

on the 29 experimental P - V - T data given by Brown (2), the average deviation of the calculated pressures using Equation 1 from the measured values was 0.22%, indicating the suitability of the equation for the calculation of thermodynamic properties of perfluoropropane.

ACKNOWLEDGMENT

Grateful acknowledgment is made to Allied Chemical Corp. for the use of their digital computer, and to members of their automation group for their assistance.

NOMENCLATURE

$A_2, A_3, A_4,$
 $B_2, B_3, B_5,$
 C_2, C_3, b = constants in the Martin and Hou equation of state
 a, b, c, d = constants in vapor pressure equation
 C_p^0 = ideal heat capacity at constant pressure, cal./gram-mole ° K.
 H = enthalpy, cal./gram-mole
 H_0 = enthalpy evaluated at base temperature and pressure
 ΔH_v = enthalpy of vaporization
 k = a parameter in the Martin and Hou equation of state, 5.475
 P = pressure, atm.
 P_c = critical pressure
 P_i = pressure at which gas is assumed to be ideal, 0.0001 p.s.i.a. or 0.6803×10^{-5} atm.

R = gas constant, 0.08205 liter-atm./gram-mole ° K.
 S = entropy, cal./gram-mole ° C.
 S_0 = entropy evaluated at base temperature and pressure
 ΔS_v = entropy of vaporization
 t = temperature, ° C.
 T = absolute temperature, ° K. = t ° C. + 273.16°
 T_c = critical temperature
 V = specific volume, liter/gram-mole
 V_g = vapor specific volume
 V_l = liquid specific volume
 V_i = initial specific volume
 V_f = final specific volume

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Equilibria in the Hydration of Propylene and of Butylenes

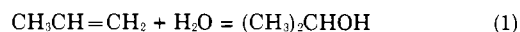
C. S. COPE

E. I. du Pont de Nemours and Co., Inc., Parkersburg, W. Va.

Precise thermochemical data which permit calculation of equilibrium states in the hydration of propylene and of the various isomers of butylene have recently become available. Comparisons are made between compositions thus calculated and reported values obtained by direct measurement. For the hydration of propylene with liquid and vapor phases simultaneously present, the thermochemical data, together with appropriate vapor-liquid equilibrium data, are used to estimate equilibrium compositions of both phases. The equilibrium constants for the hydration of the various C_2 - through C_4 -olefins show considerable similarities in behavior as functions of temperature, whereas those for the etherification of the corresponding alcohols differ more markedly. Etherification tendency decreases on progressing up the series, and is quite unfavorable for the formation of the sterically hindered *tert*-butyl ether.

A PREVIOUS ARTICLE (6) discussed equilibria in the hydration of ethylene with liquid and vapor phases simultaneously present. The importance of taking account of ethyl ether formation in this reaction system was pointed out. A comparison was made of equilibrium compositions calculated from available thermochemical and phase-equilibrium data and those measured experimentally. However, extension of the method of calculation to the propylene hydration system was severely restricted by the questionable reliability of various necessary thermochemical data. A more recent communication (5) indicated that thermochemical data of good precision have now become available for the propylene system.

One purpose of the present paper is to derive values of equilibrium constant, K_p , for the reactions



from thermochemical data, and to compare these with reported values obtained by direct measurement of equilibrium composition. Later, an analogous treatment of reactions involved in the hydration of butylenes is presented. Another purpose is to utilize the low-pressure equilibrium data, together with appropriate phase-equilibrium data for the binary system isopropyl alcohol-water, to present an approximate calculation of equilibrium compositions for the hydration of propylene under two-phase conditions.

HYDRATION OF PROPYLENE

Calculation of Equilibrium Constants from Thermochemical Data; Results of Previous Direct Measurements of Equilibrium Constant. As indicated in the preceding equations, the hydration of propylene, when carried out in the presence of dilute mineral acid catalysts, follows the familiar

Markownikoff rule to give isopropyl alcohol to the exclusion of *n*-propyl alcohol. The thermochemical data required for treating Reactions 1 and 2 are listed in Table I.

From these data, K_p values, as calculated by the usual procedure (7), are shown for Reaction 1 in conventional form in Figure 1, and are tabulated for Reaction 2 as a function of temperature in Table II. Represented in Figure 1 and in Table II are the corresponding relationships for the ethylene hydration system. While the values of K_p for the direct hydration reactions are not greatly different for the two systems, those for the etherification reaction in the propylene system average about 20-fold lower, over the temperature range from 200° to 300° C., than those for the ethylene system.

Also represented in Figure 1 are values derived from three reported sets of experimental measurements of equilibrium composition. Excellent agreement between calculated and experimental results is observed in the case of the study by Majewski and Marek (12), which was carried out at elevated pressures with two phases present. The atmospheric-pressure, vapor-phase results of Stanley, Youell, and Dymock (23) and of Shiffler, Holm, and Brooke (21) are in less good agreement, especially with respect to the temperature dependence of K_p . The tendency toward etherification in the latter study was observed to be much less than that in the ethylene system, as supported by the present thermochemical data.

No direct measurements of equilibrium composition for

Table I. Thermochemical Data for the Propylene Hydration System

Ideal Gas State at 1 Atm. and 298.2° K. (25° C.)

Substance	Heat of Formation, Kcal./Mole	Absolute Entropy, Cal./(Mole)(° K.)
Propylene ^a	+4.879	63.80
Water ^b	-57.798	45.106
Isopropyl alcohol ^c	-65.19	74.07
Isopropyl ether	-76.4 ^d	92.7 ^e

Specific Heat Equations^f

Ideal Gas State, 300° to 700° K.

$$C_p = \alpha + \beta T + \gamma T^2, \text{ Cal./ (Mole) } (^\circ \text{ K.})$$

Substance	α	$\beta \times 10^3$	$\gamma \times 10^6$
Propylene ^a	2.02	49.3	-16.3
Water ^a	7.85	-0.217	+2.656
Isopropyl alcohol ^c	0.40	80.3	-35.5
Isopropyl ether ^a	6.8	122.5	-43.0

^a (18). ^b (19). ^c (9). ^d (16). ^e Value for the liquid (15), corrected to a molecular weight of 102.17 and converted to the ideal gas state by using the heat of vaporization and vapor-pressure data of Reference (13), together with a small correction based on the modified Berthelot equation of state. ^f Fitted to tabulated data in the specific references cited. ^g The specific heat at any temperature was assumed to be greater than that given for ethyl ether (6) by an amount equal to the difference in the known specific heats of 2,4-dimethylpentane and *n*-pentane (20).

Table II. Values of Equilibrium Constant vs. Temperature

$$2ROH_{(g)} = ROR_{(g)} + H_2O_{(g)}$$

(Calculated from Thermochemical Data)

Temp., ° C.	Equilibrium Constant, K_p	
	$R = C_2H_5-$ (5)	$R = (CH_3)_2CH-$
25	251.	3.37
75	64.5	1.38
150	16.8	0.57
200	8.9	0.38
250	5.5	0.28
300	3.8	0.22

Reaction 2 are known to have been reported. The thermochemical data now available appear, however, to be reliable.

Calculation of Equilibrium Compositions for the Two-Phase System. From the K_p values for Reactions 1 and 2, as presented in the previous section, together with pertinent liquid-vapor equilibrium data (1) for the binary isopropyl alcohol-water system, a calculation has been made of the equilibrium compositions of both phases for the hydration of propylene at elevated temperatures and pressures. The same methods and procedures as those described previously (6) were employed, using analogous assumptions, including that of negligible solubility of olefin in the liquid phase. As before, the calculations are based on the extensive use of the assumption of ideal-solution behavior, the limitations of which under conditions as severe as those considered here have long been recognized. The highest temperature at which calculations could be carried out was 275° C., as insufficient data for 300° C. were available from Reference (1). At the relatively low temperature of 150° C., the method is overextended and gives unsatisfactory results.

The calculated equilibrium compositions are presented in Table III. Comparison of these figures with those given for the hydration of ethylene under similar conditions (6) generally shows the behavior which would be expected from the considerable similarities in the equilibrium constants for the direct hydration reactions and also in the binary liquid-vapor equilibria and the marked differences in the K_p values for the two etherification reactions. The calculated values of composition given in Reference (6) are not greatly affected by the revisions to the K_p values for the etherification reaction subsequently given in Reference (5).

Comparison of Reported and Calculated Values of Equilibrium Composition. For direct comparison with the calculated values of composition, the results of the aforementioned

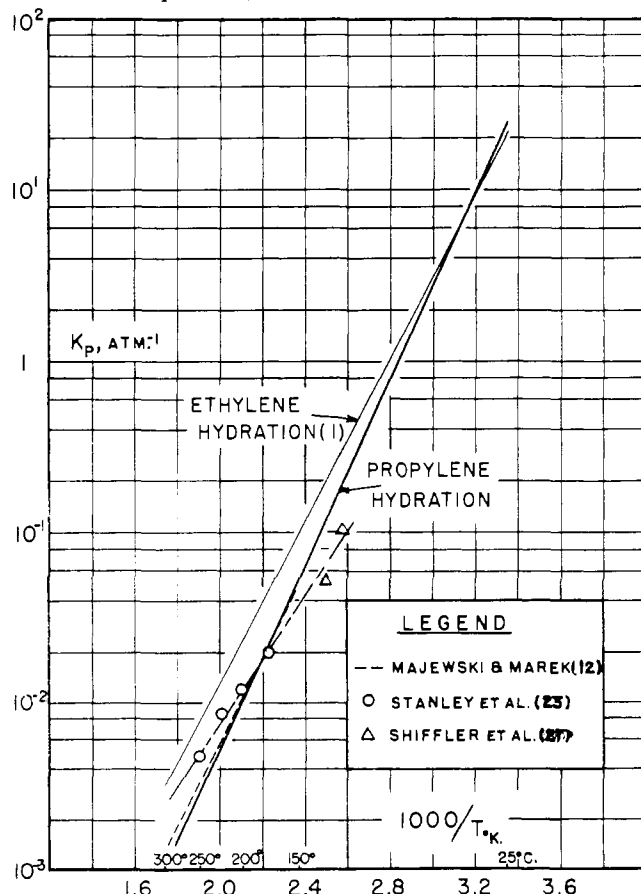


Figure 1. Logarithm of equilibrium constant vs. reciprocal absolute temperature
Solid lines represent equilibrium constants calculated solely from thermochemical data

Table III. Calculated Values of Equilibrium Composition for the Hydration of Propylene

Pressure, Atm.	Alcohol Conc. in Liquid Phase, Mole %	Concentrations in Vapor Phase, Mole %			
		Isopropyl alcohol	Water	Propylene	Isopropyl ether
200° C.					
100	3.8	17.3	23.3	54.8	4.6
200	5.5	24.0	18.9	48.8	8.3
300	6.2	28.3	18.2	43.6	9.9
400	6.3	31.2	18.8	37.6	12.4
500	5.7	35.3	19.8	31.9	13.0
250° C.					
100	1.2	7.9	49.3	42.5	0.3
200	2.1	13.0	37.6	48.6	0.8
300	2.6	14.5	36.1	48.5	0.9
400	3.2	15.3	36.1	47.5	1.1
500	3.7	15.2	37.8	45.7	1.3
275° C.					
100	0.9	3.9	69.7	26.3	0.1
200	1.6	8.1	52.0	39.7	0.2
300	2.0	9.5	49.2	41.0	0.3
400	2.3	9.8	48.5	41.3	0.4
500	2.4	9.7	51.0	38.9	0.4

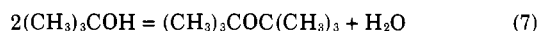
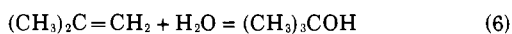
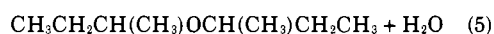
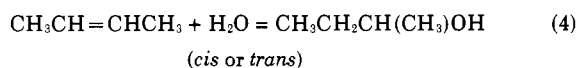
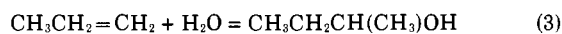
study by Majewski and Marek, carried out at temperatures from about 160° to 290° C. and at pressures from 95 to 503 atm., are available. A selected majority of their compositional data for both the liquid and vapor phases is reproduced in Table IV. Comparison of these data with those of Table III indicates the following significant features.

LIQUID PHASE. The calculated trends for the concentration of isopropyl alcohol with temperature and pressure are generally in agreement with those observed experimentally. The two sets of values are in reasonably good quantitative agreement, especially in view of several approximations and complicating factors involved.

VAPOR PHASE. At the lower temperatures, the calculated concentrations of isopropyl alcohol are in reasonable quantitative agreement with the measured values. The calculated values of concentration of water tend to be somewhat lower than the measured ones, although at higher temperatures the agreement improves. At these higher temperatures, the calculated propylene and isopropyl alcohol concentrations are higher than the measured ones, a result partially attributable to the irreversible polymerization of propylene, which is not taken into account in the calculations.

HYDRATION OF BUTYLENES

Calculation of Equilibrium Constants from Thermochemical Data; Comparison with Reported Experimental Results. At present, the treatment just applied to the hydration of propylene at elevated temperatures and pressures cannot be extended to the hydration of butylenes because of lack of appropriate vapor-liquid equilibrium data for the systems *sec*-butyl alcohol-water and *tert*-butyl alcohol-water. However, the basic thermochemical data presented in Table V are available from which K_p values can be calculated as functions of temperature for the following reactions:



Although the choice of this specific set of equations to

Table V. Thermochemical Data for the Hydration of Butylenes

Substance	Ideal Gas State at 1 Atm. and 298.2° K. (25° C.)		
	Heat of Formation, Kcal./Mole	Absolute Entropy, Cal./ (Mole) (° K.)	
1-Butene ^a	-0.03	73.04	
2-Butene (<i>cis</i>) ^a	-1.67	71.90	
(<i>trans</i>) ^a	-2.67	70.86	
<i>sec</i> -Butyl alcohol ^b	-69.84	85.81	
<i>sec</i> -Butyl ether	-86.28 ^c	111.5 ^d	
Isobutylene ^a	-4.04	70.17	
<i>tert</i> -Butyl alcohol ^e	-74.72	77.98	
<i>tert</i> -Butyl ether	-87.2 ^f	104.5 ^d	
Specific Heat Equations ^g			
Ideal Gas State, 300° to 700° K.			
$C_p = \alpha + \beta T + \gamma T^2$, Cal./ (Mole) (° K.)			
	α	$\beta \times 10^3$	$\gamma \times 10^6$
1-Butene ^a	0.33	76.9	-31.5
2-Butene (<i>cis</i>) ^a	-0.80	74.1	-27.5
(<i>trans</i>) ^a	3.41	65.6	-22.3
<i>sec</i> -Butyl alcohol ^b	2.72	93.1	-38.3
<i>sec</i> -Butyl ether ^h	6.3	166.9	-63.5
Isobutylene ^a	2.37	71.9	-28.3
<i>tert</i> -Butyl alcohol ^e	0.82	101.8	-45.8
<i>tert</i> -Butyl ether ⁱ	1.9	184.7	-72.9

^a(20). ^b(2). The more recent value of 85.69 E.U. established in Reference (4) for the absolute entropy of *sec*-butyl alcohol has an insignificant effect on the calculations made here. ^c(17). ^dSee Table VI: (Deposited with ADI). ^e(3). ^f(22). ^gFitted to tabulated data in specific references cited. ^hSpecific heat was assumed to differ from that of isopropyl ether (Table I) by the difference in the known specific heats of 3,5-dimethylheptane and 2,4-dimethylpentane (20). ⁱSpecific heat was assumed to differ from that of *sec*-butyl ether by the calculated difference in the specific heats of the corresponding paraffinic hydrocarbons, as estimated by the well-known method of Andersen, Beyer, and Watson, with both hydrocarbons derived from *n*-pentane by the appropriate methyl substitutions.

represent the over-all hydration system is necessarily arbitrary, it is believed, within the restrictions imposed by the rule of Markownikoff, to form a complete—yet not redundant—representation of the equilibrium relationships for the system. Since both Equations 3 and 4 share common reactants on either side—namely, water and *sec*-butyl alcohol—the achievement of equilibrium with respect to both reactions implicitly signifies the attainment of isomerization equilibria among 1-butene, *cis*-2-butene, and *trans*-2-butene, though the *iso*-structured olefin of Equation 6 is, of course, excluded.

While all of the reported heats of formation have been directly measured, it was necessary to estimate the absolute entropies of both *sec*- and *tert*-butyl ethers. The estimates given—perhaps correct to within ± 2 E. U.—are based on an extension of the analogy drawn in Reference (5) between the entropies of the lower ethers and those of the corresponding paraffinic hydrocarbons.

Values of K_p as calculated from the data of Table V are shown as functions of temperature in Figure 2 for Reaction 6 and in Figure 3 for Reactions 3 and 4. Included in Figure 2 are the results obtained by several groups of investigators by direct measurement of equilibrium composition. The more precise and reliable studies are those of Taft and Riesz (24) and of Eberz and Lucas (8), both of which were made at relatively low temperatures and pressures in the presence of a liquid phase. The data points shown in Figure 2 to represent their results are not those measured directly, but rather those converted to represent K_p values for reaction entirely in the vapor phase at the same corresponding temperatures, based on auxiliary thermal and vapor-pressure data either measured or estimated by the two sets of investigators. The two other investiga-

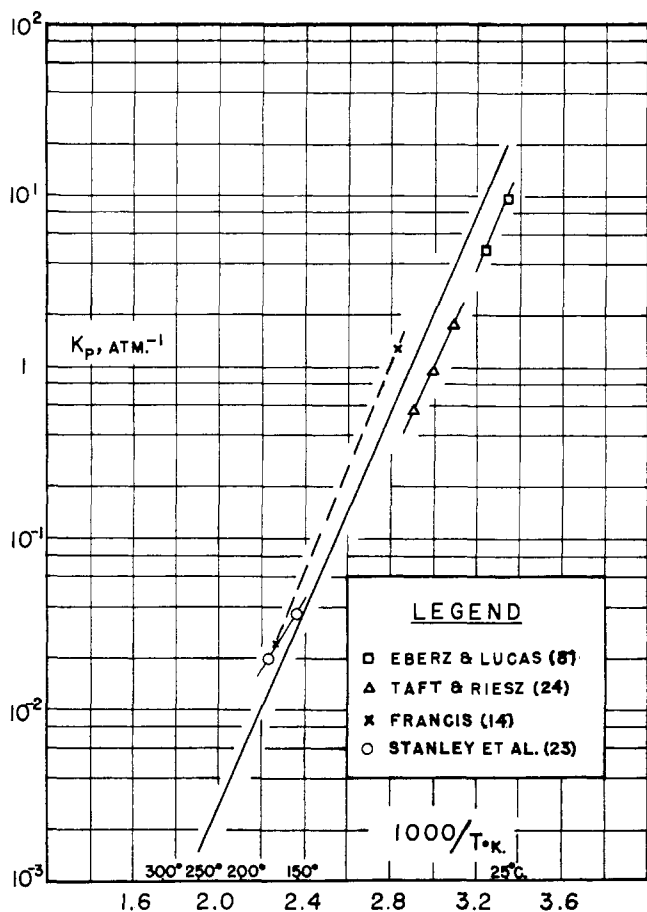


Figure 2. Logarithm of equilibrium constant vs. reciprocal absolute temperature for the hydration of isobutylene
Longest line represents equilibrium constants calculated solely from thermochemical data

tions cited were carried out in the vapor phase at atmospheric pressure and at higher temperatures; the results of Francis can only be considered approximate. The overall agreement of the K_p values as calculated from thermochemical data with those measured experimentally is considered satisfactory.

Fewer direct measurements of equilibrium compositions are available for either Reaction 3 or 4. Stanley, Youell, and Dymock studied, at atmospheric pressure, the hydration of a mixture of butylenes obtained by the dehydration of *n*-butyl alcohol over an acidic catalyst. The mixture was known to consist of 1-butene and 2-butene(s), with the latter stated to be "in excess." Under the preparative conditions employed, it appears, from general considerations of probable reaction mechanism, that the *trans* form of 2-butene would have been favored over the *cis* isomer. Since the results here lie considerably below the calculated equilibrium relationships and, thus, in the opposite direction to that observed by the same investigators for the hydration of isobutylene, it is appropriate to question the validity of the assumption made by Stanley, Youell, and Dymock that the two (actually probably three) isomeric butylenes present in their mixture could be regarded "as a single compound for practical purposes"—i.e., their K_p values were defined in terms of the measured partial pressure of total isomeric olefins present. At atmospheric pressure and over the range of temperature from 150° to 250° C. employed by Stanley, Youell, and Dymock, it may readily be calculated from the data of Table V (or Figure 3) that the equilibrium composition of the 1-butene, *cis*-2-butene, and *trans*-2-butene isomers lies within the limits of about 8–13, 30–32, and 62–55 %, respectively. Assuming that a true over-all equilibrium was achieved, and that *trans*-2-butene

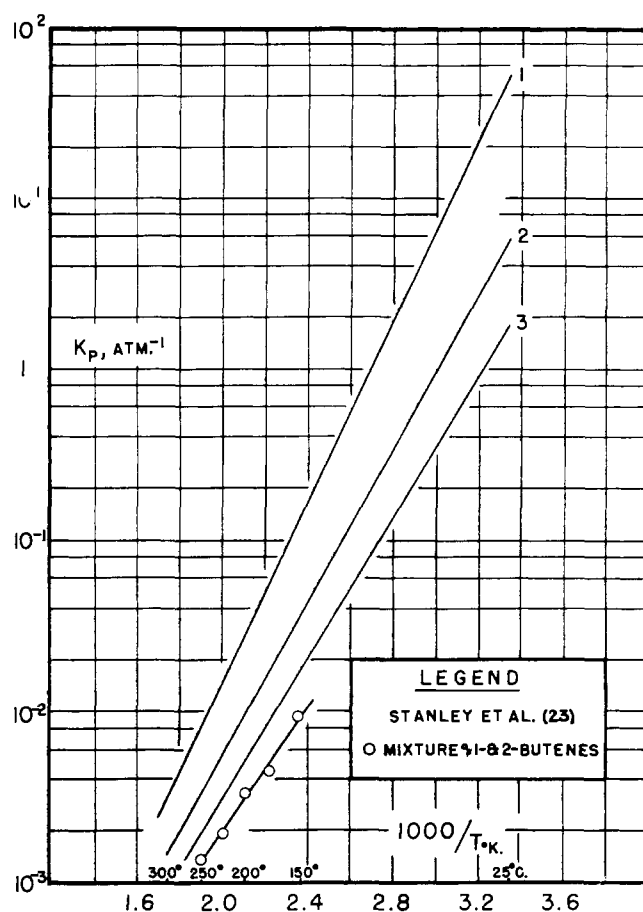


Figure 3. Logarithm of equilibrium constant vs. reciprocal absolute temperature for the hydration of butylenes
Numbered lines represent equilibrium constants calculated solely from thermochemical data

- | | | |
|---|------------------------|---------------------------------|
| 1 | 1-Butene | } + H ₂ O = sec-BuOH |
| 2 | <i>cis</i> -2-Butene | |
| 3 | <i>trans</i> -2-Butene | |

constituted about 60% of the total olefin in each run, the K_p value as defined by Stanley, Youell, and Dymock is thus reckoned to be about 40% below that calculated when the isomers are considered individually. Adjustment of the experimental results upward by this amount brings them into very good agreement with Curve 3 of Figure 3. Furthermore, the generally close agreement of the heat of reaction, as calculated from the experimental data, with the corresponding values obtained by the same investigators for the hydration of ethylene, propylene, and isobutylene tends to confirm the postulated likelihood of a relatively small variation in the equilibrium composition of the isomers over the temperature range involved. Admittedly, it is not possible, within the accuracy of the data, to state unequivocally that a condition of true equilibrium was actually achieved.

Etherification of *sec*- and *tert*-Butyl Alcohols. The calculated values of K_p at 25° C. for the etherification of *sec*-butyl and *tert*-butyl alcohols are 0.88 and 0.000023, respectively. At 250° C., these values become 0.047 and 0.00075. The increase with temperature in the latter case results from the endothermic nature of Reaction 7. The exothermic heat of reaction at 25° C. for Reaction 5 is, as might be expected, not greatly different from the corresponding values for the etherification of ethyl and isopropyl alcohols; no direct study of equilibrium in this reaction appears to have been published. The relatively low K_p values for Reaction 7 indicate that formation of *tert*-butyl ether in the hydration of isobutylene can be neglected for all practical purposes; in fact, the difficulty of synthesizing the sterically strained

tert-butyl ether by any of a variety of conventional techniques is well established (22).

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Tetrafluoromethane

Thermodynamic Properties of the Real Gas

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The thermodynamic properties, $H - H^\circ$, $S - S^\circ$, and $G - G^\circ$, of tetrafluoromethane were determined as functions of temperatures (0° to 350° C.) and molal density (0.75 to 11.0 gram-moles per liter) over a pressure range of 0 to 400 atm. The analytical and graphical correlating techniques described have produced results that reflect all of the inherent accuracy of the basic data used, and in this sense the values given are useful as comparison standards.

THE thermodynamic properties of compressed gaseous tetrafluoromethane were determined at the Bureau of Mines as part of a larger program (8, 9) to evaluate P - V - T and intermolecular potential energy relationships as well as chemical thermodynamic properties for hydrocarbons, fluorocarbons, and mixtures of hydrocarbons and fluorocarbons.

The quantities presented in this paper are the contributions that originated in the intermolecular phenomenon or nonideality of the gas. Thus, to obtain thermodynamic properties for the total or real gas, one must add to the present values the contributions for the ideal gas at the same temperature and at 1-atm. pressure. Spectroscopically based values of the ideal gas have been reported by Nagarajan (13) and by McBride and coauthors (12).

In addition to providing useful information for various direct engineering applications, the present values will qualify, when required, as standards in the sense that they reflect faithfully all of the trends that appear in the experimental data from which they were derived. Because the computations are based directly on unsmoothed experimental compressibility values (8) measured at even temperatures and densities, the introduction of spurious trends from arbitrary smoothing of the basic data was prevented.

Many of the numerical calculations were performed on a digital computer; however, a combination of analytical and graphical correlational methods was adopted to ensure full utilization of the inherent accuracy and precision of the experimental results.

Briefly, the approach to the correlations was as follows: First, the temperature-dependent slopes of the experimental isometric lines $(\partial P/\partial T)_\rho$, which appear in the integrands for enthalpy and entropy (Equations 1 and 2), were evaluated by fitting analytical functions to them, differentiating the analytic functions with respect to temperature, and adding graphically determined residuals. The integrals that contained $(\partial P/\partial T)_\rho$ were then evaluated graphically. Location of the zero density intercepts of the integrals, which usually presents a problem, was accurately placed by a method based on independently derived values of the second virial coefficients and their first derivatives with respect to temperature.

Recently, Chari (7) calculated thermodynamic properties for the saturated liquid and gas, and the superheated gas. However, his calculations for the super-heated gas were based on unpublished values of the P - V - T properties, and it seemed best, therefore, not to make a serious attempt at comparing those results with the currently derived ones.