, some others) is unstable with respect to condensation.

The data obtained make it possible to determine the thermal effect of reaction (1). Since $K_\gamma$ in the case under consideration does not depend on the composition of the gas mixture, then

$$\left(\frac{\partial \ln K_\gamma}{\partial T}\right)_P = \frac{\Delta H^0 - \Delta H}{RT^2}. \qquad (7)$$

From the relation

$$\frac{d \ln K_f}{dT} = \frac{\Delta H^0}{RT^2} \qquad (8)$$

and the equality $K_P = K_f/K_\gamma$, we obtain

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* The corresponding formulation in ([1]) contains misprints.

$$\left(\frac{\partial \ln K_P}{\partial T}\right)_P = \frac{\Delta H}{RT^2}. \tag{9}$$

Equation (5) gives

$$\Delta H = -9570 - \left(47.9 - \frac{5.83 \cdot 10^4}{T}\right) P. \tag{10}$$

At 300° and 80 atm, $\Delta H = -5263$ cal. This value differs substantially from $\Delta H^0 = -9570$ cal. Consequently, in technological calculations it is necessary to take into account the dependence of $\Delta H$ on $P$.

Physical-Chemical Institute
named after L. Ya. Karpov

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## CITED LITERATURE

1. Yu. M. Bakshi, A. I. Gelbshtein, M. I. Temkin, DAN, **126**, 314 (1959).

*Note: Figure translations are in progress. See original paper for figures.*

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