ously published (3), and the constants are given in Table 1. Equation (14) fits the isothermal $\alpha - x - P$ data within 0.0003 units of relative volatility over a temperature range of −20 to 100°F.[*]

To evaluate the saturated enthalpies from $\Delta' H$ it was first necessary to calculate the ideal gas enthalpies for both the vapor and liquid phases. This information was correlated from the data given in API Research Project 44 (*1*) pages 582 and 594 where the standard states are ideal gases at 0°R. H^V was calculated from Equation (2) using the Redlich-Kwong equation of state to determine the enthalpy deviation for the gas, $(\Delta H')^L$ was determined from Equation (4) where $\Delta' H$ was calculated from Equation (12). Finally, H^L was calculated by applying Equation (2) to the liquid phase.

RESULTS AND CONCLUSIONS

The calculated saturated enthalpies are given in Table 2 and are shown graphically in Figure 1. Obviously, the effect of mixing on the heat of vaporization is quite small and for practical purposes can be ignored. Probably the major source of error in these data is the equation to correlate the isothermal $P - x$ data. Although the use of Equation (12) to calculate $\Delta' H$ eliminates numerical differentiation problems, errors in Equation (13), whether due to the form of the equation or to the experimental data on which it is based, will be reflected in the resulting enthalpies. The results of this work and also the work on relative volatilities indicate that when applying the general coexistence equation to calculate thermodynamic properties of close boiling mixtures the greatest effort should be expended on the accurate measurement of vapor pressure.

NOTATION

C_{ij} = constants for relative volatility correlation
F = function representing vapor pressure correlation
$\hat{f}_i$ = fugacity of component i in solution, lb./sq.in.abs.
H = enthalpy, B.t.u./lb.$_m$-mole
H^{id} = ideal gas enthalpy, B.t.u./lb.$_m$-mole
$\Delta H'$ = $H^{id} - H$, B.t.u./lb.$_m$-mole
$\Delta' H$ = $[(\Delta H')^V - (\Delta H')^L]/RT_a^2$, °R.$^{-1}$
P = pressure, lb./sq.in.abs.
R = ideal gas constant, B.t.u./lb.$_m$-mole°R.
T = temperature, °F.
T_a = temperature, °R.
x = mole fraction propene in liquid
y = mole fraction propene in vapor
z_i = mole fraction component i
α = relative volatility, $[y(1-x)]/[x(1-y)]$
Γ = $\ln(\hat{\phi}_2/\hat{\phi}_1)$
$\hat{\phi}_i$ = fugacity coefficient of component i in solution

Superscripts

L = liquid phase
V = vapor phase

Subscripts

1 = propane
2 = propene

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[*] Reamer and Sage (*4*) have measured the vapor-pressures, compositions, and specific volumes of mixtures of propane and propene at 100°F. and 160°F.; and these data were used by Manley and Swift (*3*) to help calculate the relative volatility of propene to propane at 130°F. However, since the original data of this study were limited to 100°F., and since the primary purpose of this paper is to demonstrate one method of calculating heats of vaporization, no effort was made to extend the enthalpy data to 130°F.

Estimation of Effective Molecular Quadrupole Moments

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Quadrupole-dipole interactions can produce important contributions to the second virial coefficient B (*1, 2*) and compressibility factor Z_c of highly dipolar gases such as water, ammonia, the alcohols, and the ketones. The importance of quadrupole interactions in quadrupole gases such as N_2, O_2, NO, CO, CO_2, C_2H_2, C_2H_4, and F_2 is well known (*3, 4*). Although for dipolar gases B^* (σ, y, τ, γ, q) and $Z_c(T_r, P_r, \tau, \gamma, q)$, the dependency of the critical constants on τ, γ and q should be recognized in corresponding states correlations of the compressibility factor.

Quadrupole moments can be estimated from quantum mechanics (based on an assumed form of the wavefunction) or extracted from microwave line broadening, pressure-induced infrared absorption, nuclear spin relaxation, induced birefringence, anisotropy in diamagnetic susceptibility, and other measurements. A comprehensive survey of literature values before 1966 is available (*5*). Except for water, few references as yet pertain to molecules which are not cylindrically symmetric. Differences of the order of 2×10^{-26} esu-cm^2 or more are still common although values for several axially symmetric molecules such as O_2, N_2, and CO_2 are known with greater certainty. A simple estimation method applicable to any compound will be presented here together with a comparison with current literature values.

CYLINDRICALLY SYMMETRIC MOLECULES

The molecular quadrupole moment $\Theta = \Theta_{zz}$ where the charge distribution is cylindrically symmetric about the z axis, which is through the center of mass (*6*)

$$\Theta = \Theta_{zz} \equiv \frac{1}{2} \Sigma\, e_i \,(3Z_i^2 - R_i^2), \tag{1}$$

with $\Theta_{xx} = \Theta_{yy} = -\frac{1}{2}\,\Theta_{zz}$ so that the diagonal matrix of the quadrupole moment tensor is traceless.

The present estimation procedure is begun by calculation of the net charge e on each atom by dividing the bond dipole moments (*7*) by the bond distances (*8*) somewhat similar to the method proposed by Rowlinson (*9*) for water. Bond distances are shown in Figure 1. For example, $\mu(\text{C—Cl}) = 1.46$ and $\mu(\text{H—C}) = 0.4$ for methyl chloride. Then $e_{\text{Cl}} = -(1.46/1.782) = -0.819$, $e_{\text{H}} = (0.4/1.103) = 0.362$, and $e_{\text{C}} = 0.819 - 3(0.362) = -0.267$. The center of mass is located 1.235A from the carbon atom along the C—Cl bond as shown in Figure 1. Simple geometrical analysis of the CH_3 tetrahedron with known bond angles and distances shows the plane of the three hydrogen atoms to be 0.354A below the carbon atom with each hydrogen atom 1.047A from the center of the H—H—H triangle on the Z axis. By Equation (1)

$$\begin{aligned} 2\Theta_{zz} = {} & -0.819[2(1.782 - 1.235)^2] \\ & -0.267[2(1.235)^2] \\ & + 3(0.362)\,[2(1.235 + 0.354)^2 - (1.047)^2] \end{aligned}$$

or $\Theta_{zz} = +1.49$ esu-cm^2, which is in close agreement with the recently measured value of 1.23 ± 0.82 (*10*). Table 1 is a comparison of quadrupole moments calculated from the bond dipole method with the selected values of (*5*) and some recent measurements for cylindrically symmetric molecules. The numbers in parenthesis provide the range of literature values. Where the sign is not given the number should be considered the absolute value which is sufficient for equation of state calculations as the quadrupole moment appears as the dimensionless quantity $\gamma = \Theta^2/\epsilon\sigma^5$.

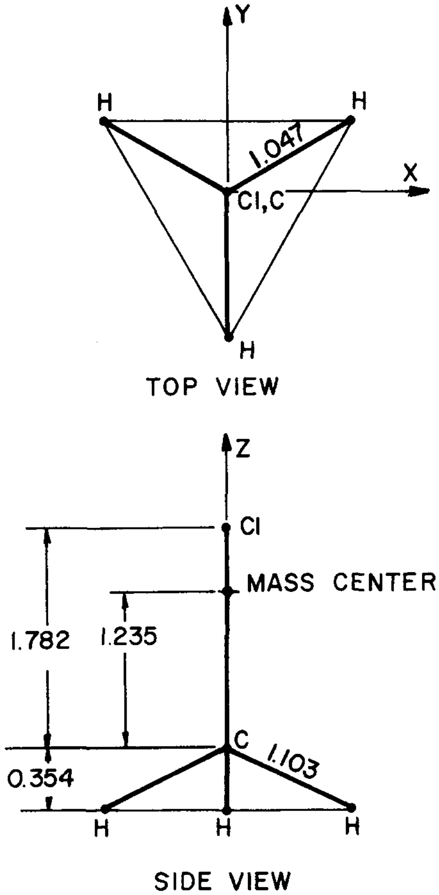

Fig. 1. Molecular geometry at methyl chloride.

The estimation method predicts no moment for diatomic molecules of one element whereas these compounds are known to have small moments — $O_2(-0.39)$, $N_2(-1.52)$, $H_2(+0.66)$, etc. The method is not recommended for diatomic moments since it also underestimates the moments of HCl, HBr, etc. by ¼ to ½ of the accepted values.

TABLE 1. COMPARISON OF QUADRUPOLE MOMENTS FOR CYLINDRICALLY SYMMETRIC MOLECULES

Compound	Θ_{zz}, esu-cm^2 × 10^{26} (bond dipole method)	Θ_{zz} (literature)
CO_2	-5.59	-4.3 (1.7, 5.9) (*5*)
N_2O	-2.07	-3.0 (2.5, 4.25) (*5*)
ClCN	-7.94	6.6 (*5*)
BrCN	-9.96	6.8 (6.8, 10.1) (*5*)
OCS	-6.06	3.1 (1.7, 4.3) (*5*)
NH_3	-1.34	-1 (-0.34, -1.9†) (*5*)
C_2H_2	$+1.80$	3.0 (*5*)
C_2H_4*	$+1.18$	$+1.5$ (1.3, 4) (*5*)
C_2H_6	$+0.26$	-0.65 (*5*)
CH_3Cl	$+1.49$	$+1.23 \pm 0.82$ (*10*)
CH_3Br	$+2.63$	$+3.55 \pm 0.79$ (*10*)
CH_3I	$+3.07$	$+5.35 \pm 0.85$ (*10*)

† A recently measured value is -1.9 ± 1.0 (*14*).
* Ethylene is not exactly symmetric but usually included in this class.

The bond dipole moments should be added vectorially to check the known molecular dipole moment during an estimation. Slight adjustment of the less well established bond moments is occasionally necessary to meet this criteria.

NONCYLINDRICALLY SYMMETRIC MOLECULES

Two components of the traceless, diagonal matrix of the quadrupole tensor are necessary to describe the quadrupole moment of molecules lacking cylindrically symmetry of the charge distribution. That is, a rectangular coordinate system can always be found such that $\Theta_{yy} = -[\Theta_{xx} + \Theta_{zz}]$ with $\Theta_{ij} = 0$ for $i \neq j$. An empirical equation

$$\Theta^2 = \frac{2}{3}\,[\Theta^2{}_{xx} + \Theta^2{}_{yy} + \Theta^2{}_{zz}] \tag{2}$$

is proposed for calculation of the effective molecular quadrupole moment Θ from the diagonal elements. The equation, which reduces to $\Theta = \Theta_{zz}$ for cylindrically symmetric molecules, is based on the average of the square of Θ_{ii} because B and Z depend on $\gamma \sim \Theta^2$ in the first order approximation.

Table 2 contains a comparison of literature diagonal elements of the traceless tensor for water with those of the bond dipole method. The origin of the coordinate system is at the mass center with the Z-axis through the oxygen atom and the y axis in the HOH plane. The values of Θ, which were calculated in each case from Equation (2), may also be compared with -1.00 selected by O'Connell and Prausnitz (*11*) and 1.81 computed by Rowlinson (*9*).

Table 3 provides the results for the remaining noncylindrical molecules. An effective moment for SO_2 of 4.4 (5) is available for comparison with the estimated value of 3.42. The coordinate system for SO_2 is analogous to that chosen for water. The Z axis for the alcohols and acetone is through the mass center and parallel to the O—C or O=C bond. The y axis is in the HOC plane for the alcohols and in the C—C—C plane for acetone. These choices of coordinate systems do not produce exactly a traceless, diagonal matrix of the quadrupole tensor. Calculations show such errors to be small (less than ± 0.1 for each Θ_{ii} of Table 3) so the present coordinate system is retained for convenience. In each case the trans rotational isomer was assumed as illustrated by Figure 2 for n-propanol.

TABLE 2. QUADRUPOLE MOMENTS OF WATER

Ref.	μ, debyes	Θ_{xx}	Θ_{yy}	Θ_{zz}	Θ
(*12*)	1.84	−0.79	+0.82	−0.03	0.93
(*13*)	1.72	−1.19	+1.05	+0.14	1.30
(*14*)		−2.0 ± 0.6	+1.6 ± 0.7	0.4 ± 0.6	2.12
Estimated	1.85	−1.34	+1.40	−0.06	1.58

TABLE 3. ESTIMATED QUADRUPOLE MOMENTS

Compound	μ	Θ_{xx}	Θ_{yy}	Θ_{zz}	Θ
Sulfur dioxide	1.633	+1.73	−3.45	+1.72	3.46
Methanol	1.70	−1.07	+0.62	+0.45	1.07
Ethanol	1.69	−0.98	+1.21	−0.23	1.28
N-propanol	1.68	−1.13	+1.89	−0.76	1.90
Iso-propanol	1.66	−1.75	+2.11	−0.36	2.26
Acetone	2.88	+0.12	+2.88	−3.00	3.40

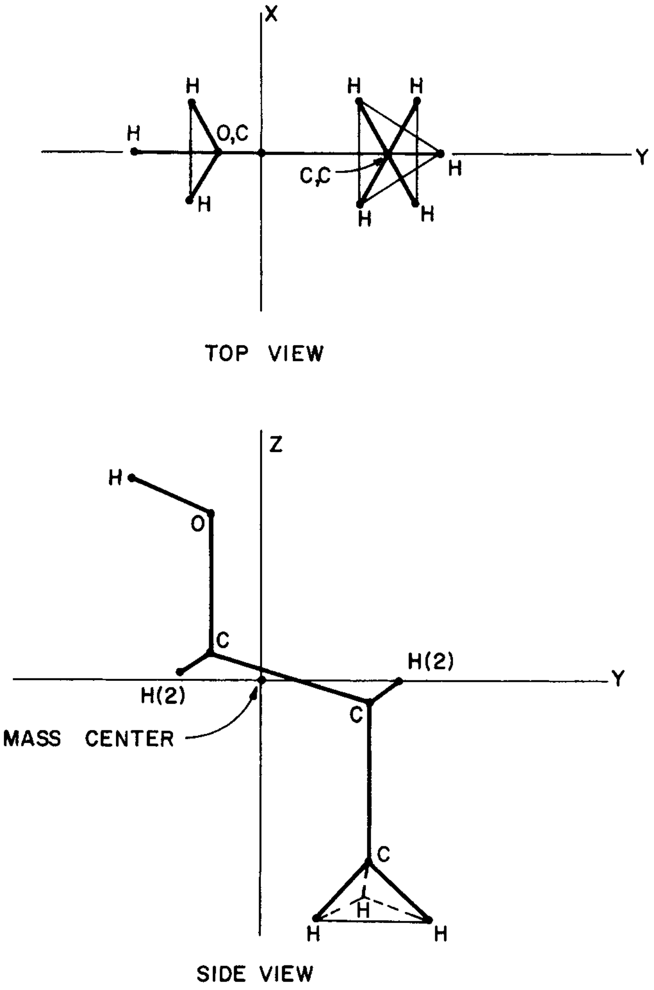

Fig. 2. Molecular geometry of n-propanol (trans).

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NOTATION

B = second virial coefficient, cm^3/g.-mole
B^* = dimensionless second virial coefficient, $B \Big/ \frac{2}{3} \pi \tilde{N} \sigma^3$
e_i = electric charge at position (Z_i, R_i)
$\tilde{N}$ = Avogadro number, 6.025 × 10^{23} molecules/g.-mole
P = pressure
P_r = pressure divided by critical pressure
q = dimensionless mean polarizability, $\bar{\alpha}/\sigma^3$
R = gas constant
R_i = distance from mass center to charge i
T = temperature
T_r = temperature divided by critical temperature
v = specific volume
y = dimensionless temperature variable $2\sqrt{\epsilon/\kappa T}$
Z_c = compressibility factor Pv/RT
Z_i = distance parallel to Z axis of charge i

Greek Letters

$\bar{\alpha}$ = mean polarizability
γ = dimensionless quadrupole moment, $\Theta^2/\epsilon\sigma^5$
$(\epsilon/\kappa), \sigma$ = intermolecular force constants
Θ = quadrupole moment esu-cm^2 × 10^{26}
κ = Boltzmann constant, 1.38054 × 10^{-16} erg/°K.
μ = dipole moment, debyes (esu-cm × 10^{18})
τ = dimensionless dipole moment, $\mu^2/\epsilon\sigma^3$

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