

Part I

PHASE EQUILIBRIA

MOLECULAR TRANSPORT

THERMODYNAMICS

Phase Behavior of the System

Hydrogen Chloride-Ethane-2-Methylpentane

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PREDICTION of the phase behavior of polar-nonpolar mixtures is difficult because of the disappearance of dipole-dipole interactions when such systems are formed (12). The hydrogen chloride-ethane-2-methylpentane system well illustrates this effect. When hydrogen chloride enters the nonpolar solution, permanent dipole interactions are replaced by interactions between permanent and induced dipoles. Because the latter interactions are small, the volatility of hydrogen chloride exceeds that of ethane more than would be predicted from their vapor pressures. Therefore, existing correlations are not applicable and experimental data are necessary to define the phase behavior accurately.

Liquid and vapor compositions for this system were measured at pressures of 10 to 30 atm. and temperatures of 40° to 180° C. Saturated liquid and vapor densities were measured under the same conditions. Because the measurements were very time-consuming, not enough points were taken to permit completely empirical interpolation. Therefore, interpolation was accomplished by setting up an equation of state for the gas phase and calculating liquid phase fugacity coefficients.

MATERIALS AND PROCEDURE

Hydrogen chloride was prepared by the action of concentrated H_2SO_4 on KCl, and was purified by passing through traps at $-125^\circ C$. and then through activated charcoal at $-78^\circ C$. It had a purity of 99.8 mole %, as indicated by mass spectrometry. Ethane (Phillips research grade) had a stated purity of 99.9 mole %, which was checked by mass spectrometry. 2-Methylpentane (Phillips research grade) had a stated purity of 99.9 mole %, which was checked by gas chromatography. The HCl and ethane were dried by passing through P_2O_5 ; 2-methylpentane was dried over sodium. Immediately before use, noncondensibles were removed from all three substances by distillation at the boiling temperature of liquid nitrogen, in a vacuum system.

The equilibrium cell (Figure 1) is a 500-cc. stainless steel, pressure vessel. The built-in valve leads to a vacuum system

VAPOR-LIQUID EQUILIBRIUM CELL

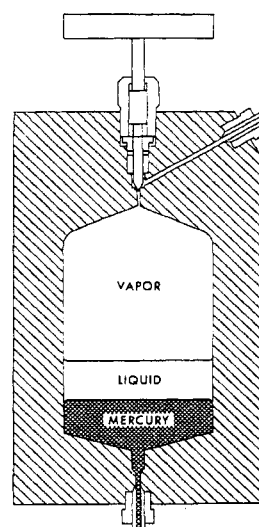


Figure 1. Vapor-liquid equilibrium cell

for analyzing vapor and liquid samples. Mercury, which acts as a confining fluid, is transmitted to a dead-weight gage and a mercury injector.

In each experiment, the cell was loaded, brought to temperature, and rocked at constant pressure to achieve equilibrium. Four samples were then taken for analysis, while mercury was injected to replace the withdrawn material. Two vapor samples were taken first; when all of the vapor had been displaced by injected mercury, two liquid samples were taken.

Temperature was measured with a platinum resistance thermometer and a Mueller bridge. Temperature was adjusted and controlled with a thermistor as sensing element.

The volume of mercury fed to the equilibrium cell was measured and adjusted with a positive-displacement pump. Gas and liquid densities were calculated from the sample

weight and the volume of mercury used to displace the sample.

Pressure was measured and controlled by a dead-weight gage; an electrical contact detected the position of the oil-mercury interface, and controlled the action of the mercury pump.

In achieving equilibrium, the cell was rocked rapidly (20 cycles per minute) for about 2 hours and then slowly (6 cycles per minute) for 2 hours.

In the analysis, the 2-methylpentane was separated by traps at -125°C . and weighed. The HCl-ethane mixture was then transferred to a bulb of known volume, and the pressure was measured with a mercury manometer and cathetometer. After the HCl was absorbed on Ascarite, the pressure of the remaining ethane was measured, and the moles of HCl were found by difference.

CHECKS ON SOURCES OF ERROR

The error of these measurements was the cumulative result of errors in measuring and controlling temperature, volume, and pressure and in analyzing vapor and liquid samples. There were also the pitfalls of taking liquid along in the vapor sample and failing to reach equilibrium between vapor and liquid.

The temperature error probably did not exceed 0.02°C . The bath was controlled to 0.01°C ., and the manufacturer's calibration of the platinum resistance thermometer was compared with a similar thermometer calibrated by the National Bureau of Standards.

Any error in volumes measured by the mercury displacement pump should be less than 0.1 cc. This amounts to less than 0.1% of the vapor sample volumes and less than 0.5% of the liquid sample volumes.

The error in pressure measurement and control was less than 0.1%. The manufacturer's calibration of the dead-weight gage was checked by measuring the vapor pressure of CO_2 at 0°C . (2). Control of pressure by the automatic injection of mercury during sampling was estimated to be within 0.003 atm.

The analyses were checked by mass spectrometry for completeness of separation of 2-methylpentane from HCl plus ethane. The completeness of HCl absorption by Ascarite was similarly checked. No detectable amount ($<0.1\%$) of ethane was adsorbed by Ascarite. To minimize the adsorption of 2-methylpentane, all pressure valves were Teflon-packed and mercury float valves were used in place of stopcocks in the vacuum system.

In the gas-measuring bulb, pressures (of about 0.5 atm.) were measured with a cathetometer reading to 0.05 mm. and a wide-bore mercury manometer, with temperature controlled to 0.05°C . Small corrections were made for the deviations of HCl and ethane from the ideal gas law. The partial pressures of HCl and ethane were found to be not quite additive, and a correction was made for this deviation from Dalton's Law. Analyses of duplicate samples agreed to within 0.001 times the mole fraction, with a lower limit of 0.0002 in mole fraction. Similar agreement was obtained when synthetic samples of known composition were analyzed.

No appreciable error is believed to have resulted from liquid entrainment in the vapor samples. The passage in front of the valve could hold 0.02 cc. of liquid at most, and it was flushed with 10 to 20 cc. of vapor immediately before taking the vapor samples.

The possibility of error due to failure to attain equilibrium was small. Sampling was not started until the volume of the vapor phase changed less than 0.01% during a half hour of slow rocking. The sufficiency of this criterion was checked by comparing the analyses of two vapor samples, one taken after rocking for 4 hours, and one after rocking for 24 hours. The possibility that equilibrium might have been disturbed during the sampling process was checked by rocking the cell slowly after taking the first vapor sample and measuring the volume change. The volume always decreased slightly, but never by more than 0.1% of the volume of the vapor phase.

As an over-all check, two runs were made on the ethane-*n*-heptane system, which has been studied by Kay (9) with a totally different experimental technique. The composition of vapor samples taken at 178.97°C . and 19.47 atm. agreed with Kay's results within 0.001 times the mole fraction (because only the smoothed data were published, points used for comparison were obtained from Professor Kay's records); the composition of liquid samples taken at 107.94°C . and 23.27 atm. agreed within 0.004 times the mole fraction.

This analysis of errors from all sources indicates that the measured equilibrium ratios (K) are probably valid within 1%.

DISCUSSION

The experimental results are listed in Table I. The subscripts 1, 2, 3, G , and L denote HCl, ethane, 2-methylpentane, gas, and liquid. Symbols x , K , and d denote mole

Table I. Equilibrium Ratios for HCl, Ethane, and 2-Methylpentane

(1 = HCl, 2 = ethane, 3 = 2-methylpentane)

Temp., $^{\circ}\text{C}$.	Pressure, Atm.	Moles/L.						
		x_1	x_2	K_1	K_2	K_3	d_G	d_L
40	10	0.0295	0.1912	6.78	3.896	0.0708	0.4185	8.22
40	10	0.0881	0.0928	6.61	3.908	0.0674	0.4127	8.14
40	10	0.1255	0.0329	6.50	3.918	0.0658	0.4122	8.13
40	30	0.0877	0.5053	2.418	1.516	0.0537	1.484	10.1
40	30	0.2338	0.2821	2.298	1.561	0.0462	1.423	10.2
40	30	0.3826	0.0965	2.154	1.596	0.0420	1.410	10.4
70	20	0.1029	0.1577	4.436	2.921	0.1120	0.7930	8.07
110	10	0.0420	0.0176	10.62	7.36	0.4512	0.3513	6.70
110	30	0.0426	0.2490	3.733	2.677	0.2460	1.156	7.33
110	30	0.1000	0.1657	3.757	2.726	0.2350	1.133	7.39
110	30	0.1073	0.1553	3.765	2.728	0.2339	1.125	7.38
110	30	0.1801	0.0544	3.775	2.769	0.2214	1.105	7.43
140	20	0.0460	0.0684	5.835	4.352	0.4897	0.7104	6.35
180	30	0.0197	0.1073	3.572	2.912	0.7069	1.191	5.42
180	30	0.0537	0.0627	3.671	2.987	0.6967	1.154	5.47
180	30	0.0851	0.0208	3.758	3.057	0.6896	1.135	5.51
180	30	0.0903	0.0141	3.763	3.065	0.6889	1.129	5.53

fraction in the liquid, mole fraction of a component in the gas divided by its mole fraction in the liquid (vapor-liquid equilibrium ratio), and density in moles per liter.

K does not increase regularly with temperature. In fact, at $p = 30$ atm. and $x_1 = 0.05$, K for HCl increases with temperature from 40° to 110° C. and then decreases between 110° and 180° C. Such behavior, though normal, causes difficulties in this case because few temperatures are available for interpolation. Hence, K must be replaced by a function that is more nearly linear with temperature. Interpolation with respect to pressure is normally done by using pK , but pK_3 in the present case changes too rapidly with pressure. Therefore, pK must be replaced by a function that varies more slowly with pressure.

One procedure in similar situations is to calculate liquid-phase activity coefficients and interpolate them. In the present case, however, two of the components were above their critical temperatures, and the pure liquid could not be used as a standard state. Therefore, only liquid-phase fugacity coefficients, which use the ideal gas as a standard state, were calculated. The fugacity coefficient turned out to be a better interpolation function than K .

Fugacity coefficients are defined by

$$\mu_{iG} = F_i + RT \ln f_{iG} = F_i + RT \ln \phi_{iG} y_i p \quad (1)$$

$$\mu_{iL} = F_i + RT \ln f_{iL} = F_i + RT \ln \phi_{iL} x_i p \quad (2)$$

where μ_i and f_i are the chemical potential and fugacity of substance i , F_i is the chemical potential of pure i at T and 1 atm. in the ideal-gas state, ϕ_{iG} is the gaseous fugacity coefficient, and ϕ_{iL} is the liquid fugacity coefficient.

At equilibrium, the chemical potentials of each species in the gas and liquid phases can be equated. Then:

$$\phi_{iL} = \phi_{iG} K_i \quad (3)$$

Therefore, ϕ_{iL} can be calculated from K (Table I) and a knowledge of ϕ_{iG} .

Equation of State for the Gas Phase. The gaseous fugacity coefficient, ϕ_{iG} , can be calculated from the gaseous equation of state. At the pressures reached in the present work, the virial gaseous equation of state could be terminated after the third term.

$$\frac{pv}{RT} = 1 + \frac{1}{v} \sum_{ij} B_{ij} y_i y_j + \frac{1}{v^2} \sum_{ijk} C_{ijk} y_i y_j y_k \quad (4)$$

where v is the molar volume of the gas phase, B_{ij} and C_{ijk} are virial coefficients, and the summation is carried out over all species in the gas phase. Equation 4 has been used (1) to calculate ϕ_{iG}

$$\phi_{iG} = \frac{RT}{pv} \exp \left(\frac{2}{v} \sum_j y_j B_{ij} + \frac{3}{2v^2} \sum_{jk} y_j y_k C_{ijk} \right) \quad (5)$$

Therefore, the calculation of ϕ_{iG} and hence ϕ_{iL} can proceed once the virial coefficients are known.

The most desirable way of obtaining these virial coefficients would be by fitting Equation 4 to the measured gas compressibilities of mixtures and pure compounds. Because measured gas densities were available only at the saturation point, this option was not open. Therefore, B and C were obtained for the pure compounds from experimental data or from well-established correlations. The mixed virial coefficients were then obtained from empirical combining rules. The resulting equation of state in the form of Equation 4 was then tested by comparing saturated-vapor densities calculated from it with the measured values in Table I.

Pitzer's correlation (10) was used to interpolate and extrapolate values of B_{11} calculated from Glockler's data (4, 5) on HCl: the differences between Pitzer's correlation and the experimental values of B_{11} at 55.5° and 95.5° C. were

interpolated and extrapolated linearly to obtain B_{11} in the range 40° to 180° C. B_{22} and B_{33} were taken directly from Pitzer's correlation. (Glockler's gas-compressibility data contain errors that must be allowed for before the data can be used to obtain virial coefficients. Plots of

$$\frac{V}{n} \left(\frac{pV}{nRT} - 1 \right) \text{ vs. } \frac{n}{V}$$

should be straight lines, with B as an intercept and C as a slope, in the pressure range of these measurements. This is the case for some of Glockler's runs, but others depart from linearity at low densities. Such curvature is usually due to an error in the number of moles, n , which is especially likely in the type of apparatus used by Glockler, in which n is very small. Therefore, the value of n was adjusted in some runs to straighten the plots. When this was done, Glockler's data became self-consistent. For example, Glockler's first run on HCl at 95.5° C. (4) gave a plot which curved so that extrapolation to zero density was not possible; his second run at 95.5° C. (5) gave a straight-line plot with an intercept of -87 cc. per mole and a slope of 0.0038 square liter per square mole. However, when n was increased by 1.3% for the run, the plot became a straight line with an intercept of -85 cc. per mole and a slope of 0.0034 square liter per square mole—in good agreement with the second run.)

C_{111} and C_{222} , which vary little with temperature, were calculated to be 0.004 ± 0.001 and 0.008 ± 0.002 square liter per square mole from Glockler's data and Pitzer's compressibility-factor tables (11), respectively. C_{333} was calculated to be 0.10 ± 0.02 square liter per square mole at 180° C. from Pitzer's tables. Because C_{333} is important only near 180° C. where y_3 is large, the value 0.10 square liter per square mole was used over the whole temperature range. These values of C_{222} and C_{333} are in essential agreement with David's correlation (3).

B_{23} was obtained by combining the constants of Pitzer's equations (10) for the 2nd virial coefficient with the Lorentz and quadratic combination rules in the manner usual for nonpolar compounds (1). However, B_{12} and B_{13} must be treated in a manner that subtracts the effects of polar forces, which almost disappear in a polar-nonpolar interaction. In order to force Glockler's HCl-propane mixed 2nd virial coefficients (5) into Guggenheim's scheme for nonpolar molecules (6), it is necessary to use a critical temperature of 230° K. for hydrogen chloride, rather than the true 325° K. (8). This low critical temperature might be considered an approximation to that HCl would have in the absence of polar interactions. Guggenheim's correlation was then used, in combination with the false critical temperature of 230° K. for hydrogen chloride, to calculate B_{12} and B_{13} .

There is no accurate method of obtaining C_{ijk} for polar-nonpolar mixtures. Fortunately, we are concerned here only with moderate pressures so that C_{ijk} is much less important than B_{ij} . Therefore, a nonattracting hard-sphere model was used to calculate C_{ijk} from C_{111} , C_{222} , and C_{333} . (Kihara (7) has calculated C_{ijk} for the square well potential. Letting $\epsilon = 0$ gives a formula for mixtures of nonattracting hard spheres. The hard-sphere diameters (σ_{ii}) were calculated from $C_{iii} = \frac{5}{8} (\frac{2}{3} \pi N \sigma_{ii}^3)^2$ (7) and combined linearly to get σ_{ij} .)

The equation of state formed from these virial coefficients (Table II) was tested by comparing saturated-vapor densities calculated from it with the values in Table I. The average difference between calculated and experimental values is $\pm 0.3\%$. Such agreement is not entirely fortuitous; although each source of virial coefficients had independent justification, it was chosen with a view to its end effect on the calculation of saturated-vapor densities. Alternate sources would have given somewhat different coefficients, and hence poorer agreement with the experimental saturated-vapor densities.

Table II. Estimated Virial Coefficients
(1 = HCl, 2 = ethane, 3 = 2-methylpentane)

Temp., ° C.	B_{11}	B_{22}	Cc./Mole			
40	128	168	1499	94	272	463
70	104	137	1190	77	222	377
110	79	106	913	61	175	290
140	65	87	763	49	152	243
180	50	68	612	40	122	192
	C_{111}		C_{222}		C_{112}	
	Liter ² /Mole ²					
40	0.004	0.008	0.006	0.005		
70	0.004	0.008	0.006	0.005		
110	0.004	0.008	0.006	0.005		
140	0.004	0.008	0.006	0.005		
180	0.004	0.008	0.006	0.005		
^a $C_{333} = 0.100$	$C_{133} = 0.037$		$C_{223} = 0.019$			
$C_{123} = 0.016$	$C_{113} = 0.013$		$C_{233} = 0.045$			

Liquid Phase Fugacity Coefficients. The estimated virial coefficients were used with the vapor-liquid equilibrium ratios in Table I and Equations 3, 4, and 5 to calculate ϕ_{iL} for each experimental point. For HCl, plots of $RT \ln p\phi_{iL}$ (the chemical potential in excess of that in an ideal gas mixture of the same composition and temperature, and at 1 atm. pressure) vs. composition are shown in Figure 2. The lines are linear with composition and the pressure effect is small. For 2-methylpentane, the improvement in the pressure effect made by using ϕ_{3L} rather than K_3 , is marked. Although pK_3 varies by 135% at 40° C., when the pressure is changed from 10 to 30 atm., $p\phi_{3L}$ varies only by 15% over the same pressure range. ϕ_{iL} is also more linear than K_i with respect to temperature, as is illustrated for HCl (Figure 3). Plots of $RT \ln p\phi_{iL}$ vs. temperature are shown in Figure 4 for HCl, ethane, and 2-methylpentane.

The curves in all of the diagrams were calculated from the equations:

$$RT \ln \phi_{1L} p = 84.95 + 0.6594t - 0.000674t^2 + \Delta_1 \quad (6)$$

$$RT \ln \phi_{2L} p = 63.78 + 0.7306t - 0.000779t^2 + \Delta_2 \quad (7)$$

$$RT \ln \phi_{3L} p = -50.16 + 0.9146t - 0.000655t^2 + \Delta_3 \quad (8)$$

$$\frac{\Delta_1}{RT} = (0.00445 - 2.0 \times 10^{-5}t) (p - 30) - (1.004 - 0.00578t)x_1 \quad (9)$$

$$\frac{\Delta_2}{RT} = -(0.00065 - 1.0 \times 10^{-5}t) (p - 30) + (0.454 - 0.00067t)x_1 \quad (10)$$

$$\frac{\Delta_3}{RT} = (0.00613 - 1.0 \times 10^{-5}t) (p - 30) + (0.279 - 0.00155t)x_1 \quad (11)$$

which were obtained by trail-and-error curve fitting. R is in liter atm. per mole ° K., p is between 10 and 30 atm., t is between 40° and 180° C., and x_1 is less than 0.25. Thus, the liquid-phase fugacity coefficients of each component can be calculated in the range of the present work.

Interpolation. To calculate the compositions of liquid and vapor in equilibrium at any given p , t , and x_1 , we must equate the fugacities in the gaseous and liquid phases and solve the resulting set of simultaneous equations:

$$p\phi_{1L}x_1 = \frac{y_1RT}{v} \exp \left(\frac{2}{v} \sum_j y_j B_{1j} + \frac{3}{2v^2} \sum_{jk} y_j y_k C_{1jk} \right) \quad (12)$$

$$p\phi_{2L}x_2 = \frac{y_2RT}{v} \exp \left(\frac{2}{v} \sum_j y_j B_{2j} + \frac{3}{2v^2} \sum_{jk} y_j y_k C_{2jk} \right) \quad (13)$$

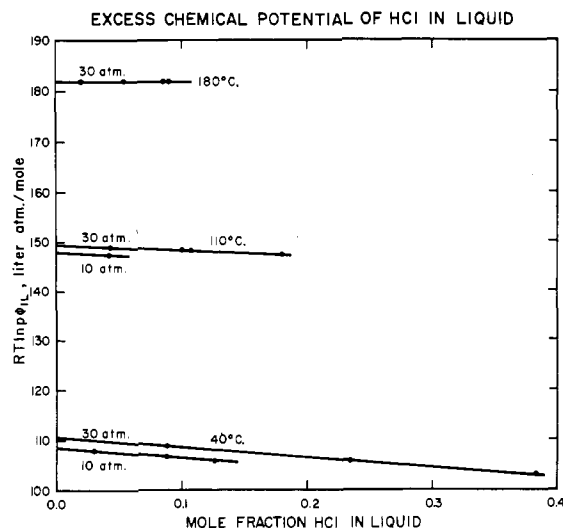


Figure 2. Excess chemical potential of HCl in liquid

$$p\phi_{3L}x_3 = \frac{y_3RT}{v} \exp \left(\frac{2}{v} \sum_j y_j B_{3j} + \frac{3}{2v^2} \sum_{jk} y_j y_k C_{3jk} \right) \quad (14)$$

$$\frac{pv}{RT} = 1 + \frac{1}{v} \sum_{ij} y_i y_j B_{ij} + \frac{1}{v^2} \sum_{ijk} y_i y_j y_k C_{ijk} \quad (15)$$

$$1 = x_1 + x_2 + x_3 \quad (16)$$

$$1 = y_1 + y_2 + y_3 \quad (17)$$

where ϕ_{1L} , ϕ_{2L} , and ϕ_{3L} are calculated from Equations 6 through 11. These equations regenerate the experimental K with an average deviation of 0.4% and a maximum deviation of 0.8%.

APPLICATION

Solution of the six simultaneous equations with a desk calculator is tedious. Therefore, in order to present a more usable interpolation method, liquid and vapor compositions were calculated from Equations 6 through 17 at many values of t , p , x_1 on a digital computer. These values were then fitted within a few tenths of 1% by least squares, to empirical functions of temperature and pressure at several values of x_1 . The resulting equations, which make it a simple matter to calculate liquid and vapor composition anywhere within the range of the experimental data, are

$$x_1 = 0.00: \log pK_1 = 1.9554 + 0.4982z - 1.2467z^2 + 0.8084z^3 - 0.2120z^4 + 0.003250p - 0.0000337p^2 - 0.003143pz + 0.008414pz^3 - 0.006007pz^4$$

$$x_1 = 0.05: \log pK_1 = 2.0068 + 0.3423z - 1.1028z^2 + 0.8052z^3 - 0.2529z^4 + 0.001697p - 0.0000180p^2 + 0.002575pz^3 - 0.001943pz^4$$

$$x_1 = 0.10: \log pK_1 = 2.0030 + 0.2905z - 1.0018z^2 + 0.7435z^3 - 0.2565z^4 + 0.002703p - 0.0000291p^2 + 0.000614pz^4$$

$$x_1 = 0.20: \log pK_1 = 2.0565 - 0.1243z - 0.1679z^2 + 0.002467p$$

$$x_1 = 0.00: \log pK_2 = 1.8323 + 0.3798z - 1.2916z^2 + 0.9311z^3 - 0.3033z^4 + 0.004721p - 0.0000411p^2 - 0.004573pz + 0.002023pz^2 + 0.0000683pz^2$$

$$x_1 = 0.05: \log pK_2 = 1.8962 + 0.2207z - 1.1041z^2 + 0.7927z^3 - 0.2574z^4 + 0.002019p - 0.0000030p^2 - 0.000974pz + 0.002252pz^2$$

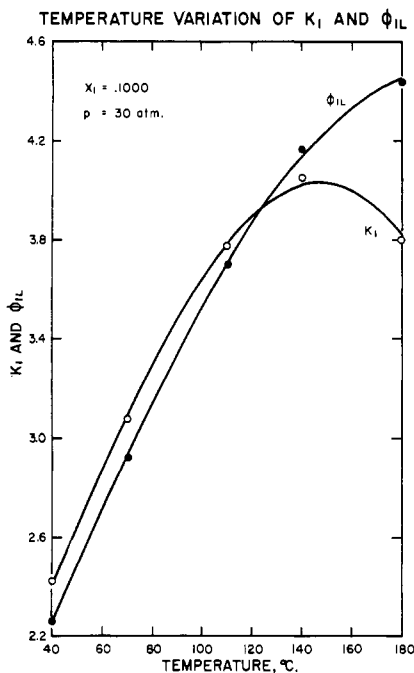


Figure 3. Temperature variation of K_1 and ϕ_{1L} .

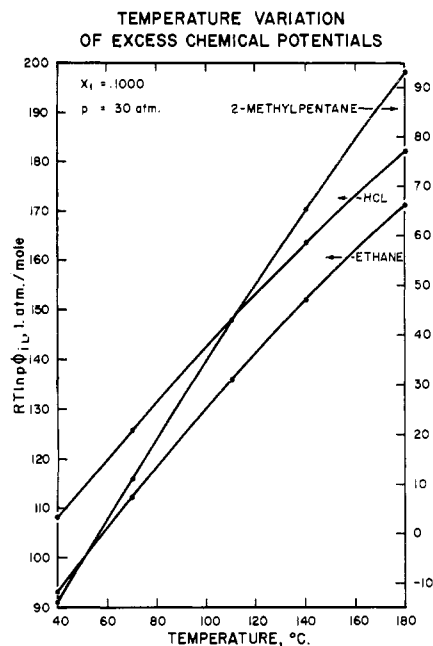


Figure 4. Temperature variation of excess chemical potentials.

$$x_1 = 0.10: \log pK_2 = 1.9202 + 0.1559z - 1.0211z^2 + 0.7322z^3 - 0.2353z^4 + 0.001606p + 0.001719pz^2$$

$$x_1 = 0.20: \log pK_2 = 1.9416 - 0.2196z - 0.1587z^2 + 0.003167p$$

$$x_1 = 0.00: \log pK_3 = 1.0423 - 1.0620z - 0.4847z^2 + 0.1907z^3 + 0.010437p - 0.0000284p^2 + 0.003018pz^2 + 0.0001930p^2z^2$$

$$x_1 = 0.05: \log pK_3 = 1.0489 - 1.0861z - 0.4804z^2 + 0.1900z^3 + 0.009805p - 0.0000209p^2 + 0.003991pz^2 + 0.0001585p^2z^2$$

$$x_1 = 0.10: \log pK_3 = 1.0452 - 1.0984z - 0.4852z^2 + 0.1894z^3 + 0.009196p - 0.0000068p^2 + 0.005554pz^2 + 0.0001075p^2z^2$$

$$x_1 = 0.20: \log pK_3 = 1.2617 - 1.8296z + 0.1464z^2 - 0.002245p + 0.016418pz$$

where $z = [1000/(t + 273.16)] - 2.2067$, t is between 40° and 180° C., p is between 10 and 30 atm., and x_1 is less than 0.25. Equilibrium ratios at uneven values of x_1 may be obtained by linear interpolation or extrapolation of K_1 .

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NOMENCLATURE

B = second virial coefficient
 C = third virial coefficient
 F = chemical potential of pure substance in the ideal gas state at T , $^\circ$ K. and 1 atm.
 K = vapor-liquid equilibrium ratio ($K = y/x$)
 N = Avagadro's number
 R = gas constant, 0.082054 liter atm. per mole $^\circ$ K.
 T = temperature, $^\circ$ K. ($T_0 = 273.16^\circ$ K.)
 V = volume, liters
 d = density, moles per liter
 n = moles
 p = pressure, atm.

t = temperature, $^\circ$ C.

v = molar volume, liters per mole

x = mole fraction in liquid

y = mole fraction in vapor

ϵ = depth of the well in an intermolecular potential energy function

μ = chemical potential

ϕ = fugacity coefficient

σ = hard-sphere diameter of a molecule

Subscripts

G = gas

L = liquid

i = any compound

1 = HCl

2 = ethane

3 = 2-methylpentane

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