The experimental high pressure viscosities available for water (*27*) were found to be inconsistent with those of the other polar substances investigated. Jossi, Stiel, and Thodos (*11*) have presented a fourth degree polynomial relationship between $(\mu - \mu^*)\xi$ and ρ_R for this substance. This relationship is higher than that of Figure 1 at low densities and lower at high densities. The reason for the abnormal behavior of water is uncertain, but may be owing to its excessive hydrogen bonding effects. Considerable deviations among the data of the individual investigators have been obtained for this substance (*27*). The relationships developed in this and the previous study (*11*) indicate that the viscosity of both nonpolar and polar substances for high densities in the liquid region (for which μ^* is insignificant compared to μ) is extremely dependent on density. Baschinski (*3*) proposed the following relationship for the viscosity of liquids:

$$\mu = \frac{c}{v - b} \qquad (7)$$

Here c and b are specific constants for each substance, and v is the molar volume. Souders (*22*) has suggested that for organic liquids the quantity log (log μ) is proportional to the density. The relationship of Figure 1 is essentially consistent with such a form at high densities as shown in Equation (6). Experimental data for argon and nitrogen (*30, 31*) indicate that a unique dependence between liquid viscosity and density is exactly correct only at a reduced density of 2.0 and approximately correct at lower reduced densities. At higher reduced densities the relationship between viscosity and density may be quite dependent on temperature. However, in the present study the effects of other variables could not be observed because of the extreme sensitivity of the group $(\mu - \mu^*)\xi$ on ρ_R.

NOTATION

b, c = constants in Equation (7)
m, n = exponents in Equation (3)
M = molecular weight
P_c = critical pressure, atm.
R = gas constant, 82.055 cc. atm./g.-mole °K.
T = temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
v = molar volume, cc./g.-mole
v_c = critical volume, cc./g.-mole
z_c = critical compressibility factor, $P_c v_c / RT_c$

Greek Letters

α = proportionality constant in Equation (3)
μ = viscosity, centipoises
μ^* = gaseous viscosity at approximately atmospheric pressure, centipoises
ξ = viscosity parameter, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c

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Equilibria in the Hydration of Ethylene and of Propylene

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In a previous article by Cope and Dodge (*1*), it was shown that two simultaneous reactions occur when ethylene is hydrated at elevated temperatures and pressure in the presence of a dilute mineral acid as catalyst:

$$C_2H_4 + H_2O = C_2H_5OH \qquad (1)$$

$$2\,C_2H_5OH = C_2H_5OC_2H_5 + H_2O \qquad (2)$$

It was further shown that, while the agreement between directly measured values of equilibrium composition at various temperatures and those calculated from thermochemical data was reasonably good for reaction (1), such was not the case for reaction (2). Based on an analysis of the various thermochemical data then available, it was concluded that the most likely source of the discrepancy lay in the value of the absolute entropy of ethyl

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ether. Two recent papers have now served to resolve considerably the conflict of the data.

Results of a further direct measurement (*2*) of equilibrium composition indicate the equilibrium constant, *Kp*, to be 24.7 ± 0.1 at 120.8°C. This measurement appears to be of good reliability; equilibrium was approached from both sides, and the absence of side reactions was established. As may be seen in Figure 1, this result lends strong support to that measured at 135°C. by Atherton as cited in reference *1*.

A precise determination (*3*) of the heat of formation of ethyl ether indicates that the value of −58.6 kcal./mole (at 25°C.) selected in reference *1* after analysis of older measurements should be changed to −60.28 ± 0.19 kcal./mole.

Previous analyses (*1*, *2*) of the best available data had indicated that an increase of about 3.4 cal./(mole) (°K.) in the value of 81.85 entropy units (E.U.) for the absolute entropy of gaseous ethyl ether at 25°C., as derived in reference *1* from the low-temperature specific-heat measurements of Parks and Huffman, would be required to bring the thermochemical data into agreement with the preferred values of directly measured equilibrium composition. The value of the absolute entropy, as obtained by means of the standard method of calculation (*4*) from the newer figures for the equilib-

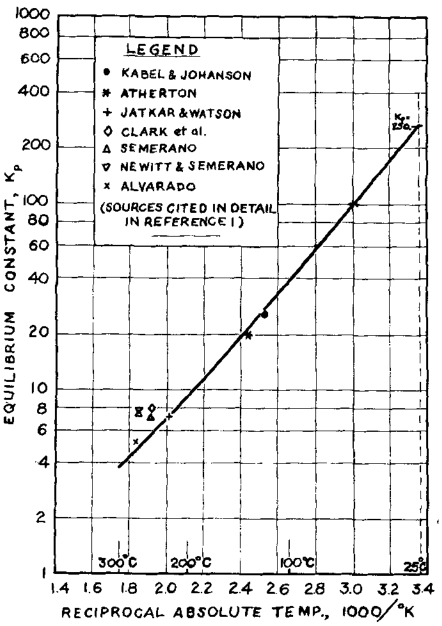

Fig. 1. Logarithm of equilibrium constant vs. reciprocal absolute temperature: $2C_2H_5OH_{(g)} = C_2H_5OC_2H_{5(g)} + H_2O_{(g)}$. The curve represents *equilibrium constants calculated entirely from thermochemical data.*

INFORMATION RETRIEVAL*

Use of adiabatic experiments for kinetic studies in fixed catalyst beds, Schmidt, J. P., H. S. Mickley, and S. L. Grotch, **A.I.Ch.E. Journal, 10,** No. 2, p. 149 (March, 1964).

Key Words: Cumene, Catalyst, Cracking-1, Benzene, Propylene-2, Di-isopropylbenzene-3, Silica-Alumina Catalyst-4, Adiabatic, Gas-5, Temperature, Pressure-6, Reaction Rate, Kinetics-7, Catalysis, Heterogeneous Reaction-8, Kinetics, Experimental Method-9, Adiabatic Reactor-10.

Abstract: A method is presented for using an adiabatic reactor to study the kinetics of reactions of gases on solid catalysts. The method was demonstrated by an experimental study of cumene cracking on silica-alumina catalyst at 420° to 480°C. Areas of application of the adiabatic method are suggested.

Diffusion through the liquid-liquid interface, Ward, W. J., and J. A. Quinn, **A.I.Ch.E. Journal, 10,** No. 2, p. 155 (March, 1964).

Key Words: Diffusion-6, Liquid-Liquid Interface-8, Benzene-9, Toluene-9, Water-0, Interfacial Resistance-8, Mass Transfer-8, Equilibrium-8, Contact Time-8, Solubility-8.

Abstract: A dynamic method has been developed for measuring transient rates of diffusion through the liquid-liquid interface. Measurements are reported on the diffusion of benzene and toluene into water at 25°C. The measured transfer rates agree well with predictions based on the assumption of interfacial equilibrium. The results indicate that any interfacial resistance present in these systems must be less than approximately 10 sec./cm.

Pure diffusional mass transfer in zone melting, Wilcox, W. R., and C. R. Wilke, **A.I.Ch.E. Journal, 10,** No. 2, p. 160 (March, 1964).

Key Words: Diffusion-6, Mass Transfer-7, Separation-8, Segregation-8, Purification-8, Refining-8, Zone Melting-9, Eutectics-9, Solidification-9, Fusing-9, Crystallization-9, Mathematics-10, Computations-10.

Abstract: The differential equation and boundary conditions for pure diffusional mass transfer in zone melting are derived. Numerical solutions are obtained and approximated algebraically for eutectic forming systems. An analytical solution for constant distribution coefficient is obtained. Graphs are given which permit rapid approximation of concentration profiles resulting from one zone pass. Example problems are provided which illustrate the use of the calculation techniques developed.

Calculation of concentration response to intermittent irradiation, Hill, F. B. **A.I.Ch.E. Journal, 10,** No. 2, p. 166 (March, 1964).

Key Words: Differential Equations-1, Difference Equations-1, Equations-2, Intermittent Radiation-4, Irradiator Type-6, Kinetic Mechanism-6, Frequency of Irradiation-6, Mixing-6, Concentration Transients-7, Steady State Concentrations-7, Intermittent Irradiation-8, Irradiator Design-9, Chemical Reaction Engineering Research-9, Photochemistry-9, Radiation Chemistry-9, Photobiology-9, Irradiator-10, Chemical Reactor-10, Nuclear Reactor-10, Visible Light-, Ultraviolet Light-, Ionizing Radiation-, Neutrons-, X-rays-.

Abstract: Initiation of reactions by intermittent irradiation is frequently encountered in chemical, physical, and biological systems. Mathematical expressions for transient and steady state concentrations of reactive species in these systems are useful for predicting performance and for research purposes. Methods of formulation and solutions of the transient and steady state intermittent irradiation problem are presented herein for a number of irradiator types, for first- and second-order reactions of intermediate species, and for consecutive first-order reactions.

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*For details on the use of these key words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr.,** 57, No. 5, p. 55 (May, 1961), No. 6, p. 73 (June, 1961); **58,** No. 7, p. 9 (July, 1962).

NOTE: Additional pages of information retrieval abstracts and key words in this issue are available on request.

Table 1.

Formula	Absolute entropy* (ideal gas, 1 atm., 25°C.) cal./(mole)(°K.)	Δ
CH_3OCH_3	63.74	(18.11)
$CH_3CH_2OCH_2CH_3$	(81.85)	
$CH_3CH_2CH_3$	64.51	18.89
$CH_3CH_2CH_2CH_2CH_3$	83.40	

* References *1*, *5*, and *7*.

rium constant and heat of formation cited above, together with pertinent auxiliary thermochemical data presented in reference *1*, is 81.72 E.U., in close agreement with the results of Parks and Huffman. The basic source of discrepancy in the thermochemical data thus appears to have been in the value of heat of formation, rather than of the absolute entropy as concluded in reference *1* and reiterated in reference 2.

Further indication that the value of 81.85 E.U. is probably about correct comes from a consideration of the absolute entropies of several compounds related structurally to ethyl ether, as indicated in Table 1.

The entropy values shown for methyl ether, propane, and *n*-pentane are well established, both from direct specific-heat measurements and by statistical mechanical calculations. (No estimation of the entropy of ethyl ether by the latter method has yet been published, insofar as the author is aware.) The differences in the entropies of corresponding members of the above two homologous series are in reasonably good agreement and suggest that the entropy of ethyl ether should hardly be expected to exceed 63.74 + 18.89 = 82.63 E.U.

The curve representing the equilibrium constant for reaction (2) as a function of temperature, as calculated solely from thermochemical data, is shown in the conventional log Kp vs. T^{-1} form in Figure 1. Shown for comparison are the values obtained by various investigators by direct measurement of composition. We have omitted portions or all of the results of several investigators which were previously shown (*1*) to be substantially in error. Although most of the experimental results in the neighborhood of 250°C. lie somewhat above the curve, the divergence is greatly reduced from that shown in Figure 2 of reference *1* and by no means exceeds the various uncertainties in the several individual items of data on which the curve is based. The two experimental values at lower temperatures lie only slightly below the curve. It is difficult to specify the most likely source or sources of whatever discrepancy may remain.

EQUILIBRIUM CALCULATIONS FOR THE HYDRATION OF PROPYLENE

Sufficient data have also now accumulated to permit a calculation, using the methods described in reference *1* for the analogous case of the hydration of ethylene, of equilibrium compositions satisfying the two corresponding simultaneous reactions which occur in the hydration of propylene at elevated pressures and temperatures. Such calculations could be compared with the direct measurements of both liquid- and vapor-phase compositions as reported by Majewski and Marek (*6*). Confidence in the value for the absolute entropy of isopropyl ether as measured by Parks, Huffman, and Barmore (*7*) is strengthened by the considerations presented above for the case of ethyl ether, and a value for the heat of formation of isopropyl ether is now available (*8*). Comprehensive thermochemical and related data of high reliability are also available for isopropanol (*9*). Critical-point constants for isopropyl ether have been determined (*10*). A very limited number of auxiliary thermal data would have to be estimated for isopropyl ether, but the requirements on their precision would fortunately not be stringent.

ACKNOWLEDGMENT

The author wishes to thank Professor B. F. Dodge of Yale University, New Haven, Connecticut, and W. M. D. Bryant of E. I. du Pont de Nemours and Company, Incorporated, for their suggestions.

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