III are for the b_{2g}, b_{1g}, and a_{1g} orbitals (which are almost pure 3d in character), namely 8.55 to 10.36 eV. For the $4e_g$ orbital, however, where the 3d character is substantially reduced by 3d $\rightarrow \pi^*$ back-donation, the relaxation energy is much less, 3.55 eV.

The ΔSCF ionization potentials for the eclipsed and staggered conformers are compared in Figure 3. As expected, there are no large differences, confirming one's intuitive feeling that the D_{4h} and D_{4d} electronic structures are rather similar. As noted above, the doubly degenerate $3e_2$ orbital of the staggered conformer splits into the eclipsed orbitals $2b_{2g}$ and $3b_{1g}$, separated by 0.33 eV. A larger splitting occurs within the orbitals primarily of C–C σ bond character. Figure 3 shows that the D_{4d} orbital $4e_2$ splits into $1b_{1u}$ and $1b_{2g}$ components, separated by 0.77 eV. Finally, the small $D_{4h} - D_{4d}$ separation of about 1 kcal is not readily explained in terms of Figure 3. For example, the splittings of the D_{4d} $3e_2$ and $4e_2$ orbitals are relatively symmetric (i.e., one orbital is energetically favored, the other energetically disfavored) as the molecule proceeds from D_{4d} to D_{4h} symmetry.

It is also of considerable interest to compare Figure 3 with the qualitative textbook correlation diagram of Figure 1. The biggest difference is that four orbitals ignored in Figure 1 actually lie higher in energy than the $7a_{1g}$ orbital, which is clearly a π orbital. These four orbitals are primarily cyclobutadiene σ-like in character and disprove once again the literal notion (widely accepted 20 years ago) of σ–π separability.

Some features of Figure 1 are confirmed in Figure 3. For example, the ordering of CBD π orbitals as a_{1g}, a_{2u} (inadvertantly left out by Hall[10] in his version of Figure 1), e_u is that given by qualitative theory. Also the 3d ordering e_g, a_{1g}, $b_{1g} = b_{2g}$ is reproduced by the ab initio theory, although the $3b_{1g}$ and $2b_{2g}$ IP's actually differ by 0.33 eV, rather than being precisely equal. Furthermore, the placement of the $6e_u$ orbital (π-like) among the 3d-like orbitals is not unreasonable, since the corresponding bands in the photoelectron spectra of $(C_4H_4)Fe(CO)_3$ are quite close in energy.[29] The a priori theory places this π orbital in roughly the center of gravity of the d orbitals, while Hall's diagram places the $6e_u$ orbital somewhat lower. A more serious discrepancy between Figures 1 and 3 concerns the energy scale. In Figure 1 there is a large gap between the (b_{1g}, b_{2g}) pair of d orbitals and the $8a_{1g}$ orbital. The ΔSCF diagram, Figure 3, suggests that the four 3d-like orbitals fall in a much smaller energy range, only 1.44 eV, from which the two lower π orbitals are quite far removed.

Concluding Remarks

A reasonably comprehensive optimization of the geometry of $Ni(C_4H_4)_2$ has been carried out here with use of the restricted Hartree–Fock theory in conjunction with a relatively large basis set of one-electron functions. The resulting final wave functions allow us to make a detailed examination of the electronic structure of bis(cyclobutadiene)nickel in both its eclipsed and staggered conformations. We hope this theoretical research will provide a stimulus for the experimental determination of the properties of $Ni(C_4Ph_4)_2$, the first known cyclobutadiene sandwich compound.[5] A crystal structure would be particularly welcome. Furthermore, it is to be hoped that the unsubstituted parent compound will be synthesized in the near future.

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(29) M. B. Hall, I. H. Hillier, J. A. Connor, M. F. Guest, and D. R. Lloyd, *Mol. Phys.*, **30**, 839 (1975).

Comparison of Equilibrium Constants in Gas and Liquid Phases

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Abstract: Available vaporization data have been used to compare gas-phase and liquid-phase equilibrium constants, K_l/K_g, for associative equilibria of hydrocarbons. For most equilibria involving *n*-paraffins K_l/K_g is close to unity over the entire range of temperature and molecular size for which vapor pressures of *n*-paraffins are available. However, when methane is a reactant, K_l/K_g values become considerably greater than unity. While this effect can be ascribed to the relatively low solubility of methane in *n*-paraffins, it also appears to be an example of a general phenomenon that arises when small molecules are involved in associative equilibria. Atoms and small molecules are inherently less stable in solution than are larger molecules. For equilibria involving hydrocarbons other than *n*-paraffins, the general finding is that $K_l/K_g \sim 1$ when solvation effects are not significant and when reactants and products do not have major structural differences. These results imply that bimolecular rate constants for sufficiently large reactant molecules will not be significantly different in the liquid and gas phase unless solvation or diffusion effects are present. For reactions involving small reactant species, such as methyl radicals or H atoms, rate constants *may* be significantly greater in solution than in the gas phase. These ideas have been applied to selected aspects of free-radical thermochemistry and kinetics.

In order to use empirical and estimated gas-phase thermokinetic data for interpretation of solution-phase chemistry, a reliable means for gas-to-liquid conversion of such data is needed. While relationships between gas- and liquid-phase rate and equilibrium constants have been of concern for many years, research directly focused on this area has been reported only intermittently, and much of this research has been based on a rather limited data base.

Both collision theory and transition-state theory have been used by a number of workers to estimate relative liquid-phase and gas-phase bimolecular rate constants, $k_{b,l}/k_{b,g}$. A general conclusion of that work is that in the absence of solvation effects bimolecular rate constants in the liquid phase, $k_{b,l}$, are greater than rate constants for corresponding reactions in the gas phase, $k_{b,g}$. Early theoretical work by Rabinowitch[1] indicated that liq-

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uid-phase collision frequencies are 2–3 times greater than gas-phase collision frequencies due to excluded volume effects in liquids, hence, on the basis of collision theory, $k_{b,l}/k_{b,g} = 2\text{–}3$. In the same time period, Bell[2] used measured values for entropies and enthalpies of solution of gases to show that transition-state theory also indicates that $k_{b,l}/k_{b,g} = 2\text{–}3$. On the basis of collision theory and intuitive free-volume arguments, Bell[2] and more recently Mayo[3] deduced that $k_{b,l}/k_{b,g} \lesssim 4$. Finally, use of a transition-state theory approach in which vapor pressures were estimated, using approximate expressions from free-volume theory has led to the conclusion that $k_{b,l}/k_{b,g} \sim 50\text{–}100$.[4]

Rather few absolute rate constants for bimolecular reactions have been determined in both gas and liquid phases. Some of this work has been summarized by Martin,[5] who found that $k_{b,l}/k_{b,g} = 0.9\text{–}10$, but in most cases this ratio fell in the range 1–3. Since many of the reactions considered by Martin involved polar species, and because of possible mechanistic complexities, this analysis does not provide convincing evidence that $k_{b,l}/k_{b,g} > 1$ in the absence of solvation effects, although it does indicate that $k_{b,l}/k_{b,g} \ll 50\text{–}100$.

For unimolecular reactions, both rate data[5-7] and semiquantitative theoretical arguments[4] indicate that these reactions should possess comparable rate constants and rate parameters in gas and liquid phases.

The same free-volume calculations which predict that $k_{b,l}/k_{b,g} > 1$ lead to the prediction that the ratio of equilibrium constants for association in the liquid phase and gas phase, K_l/K_g, is also greater than unity. Moreover, if it is assumed that $k_{b,l} > k_{b,g}$ for the associative reaction

$$A + B \underset{k_u}{\overset{k_b}{\rightleftharpoons}} AB$$

and $k_{u,g} \sim k_{u,l}$, then microscopic reversibility implies that $K_l > K_g$ for this reaction. These arguments imply that associative equilibria are inherently favored in solution for reasons other than simple concentration differences and that as the change in number of moles in a reaction, Δn, decreases the ratio K_l/K_g increases.

Recent theoretical work by Pratt and Chandler[8] provides a means of calculating K_l/K_g from molecular properties. Assuming only hard-sphere interactions, these workers estimated $K_l/K_g \sim 10^3$ for the reaction $2NO_2 \rightleftharpoons N_2O_4$ in $CHCl_3$, in agreement with experiment. This high value implies that effects of "free volume" on associative equilibria can be much greater than is commonly thought.

Very few equilibria have actually been examined in both the gas phase and liquid phase. This area has recently been reviewed by Benson and Mendenhall,[9] who emphasized the importance of using vaporization heat capacities when converting gas- and liquid-phase equilibrium constants to a common temperature for comparison. The paucity of experimental data and possible influence of solution non-ideality prevent general conclusions concerning the magnitude of (K_l/K_g) from being made.

In summary, present theoretical arguments indicate that in the absence of solvation effects, both $k_{b,l}/k_{b,g}$ and K_l/K_g are greater than unity although the actual magnitude predicted depends on the type of analysis. Available empirical data are too limited to make meaningful generalizations concerning these ratios.

In the present work (K_l/K_g) values are computed for selected associative equilibria of hydrocarbons, using empirical vaporization and solubility data. For equilibria involving large molecules in which there are no major structural and solvation differences between reactants and products, calculations show that $K_l/K_g \sim 1$. When a small molecule is a reactant, K_l/K_g may be considerably greater than unity. Some applications of this approach to free-radical thermochemistry and kinetics are discussed.

Method for Calculating K_l/K_g

This work focuses on the estimation of relative gas-phase and liquid-phase equilibrium constants for the associative equilibrium

$$A + B \rightleftharpoons AB \qquad (1)$$

Associative equilibria are of special interest because of their relevance to transition-state theory descriptions of bimolecular reactions. Equation 2[4,5] is the basis for most calculations

$$\frac{K_l^c}{K_g^c} \equiv \mathbf{R} = \frac{P^\circ{}_A P^\circ{}_B}{P^\circ{}_{AB}}\left(\frac{V_s}{RT}\right) \qquad (2)$$

where $P^\circ{}_A$ is the ideal-gas vapor pressure of pure liquid A, and V_s is the volume occupied by a mole of molecules in solution (this includes A, B, AB, and solvent molecules). In a highly dilute solution V_s becomes the molar volume of the solvent. Equation 2 is of direct utility for ideal solutions since for this case K_l^c is simply equal to the equilibrium quotient of concentrations, C_{AB}/C_AC_B. Since this work focuses primarily on hydrocarbon mixtures which do not strongly deviate from ideality (i.e., from Roault's law) and the level of precision required for drawing useful conclusions about the magnitude of K_l/K_g is not high, non-ideal corrections will not be made in this work. Besides, non-ideal effects are expected to raise some K_l/K_g values while lowering others so that calculations based on ideal solutions will provide K_l/K_g values that are, more or less, averages for real solutions. A more detailed discussion of eq 2 in the context of this work is presented in the Appendix.

n-Paraffin Equilibria

Comparisons of gas- and liquid-phase equilibrium constants for reactions involving *n*-paraffins are especially informative because of the wealth of vaporization data available for these substances[10] and because of the fact that solution of *n*-paraffins are known to closely follow Roault's law even for mixtures containing components of widely differing molecular weights.[11] Data obtained by Patterson,[12] for instance, indicate that in a dilute solution of $n\text{-}C_6H_{14}$ in $n\text{-}C_{16}H_{34}$ at 298 K, $n\text{-}C_6H_{14}$ has a vapor pressure only 11% below the value predicted by Roault's law despite a difference of a factor of 2.2 in molar volumes of solute and solvent. An equimolar mixture of $n\text{-}C_6H_{14}$ and $n\text{-}C_{16}H_{34}$ has a vapor pressure only 3% lower than that expected for an ideal solution.[12]

The following hypothetical equilibrium will be examined.

$$\underset{(n)}{n\text{-}C_nH_{2n+2}} + \underset{(m)}{n\text{-}C_mH_{2m+2}} \rightleftharpoons \underset{(n+m)}{n\text{-}C_{n+m}H_{2n+2m+2}} + H_2\text{ (gas)} \qquad (3)$$

Let K_l^c(*n*-paraffin) and K_g^c(*n*-paraffin) be equilibrium constants for reaction 3 in concentration standard states where the *n*-paraffins are in the liquid phase and gas phase, respectively. Gas-phase hydrogen in reaction 3 serves only to balance the reaction; its thermodynamic properties do not influence the magnitude of the ratio K_l^c(*n*-paraffin)/K_g^c(*n*-paraffin).[13]

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(1) Rabinowitch, E. *Trans. Faraday Soc.* **1937**, *33*, 1225.

(2) Bell, R. P. *Trans. Faraday Soc.* **1939**, *35*, 342.

(3) Mayo, F. R. *J. Am. Chem. Soc.* **1967**, *89*, 2654.

(4) See, for example: (a) Benson, S. W. "Foundations of Chemical Kinetics"; McGraw Hill, Inc.: New York, 1960; Chapter 15. (b) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism"; Wiley and Sons: New York, 1961; 2nd ed.

(5) Martin, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 78.

(6) Benson, S. W.; Shaw, R. In "Organic Peroxides", Swern, D., Ed.; Wiley Interscience: New York, 1970; Chapter 2.

(7) Preliminary details are reported by: Miller, R. E.; Stein, S. E. *Prepr. Div. Fuel Chem., Am. Chem. Soc.* **1979**, *24* (*3*) 271.

(8) Chandler, D.; Pratt, L. R. *J. Chem. Phys.* **1976**, *65*, 2925.

(9) Mendenhall, G. D.; Benson, S. W. *J. Am. Chem. Soc.* **1976**, *98*, 2046.

(10) (a) Zwolinsky, B. J.; Wilhoit, R. C. "Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds"; API Project 44, Thermodynamics Research Center, College Park, TX, 1971. (b) "Selected Values of Properties of Hydrocarbons and Related Substances"; API Research Institute, Project 44, Thermodynamics Research Center, Texas A&M University, College Station, TX (extant 1967).

(11) (a) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. "Regular and Related Solutions"; Van Nostrand Reinhold Co.: New York, 1970. Rowlinson, J. S. "Liquids and Liquid Solutions"; Butterworths: London, 1969; 2nd ed.

(12) Barbe, M.; Patterson, D. *J. Phys. Chem.* **1978**, *82*, 40 and references given therein.

(13) While it may appear at first that the greater number of H atoms in the reactants compared to the product hydrocarbon might lead to greater solvation of the reactants, in fact at 298 K the internal energy of vaporization of a methylene group is actually very slightly greater than that for a methyl group[12] ($\Delta U_{vap,298\,K}$ (reaction 3) $\sim$ +76 cal). A related equilibrium system in which no hydrogen is needed to balance the reaction is considered later (reaction 8).

Table I. Temperature Dependence of Entropy and Enthalpy Contributions to $\mathbf{R}_{np}$[a]

	300 K	400 K	500 K	600 K	700 K
$\mathbf{R}_{np}$	1.1	1.2	1.2	0.95	0.73^b
$\exp(+\Delta\Delta S_{soln}/R)$	1.5	1.3	0.56	0.36	0.24^b
$\exp(-\Delta\Delta H_{soln}/RT)$	0.75	0.95	2.0	2.6	3.1^b

[a] For hypothetical equilibria $2n\mathrm{C}_n\mathrm{H}_{2n+2} \rightleftarrows n\mathrm{C}_{2n}\mathrm{H}_{4n+2} + \mathrm{H}_2$ (gas) in $n\mathrm{C}_n\mathrm{H}_{2n+2}$ solvent. Assumes $(V_{2n}/V_n) = 1.7$, independent of temperature. $\mathrm{R}_{np} = \exp\{-\Delta H_{soln}/RT + \Delta S_{soln}/\mathrm{R}\}$. ΔH_{soln} and ΔS_{soln} were derived from temperature dependence of (α/RT) by graphical methods. [b] Extrapolated from lower temperature values by graphical methods.

Recent work has demonstrated that ideal-gas vapor pressures $P°_m$ (i.e., liquid fugacities) of n-paraffins, n-C_mH_{2m+2}, below reduced temperatures of ~0.7, closely follow the empirically derived expression[14]

$$P°_m = \alpha/\beta^m V_m \tag{4}$$

where α and β are empirically determined, temperature-dependent constants and V_m is the molar volume of pure liquid n-C_mH_{2m+2} under its own vapor pressure.

Insertion of formula 4 into eq 2 yields,

$$\mathbf{R}_{np} \equiv \frac{K_l^{c}(n\text{-paraffin})}{K_g^{c}(n\text{-paraffin})} = \left(\frac{\alpha}{RT}\right)\left(\frac{V_{n+m}V_s}{V_nV_m}\right) \tag{5}$$

The quantity (α/RT) is relatively insensitive to temperature. Values of this quantity from 250 K to 600 K are:[14] 0.650 (250 K); 0.664 (298 K); 0.688 (350 K); 0.712 (400 K); 0.701 (450 K); 0.658 (500 K); 0.561 (600 K). Therefore, eq 5 becomes,

$$\mathbf{R}_{np} = (0.64 \pm 0.08)\left(\frac{V_{n+m}V_s}{V_nV_m}\right) \tag{6}$$

Equation 6 implies that associative equilibria involving n-paraffins that obey eq 4 are not inherently "favored" in solution. Consider, for instance "dimerization" of an n-paraffin solvent, C_nH_{2n+2}, to form $\mathrm{C}_{2n}H_{4n+2}$. In this case $V_{n+m} = V_{2n}$ and $V_n = V_s$, and since $V_{2n}/V_n = 1.7 \pm 0.3$,[10b] one finds $\mathbf{R}_{np} = 1.1 \pm 0.3$. If the above reaction were carried out in the solvent n-$\mathrm{C}_{2n}H_{4n+2}$, then $\mathbf{R}_{np} = 1.8 \pm 0.5$. Another general case is the "addition" of a small solvent molecule, n-C_nH_{2n+2}, to a large dilute n-paraffin, n-C_mH_{2m+2}, where one finds $\mathbf{R} = 0.64 \pm 0.08$.[15] Therefore, even though $\mathbf{R}_{np}$ is proportional to the molar volume of the solution, in many actual situations $\mathbf{R}_{np} \sim 1$ (or 0.5–2).

Note also that eq 5 implies that $\mathbf{R}_{np}$ is rather insensitive to temperature since both terms on the right side of this equation depend only weakly on temperature.

Since $\mathbf{R}_{np} \sim 1$ over a wide temperature range, as a first approximation $\Delta\Delta H_{soln}$ [$\equiv\Delta H_l$(reaction 3) − ΔH_g(reaction 3)] ~ 0, $\Delta\Delta S_{soln} \sim 0$, and $\Delta\Delta G_{soln} \sim 0$ (all in concentration standard states). Of course, this is only a rough approximation. By assuming that the term $(V_{n+m}V_s/V_nV_m)$ is temperature independent, the temperature dependence of (α/RT) may be used to estimate contributions of $\Delta\Delta H_{soln}$ and $\Delta\Delta S_{soln}$ to $\mathbf{R}_{np}$. Derived values for the solvent "dimerization" case mentioned above are given in Table I. Clearly, contributions to $\mathbf{R}_{np}$ from enthalpy and entropy terms largely cancel one another at all temperatures. It should be kept in mind that at higher temperatures the term α is subject to appreciable error since at higher temperatures α is obtained by a rather long extrapolation of empirical $P°$ values.[14]

When an n-paraffin in reaction 3 is near or above its own critical temperature, eq 4–6 are unreliable for two reasons. First, eq 4 underestimates $P°$ in the region $0.7 \sim P_{vap}/P_{crit} \sim 1$[14] ($P_{vap}$ is the vapor pressure and P_{crit} is the critical pressure), and is of dubious value above the critical temperature. Furthermore, mixing of a liquid near its own critical temperature with another liquid far below its critical temperature can result in considerable non-ideality.[16] A more reliable estimate of $\mathbf{R}$ for these equilibria is obtained by using Henry's law for components near or above their critical temperature. If n-C_mH_{2m+2} in eq 3 is such a component, then $P°_m$ in eq 2 should be replaced by its Henry's law constant $K_{\mathrm{H},m}$,

$$\mathbf{R}_{np} = \frac{P°_n K_{\mathrm{H},m}}{P°_{n+m}}\left(\frac{V_s}{RT}\right) \tag{7}$$

Table II. Gas and Liquid Phase Equilibria Involving Small n-Paraffins[a]

reactants[b,c]	$\mathbf{R}_{np}$	ΔS_{soln},[c] cal mol^{-1} K^{-1}	$-\Delta H_{soln}$,[c] kcal mol^{-1}
$\mathrm{CH_4} + n\text{-}\mathrm{C_6H_{14}}$	3.5	−1.6	1.22
$\mathrm{C_2H_6} + n\text{-}\mathrm{C_6H_{14}}$	1.8	−1.7	0.86
$\mathrm{C_3H_8} + n\text{-}\mathrm{C_6H_{14}}$	1.6^d		
$\mathrm{C_4H_{10}} + n\text{-}\mathrm{C_6H_{14}}$	1.3	0.15	0.11
$\mathrm{CH_4} + n\text{-}\mathrm{C_7H_{16}}$	5.6	0.6	0.86
$\mathrm{C_2H_6} + n\text{-}\mathrm{C_7H_{16}}$	2.0	0.5	0.28
$\mathrm{C_4H_{10}} + n\text{-}\mathrm{C_7H_{16}}$	1.4	0.32	0.105
$\mathrm{CH_4} + n\text{-}\mathrm{C_8H_{18}}$	7.5	1.3	0.80
$\mathrm{C_2H_6} + n\text{-}\mathrm{C_8H_{18}}$	2.0		
$\mathrm{C_3H_8} + n\text{-}\mathrm{C_8H_{18}}$	1.8^d		
$\mathrm{C_4H_{10}} + n\text{-}\mathrm{C_8H_{18}}$	1.6	0.61	0.095
$\mathrm{CH_4} + n\text{-}\mathrm{C_{11}H_{26}}$	16.0	2.8	0.82
$\mathrm{C_2H_6} + n\text{-}\mathrm{C_{11}H_{26}}$	2.6		
$\mathrm{C_4H_{10}} + n\text{-}\mathrm{C_{11}H_{26}}$	2.0	1.21	0.05

[a] From empirical data at 298 K given in ref 14 except where noted. [b] Products are a n-paraffin and $\mathrm{H_2}$ (gas), see reaction 3. [c] Assumes that second reactant is the solvent. [d] Thomson, E. S.; Gjaldback, J. C. *Acta Chem. Scand.* 1963, *17*, 134.

In Table II, $\mathbf{R}_{np}$ is obtained from eq 7 for equilibria in which $m = 1$, 2, and 3. For comparison, this table also gives $\mathbf{R}_{np}$ values for equilibria with $m = 4$ as derived from eq 2. For equilibria where $m = 2$–4, $\mathbf{R}_{np}$ values do not differ greatly from on another, although these values tend to increase with decreasing m. Values of $\mathbf{R}_{np}$ for $m = 1$ are unexpectedly high due to the relatively low solubility of $\mathrm{CH_4}$. Note that variations of $\mathbf{R}_{np}$ with solvent type when $m = 1$ are primarily due to entropy differences. Even more drastic effects occur for the equilibrium $2\mathrm{CH_4} \rightleftharpoons \mathrm{C_2H_6}$ ($+\mathrm{H_2}$) where solubility data[14] show that $\mathbf{R}$ varies from 7 in n-$\mathrm{C_6H_{14}}$ to 40 in n-$\mathrm{C_{12}H_{26}}$ solvent.

Equilibria Involving Other Substances

Because of the simple mathematical description of $\mathbf{R}$ for n-paraffin equilibria, as exemplified by eq 6, relative gas/liquid equilibria involving other types of hydrocarbons are most easily examined by comparison to corresponding n-paraffin equilibria. The fact that many hydrocarbons possess vapor pressures within ca. 25% of the vapor pressures of n-paraffins of the same carbon number immediately implies that the earlier conclusion that $\mathbf{R} \sim 1$ for n-paraffins also applies to equilibria involving other classes of hydrocarbons. Equilibria whose $\mathbf{R}$ values differ substantially from unity therefore must either contain components whose vapor pressures differ substantially from corresponding n-paraffins or exhibit substantial deviations from Roault's law.

In order to more closely examine influences of different molecular structures on $\mathbf{R}$, each structural group is assumed to contribute a specific amount toward the Gibbs energy of vaporization (or vapor pressure).[17] This idea is supported, to some degree, by previous correlations of vapor pressures of branched hydrocarbons with molecular structure.[18,19] To the extent that

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(14) Stein, S. E. *J. Chem. Soc. Faraday Trans. 1* **1981**, *77*, 1457.

(15) Actually, the Flory–Huggins theory (see reference 11a, page 25, for a discussion and further references) may be used to estimate activity coefficients when $m \gg n$. Such calculations tend to increase $\mathbf{R}_{np}$.

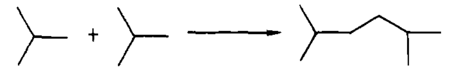
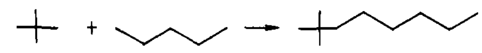
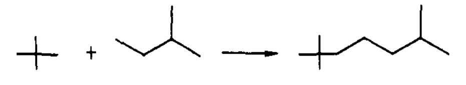
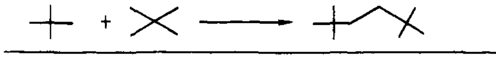
(16) Orwall, R. A.; Flory, P. J. *J. Am. Chem. Soc.* **1967**, *87*, 6814.

(17) This assumption implies that $\Delta G°_{vap}$ for a molecule is equal to the sum of $\Delta G°_{vap}$ for each of the structural groups of which it is composed. In ref 14, this has been shown to apply quite well for the methyl and methylene groups in n-paraffins.

(18) Greenshields, J. B.; Rossini, F. D. *J. Phys. Chem.* **1968**, *62*, 271.

(19) Kudchaker, A. P.; Holcomb, W. D.; Zwolinski, B. J. *J. Chem. Eng. Data* **1968**, *13*, 182.

Table III. **R** for Associative Equilibria Involving No Change in Branching

	T, K	**R**/**R**$_{np}$^{a}
	298	1.06
	298	1.04
	298	1.04
	298	1.09
	320	1.02
	320	1.12
	320	1.08
	320	1.18

^{a} Vapor pressure data taken from ref 10 and corrected for gas non-ideality, using methods given in ref 20.

this assumption holds and in the absence of significant structural differences between reactants and products, **R** ~ **R**$_{np}$. An examination of this assumption for selected associative equilibria of hydrocarbons involving no net change in branching is given in Table III. It is evident from this table that this assumption holds when branched structures are sufficiently well separated within a molecule.

Table IV lists vapor pressures for hydrocarbons containing specific molecular structures relative to *n*-paraffins of the same carbon number, P_{vap}/P_{vap}(*n*-paraffin). These quantities may be used to roughly examine influences of particular structural groups on **R**. Each of these molecular groups present in a reactant molecule will tend to increase **R** by a factor of $[P_{vap}/P_{vap}$(*n*-paraffin)] relative to **R**$_{np}$. For such groups in a product molecule, **R** will tend to be lowered by this factor.

It may be seen from Table IV that with increasing temperature P_{vap} for branched hydrocarbons, alkenes, and alkynes tends to approach P_{vap}(*n*-paraffin). It appears to be a general rule that the more P_{vap} deviates from P_{vap}(*n*-paraffin) at a particular temperature, the more rapidly P_{vap} will approach P_{vap}(*n*-paraffin) with increasing temperature (this idea also applies to non-hydrocarbon species).

It is useful to show that the presence of H_2 (gas) in reaction 3 has no major influence on the magnitude of **R** for associative equilibria. With the use of data in Table IV and ref 10 one finds for the associative equilibrium (Δn is strictly equal to −1),

$$\underset{(n)}{1\text{-}n\text{-}C_nH_m} + \underset{(m)}{n\text{-}C_mH_{2m+2}} \rightleftarrows \underset{(n+m)}{n\text{-}C_{m+n}H_{2n+2}} \qquad (8)$$

that between 298 K and 600 K $\mathbf{R} = 0.70 \pm 0.12\text{-}(V_{n+m}V_s/V_nV_m)$ which is only ca. 10% greater than **R**$_{np}$.

For equilibria involving significant differences in aromaticity between reactants and products, **R** may substantially differ from unity. This arises from the fact that vapor pressures of condensed aromatic species are strongly influenced by π–π interactions which are not necessarily proportional to the number of carbon atoms. Increasing aromaticity leads to decreasing vapor pressure as is evident from $[P_{vap}/P_{vap}$(*n*-paraffin)] values for polyaromatic molecules given in Table V.

It is difficult to make generalizations concerning the magnitude of **R** for equilibria containing non-hydrocarbon components. Simple group additivity cannot be reliably applied to vaporization properties of these compounds. For instance, the fractional lowering of vapor pressure of an alkane upon replacement of a methylene group by a carbonyl group may depend strongly on the size of the molecule and on the position of substitution. Furthermore, such molecules often form highly non-ideal solutions. However, it is noteworthy that the influence of both of the above factors on **R** tends to diminish with increasing temperature. To account for solution non-ideality one may use Regular Solution Theory[11a] or some other technique for estimating activity coefficients in solution.[20]

Free-Radical Reactions

The major difficulty in applying the methods discussed above to free-radical reactions is the treatment of possible radical/solvent complexation. In other words, free radicals, R·, may interact more strongly with solvent molecules than do corresponding molecules, RH, i.e., $K_H(R\cdot) < P°(RH)$ (or $K_H(RH)$). This problem is expected to be most severe for reactions in which free-radical centers are created or destroyed, as in bond-homolysis equilibria,

$$\mathrm{A}\cdot + \mathrm{B}\cdot \underset{k_d}{\overset{k_r}{\rightleftharpoons}} \mathrm{A{-}B} \qquad (9, -9)$$

Therefore, reaction 9 will be examined first.

Unfortunately, accurate values of the four rate constants needed to evaluate **R** (reaction 9), namely $k_{d,l}$, $k_{d,g}$, $k_{r,l}$, and $k_{r,g}$, for a specific reaction are not available. Available data, however, suggest that $k_{d,l}/k_{d,g} \sim 0.3\text{–}3^{6,7,21}$ and $k_{r,l}/k_{r,g} \sim 0.3\text{–}1.^{20}$ After accounting for the general observation that changes in solvent viscosity tend to change both $k_{d,l}$ and $k_{d,g}$ in the same direction, we estimate **R** (reaction 9) ~ 0.2–2. Therefore, such association often tends to be disfavored in solution. This is presumably due to some degree of radical/solvent complexation.

Empirical trends in $k_{d,l}$ and $k_{r,l}$ for reactions in *n*-paraffin solvents may be used to examine free-radical thermodynamics in solution in more detail. First, if it is arbitrarily assumed that AB, A·, and B· follow Roault's law, then $k_{d,l} \propto k_{r,l}V_s$ (cf. eq 7). If this relation is combined with the observation that $k_{r,l} \propto V_s^{-1.5}$ (ref 22a) in a series of *n*-paraffin solvents then $k_{d,l} \propto V_s^{-2.5}$. However, empirical homolysis rate constants do not show such a strong dependence of $k_{d,l}$ on V_s. Typically, $k_{d,l} \propto V_s^{-0.5}$.[21a] Thermochemical predictions may be brought into good agreement with experiment if it is assumed that AB obeys Roault's law and that free-radical "vapor pressures" are the same in different solvents if their concentrations, rather than their mole fractions, are the same. In this case, assuming $k_{r,l} \propto V_s^{-1.5}$ (as above), k_d is predicted to be proportional to $V_s^{-0.5}$ in agreement with experiment.

Relative liquid/gas bimolecular rate constants may be examined if species AB in reaction 1 is considered to be a transition state. For free-radical reactions involving a single free-radical center, contributions of radical/solvent complexation of the reactant to $k_{b,l}/k_{b,g}$ are expected to be compensated to some degree by related complexation of the transition state. Therefore, as a first approximation, for reactions involving large molecules, one expects $k_{b,l} \sim k_{b,g}$. In the literature this view is occasionally assumed to hold on more or less intuitive grounds since it usually does not seriously conflict with available data. Moreover, it is generally found that relative rate constants in the gas phase differ little from corresponding relative rate constants in solution. On the other hand, the present calculations of **R** for equilibria involving CH_4 as well as ideas from the Pratt–Chandler theory[8] indicate that it is possible for $k_{b,l}$ to differ substantially from $k_{b,g}$ when small radicals are involved even when no obvious "solvation" effects are present. If, for example, $K_H(\cdot CH_3)/K_H(\cdot C_2H_5) \sim K_H(CH_4)/K_H(C_2H_6)$, then H-atom transfer or addition reactions of methyl radicals relative to ethyl radicals are predicted to occur significantly faster (a factor of 2–6) in *n*-paraffin solvents than in the gas phase (see Table III). Also, if H atoms were as soluble as He in a

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(20) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids"; McGraw-Hill, Inc.: New York, 1977; 3rd ed.

(21) (a) Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 5403. (b) Walling, C.; Waits, H. P. *J. Phys. Chem.* **1967**, *71*, 2361.

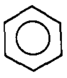
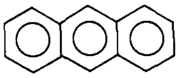
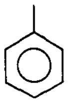
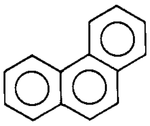
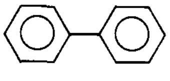
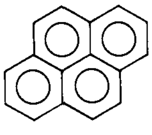
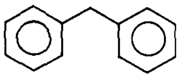
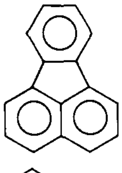
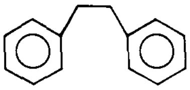
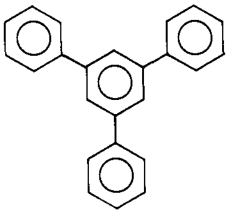
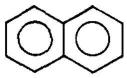
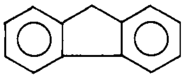
(22) (a) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 491. (b) Carlsson, D. J.; Ingold, K. U. *Ibid.* **1968**, *90*, 7048. (c) Kochi, J. K., Ed. "Free Radicals"; Wiley and Sons: New York, 1973; Chapters 1 and 2.

Table IV. Vapor Pressure Relative to *n*-Paraffins

substance or class of substances	P_{vap}/P_{vap}(*n*-paraffin)[a]						
	250 K	298 K	350 K	400 K	450 K	500 K	600 K
1-*n*-alkenes	1.30 ± 0.03	1.24 ± 0.01	1.16 ± 0.01	1.12 ± 0.01	1.09 ± 0.01	1.07 ± 0.01	1.03 ± 0.01
2-*n*-alkenes	1.00 ± 0.14	1.05 ± 0.05	1.03 ± 0.04				
1-*n*-alkyne	0.65 ± 0.10	1.80 ± 0.05	1.25 ± 0.10	1.2 ± 0.1			
2-*n*-alkyne	0.30 ± 0.05	0.40 ± 0.05	0.6				
cyclopentane	0.54	0.62					
n-alkylcyclopentane		0.88 ± 0.02	0.88 ± 0.02	0.86			
cyclohexane		0.65	0.69				
n-alkylcyclohexanes		0.95 ± 0.05	0.91 ± 0.04	0.83 ± 0.03	0.81		
singly branched alkanes	1.5 ± 0.1	1.4 ± 0.1	1.25 ± 0.10	1.2 ± 0.1			
doubly branched alkanes[b]	3.1 ± 0.3	2.2 ± 0.4	1.7 ± 0.2	1.0 ± 0.1			

[a] P_{vap} and P_{vap}(*n*-paraffin) pertain to substances containing the same number of carbon atoms per molecule. Data are taken from ref 10. Uncertainty range spans empirical values for different members of the series. [b] Both branches are on the same carbon atom (i.e., substance contains one quaternary carbon atom).

Table V. P_{vap}/P_{vap}(*n*-paraffin) for Aromatics and Polyaromatics[a]

	350 K	500 K		500 K
	0.71			0.13
	0.68			0.14
	0.27	0.40		0.055
	0.56	0.51		0.11
	0.73	0.49		0.14[c]
	0.24	0.38[b]		0.23

[a] Except where noted P_{vap} was from published compilations (for example, Boublik, T.; Fried, V.; Hala, E. "The Vapor Pressures of Pure Substances"; Elsevier: Amsterdam, 1973). P_{vap}(*n*-paraffin) values given in ref 10. [b] P_{vap}(*n*-paraffin) obtained by extrapolation of data compiled in ref 14. [c] P_{vap} from: Malaspina, L.; Bardi, G.; Gigli, R. *J. Chem. Thermodyn.* 1974, *6*, 1053.

hydrocarbon, say *n*-$C_{12}H_{26}$, then it may be shown that rate constants for H-atom reactions in this solvent should be a factor of 40 greater than those in the gas phase.[23] These considerations imply that if it is found that $k_{b,l} \sim k_{b,g}$ for such reactions then the small reactant species must be significantly solvated. Measurements of relative reaction rates of different atoms or radicals with a single substrate in both gas and liquid phases could be used to test and refine these ideas. Unfortunately, such data are not now available.

Comparison with Other Methods

Bell[2] introduced a general method for estimating relative bimolecular rate constants in the gaas and liquid phase for reactions in which the Arrhenius activation energy is the same in the two phases, using linear free-energy relationships in conjunction with transition-state theory. We have employed this approach as follows. If the Arrhenius activation energy is the same in the gas and liquid phase, then it may be shown[4] that $\Delta H^{\ddagger}_{gas} + RT = \Delta H^{\ddagger}_{liq}$. If it is further assumed that vaporization (or solution) entropies and enthalpies of reactants and transition state follow the relationship

$$\Delta S^{\circ}_{vap} = a\Delta H^{\circ}_{vap} + b \qquad (10)$$

then, one finds

$$\frac{k_{b,l}}{k_{b,g}} = \left(\frac{V_s(\text{atm})}{RT}\right)e^{1-a(\cdot\text{K})}e^{b/R}$$

Bell found $k_{b,l}/k_{b,g}$ = 2–4 at 298 K, using *a* and *b* values derived from gas solubility data. Using more recent gas solubility data at 298 K,[24] we find $k_{b,l}/k_{b,g}$ = 2.2 in benzene solution and $k_{b,l}/k_{b,g}$ = 2.4 in heptane, in agreement with Bell's calculations. Gas solubility data in several other solvents lead to very similar predicted values for $k_{b,l}/k_{b,g}$. It should be kept in mind however that eq 10 does not apply equally well to all solvents and solutes. For example, we find that this equation does not adequately correlate data for gas dissolution in *n*-$C_{12}H_{26}$.[24]

If values for *a* and *b* are derived from vaporization thermodynamics of *n*-paraffins ($a = 1.375\ \text{K}^{-1}$, $b = 11.81$ cal mol^{-1} K^{-1} at 298 K[14]), then at 298 K, $k_{b,l}/k_{b,g} = 10.74V_m(\text{l}^{-1})$ or $k_{b,l}/k_{b,g}$ = 1.2 for *n*-C_5H_{12} solvent and $k_{b,l}/k_{b,g}$ = 2.1 for *n*-$C_{10}H_{22}$ solvent. The above *a* and *b* values may be shown to apply to vaporization properties of numerous nonassociated liquids.[25] Apparently $k_{b,l}/k_{b,g}$ values derived from gas solubility data tend to be slightly greater than values from liquid vaporization data.

The reason that Bell's approach yields much lower **R** values than ours for reactions involving small molecules may be traced to the assumption in Bell's approach that reaction enthalpies (or activation energies) are the same in the gas and liquid phase. Reaction enthalpies can differ substantially in the gas and liquid phase even in the absence of obvious solvation effects.

Other attempts to find general values for $k_{b,l}/k_{b,g}$ have used eq 2 along with estimates of vaporization entropy, using the free-volume theory formalism. As indicated earlier, this approach has led to $k_{b,l}/k_{b,g}$ values between 50 and 100.[4] This approach appears to fail because it does not account for variations of formal "free volumes" with molecular size.

The Pratt–Chandler theory[8] referred to earlier allows, in principle, the calculation of **R** values from molecular properties. As far as we are aware, the only chemical equilibrium system yet

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[23] Based on eq 7, assuming $K_H(\text{H}\cdot) = K_H(\text{He})$, using $K_H(\text{He})$ given in reef 22.

[24] Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.

[25] Stull, D. R.; Westrum, E. F.; Sinke, G. C. "Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.

examined by this theory is $2NO_2 \rightleftharpoons N_2O_4$ in $CHCl_3$ solvent.[8] This analysis treated NO_2 units and solvent molecules as hard spheres and yielded a value of **R** in good agreement with experiment ($\sim 10^3$). This analysis indicated that "dissociation of N_2O_4 is less favorable in liquid chloroform than in the gas phase because the liquid molecules drive pairs of NO_2 groups together in order to save space in the dense fluid medium". Hence, this high **R** value is not a result of what is usually thought of as solvation effects since intermolecular interaction potentials do not differ for reactants and products.

Our results do not really disagree with those of Pratt and Chandler since our work deals primarily with large molecules and their's has been applied only to small molecules. In fact, our observation that when CH_4 is a reactant **R** is considerably greater than unity is in qualitative agreement with Pratt and Chandler's prediction. Furthermore, using available data for gas solubility in *n*-paraffins,[22] we estimate that for hydrogenation, H_2 + 1-*n*-$C_nH_{2n} \rightleftharpoons n\text{-}C_nH_{2n+2}$, **R** = 10–20 and for the ficticious equilibrium, $2He \rightleftharpoons He_2$, assuming He_2 to be as soluble as H_2, **R** = 50–100.

The use of simple collision theory arguments for estimating relative preexponential factors in the gas and liquid phase appears to be of little value since the definition of a collision in the liquid phase is rather arbitrary.

Conclusions

Available vaporization and solubility data have been used for estimation of relative equilibrium constants for association of hydrocarbons in the gas phase and ideal liquid phase. These calculations indicate that associative equilibrium constants for large molecules in the absence of changes in branching and aromatization are nearly the same in gases and liquids. Relatively low solubilities of certain small molecules and atoms suggest that equilibria will be shifted away from such small species in solution.

These results imply that in the absence of solvation effects, rate constants for non-diffusion-controlled reactions of large free radicals are nearly the same in the gas and liquid phase, while for smaller species, solution phase rate constants may be significantly greater than gas phase values. Limited kinetic data indicate that relative stabilities of free radicals in different solvents are more directly related to radical concentrations than to radical mole fractions.

Appendix. Discussion of Equation 2

The quantity **R** may be viewed as a generalized equilibrium constant for the transfer of reaction 1 from the gas phase to the liquid phase. The Gibbs energy for this process may in general be written

$$\Delta G = [\Delta G(\text{products}) - \Delta G(\text{reactants})]_{\text{soln}} - [\Delta G(\text{products}) - \Delta G(\text{reactants})]_{\text{gas}}$$

If this equation is rearranged as follows,

$$\Delta G = [\Delta G(\text{products})_{\text{soln}} - \Delta G(\text{products})_{\text{gas}}] - [\Delta G(\text{reactants})_{\text{soln}} - \Delta G(\text{reactants})_{\text{gas}}]$$

it becomes apparent that only Gibbs energies of vaporization of the individual substances involved in a reaction are required to evaluate ΔG, hence **R** ($\Delta G = -RT \ln \mathbf{R}$). A more detailed derivation of **R** for reaction 1 follows.

In order to directly compare equilibrium constants in the gas and liquid phase, it is most convenient to express both of these equilibrium constants in concentration (molarity) standard states. For liquid-phase associative equilibria, reaction 1, equilibrium constants in the pure liquid standard state, K_l^x (x denotes mole fraction in the liquid) are related to equilibrium constants in concentration standard states, K_l^c, as follows,

$$K_l^x = \frac{\gamma_{AB}^x X_{AB}}{(\gamma_A^x X_A)(\gamma_B^x X_B)} = \frac{\gamma_{AB}^x (C_{AB,l}/C_s)}{\gamma_A^x (C_{A,l}/C_s) \gamma_B^x (C_{B,l}/C_s)} = \frac{K_l^c}{V_s} \tag{11}$$

where $C_{AB,l}$, $C_{A,l}$, and $C_{B,l}$ are molar concentrations of AB, A, and B in the liquid phase, respectively, γ_{AB}^x, γ_A^x, and γ_B^x are their corresponding activity coefficients and $V_s \equiv C_s^{-1}$ is the volume of a mole of molecules in the liquid solution. Note that $K_l^c = (\gamma_{AB}^x/\gamma_A^x\gamma_B^x)(C_{AB}/C_AC_B)$. Mole fractions are employed in these calculations because many liquid mixtures of hydrocarbons are known to closely obey Roault's law, so for these mixtures γ_i^x values are near unity.

While there has been considerable work aimed at elucidation of non-ideality in nonpolar liquids, such effects are expected to exert only a small influence on conclusions drawn in this work. For instance, the interesting non-idealities exhibited by hydrocarbon mixtures observed by Patterson and co-workers[12] are generally based on the excess enthalpies of mixing, H^E. When such values become large, it generally is found that their effects on G^E are substantially compensated for by a TS^E term. In paraffin mixtures one does not generally expect solution non-idealities to change **R** by more than 30%.[11,12]

The gas-phase equilibrium constant for associative reactions in atmosphere, ideal-gas standard states, K_g^P, is related to the equilibrium constant in molarity standard states, K_g^c, simply by

$$K_g^P = K_g^c/(RT) \tag{12}$$

Division of eq 11 by eq 12 leads to the following expression for the ratio of liquid- and gas-phase equilibrium constants in concentration standard states,

$$\frac{K_l^c}{K_g^c} \equiv \mathbf{R} = \frac{K_l^x}{K_g^P}\left(\frac{V_s}{RT}\right) \tag{13}$$

The ratio (K_l^x/K_g^P) in eq 13 is related to the Gibbs energies of AB, A, and B as follows,

$$\begin{aligned}\frac{K_l^x}{K_g^P} = {} & \exp\left\{-\frac{\Delta G_l^*(\text{reaction 1})}{RT}\right\} \Big/ \exp\left\{-\frac{\Delta G^\circ{}_g(\text{reaction 1})}{RT}\right\} \\ & = \exp\{(-G_{AB}^* + G_A^* + G_B^* + G^\circ{}_{AB} - G^\circ{}_A - G^\circ{}_B)/RT\} \\ & = \exp\{[(G^\circ{}_{AB} - G_{AB}^*) - (G^\circ{}_A - G_A^*) - (G^\circ{}_B - G_B^*)]/RT\}\end{aligned} \tag{14}$$

where G_{AB}^*, G_A^*, and G_B^* are the Gibbs energies of the pure liquids AB, A, and B under their own vapor pressures and $G^\circ{}_{AB}$, $G^\circ{}_A$, and $G^\circ{}_B$ are Gibbs energies of AB, A, and B as ideal gases at 1 atm. For convenience eq 14 may be expressed in terms of ideal-gas vapor pressures, $P^\circ{}_A$, $P^\circ{}_B$ and $P^\circ{}_{AB}$, using the relation,

$$P^\circ{}_i/\text{atm} = \exp\{-(G^\circ{}_i - G_i^*)/RT\} \tag{15}$$

These $P^\circ{}_i$ values are, in effect, vapor pressures of pure i in atmosphere units that would be observed if the vapor were an ideal gas. This quantity is sometimes referred to as liquid fugacity or the liquid's "escaping tendancy".[26]

By combining eq 13, 14, and 15, the desired equation is obtained,

$$\mathbf{R} = \frac{P^\circ{}_A P^\circ{}_B}{P^\circ{}_{AB}}\left(\frac{V_s}{RT}\right) \tag{2}$$

For more general equilibria

$$aA + bB + \ldots \rightleftharpoons pP + qQ + \ldots$$

it is straightforward to show

$$\mathbf{R} = \frac{(P^\circ{}_A)^a (P^\circ{}_B)^b \ldots}{(P^\circ{}_P)^p (P^\circ{}_Q)^q \ldots}\left(\frac{RT}{V_s}\right)^{\Delta n} \tag{16}$$

where $\Delta n = p + q + \ldots - a - b - \ldots$.

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[26] Lewis, G. N.; Randall, M. "Thermodynamics"; McGraw-Hill, Inc.: New York, 1961; 2nd ed., revised by Pitzer, K. S.; Brewer, L.