

intensity, the absorption steps in the ionic manifold will be saturated before the absorption steps in the neutral manifold. In this case the intensity dependence measured¹ for the nonresonant background between 3.1 and 3.3 eV, with exponent $n = 2-3$, does not reflect the true order of the process, but sets a lower limit to the total photon uptake. The total number of 3.1-3.3-eV photons necessary to generate Ni^+ from NiCp_2 is at least four (see above and ref 1), in agreement with the mass spectrometric appearance potential ($\text{AP}(\text{Ni}^+) = 13.6 \text{ eV}$).

Ferrocene. The nonresonant ion background signal was also found to be almost exclusively due to Fe^+ . The analysis is, however, characteristically different from that of nickelocene in several respects: the nonresonant background is strongly structured and extends from 3750 to 4200 Å (3.3 - 2.95 eV); as the adiabatic ionization potential of ferrocene is 6.72 eV,⁹ two-photon molecular photoionization is not possible for photon energies up to 3.3 eV. On the other hand, uptake of two photons is sufficient to induce at least partial dissociation:



Nonresonant production of Fe^+ hence probably proceeds through the Fecp intermediate.

A comparison of mass spectra obtained by electron impact (EI) at electron energies of 20¹⁴ and 50 eV¹⁵ and those obtained by laser MPD/MPI is shown in Figure 3. The amount of energy transferred to the molecular system on electron impact is not well-known and is represented by

a broad distribution (the "deposition function"); however, the two EI mass spectra show very similar fragmentation patterns, despite the large difference in electron energies. The laser MPD/MPI mass spectrum is qualitatively completely different, reflecting the multitude of dissociation and predissociation processes occurring when energy is delivered to the molecule in quanta which are commensurate with metal-ligand bond energies but smaller than the molecular ionization potential.

In conclusion, we summarize the main points of this study as follows: (a) confirmation of the collision-free, truly intramolecular nature of laser MPD/MPI processes in metallocenes; (b) unequivocal identification of the ions produced, being almost exclusively the metal ions Fe^+ and Ni^+ , both at atomic resonances as well as throughout the nonresonant ion background signal region; (c) independence of the MPD/MPI spectra on cooling in supersonic jets, indicating that the first absorption step is truly diffuse, even at very low temperatures. Clarification of laser MPD/MPI processes in metallocenes have shown them to be a unique pulsed, efficient, intense, room-temperature source of pure metal ions in the gas phase. An obvious multitude of applications in gas-phase ion physics and ion chemistry can be foreseen.

Acknowledgment. S.L. acknowledges the support of the Stiftung für Stipendien auf dem Gebiete der Chemie, Basel, Switzerland. This research was supported in part by the U.S.-Israel Binational Science Foundation (Grant 2461) and by the U.S. Army European Research Office.

Latent Heat of Vaporization of a Fluid

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(Received: August 7, 1981)

Renormalization-group theory is applied to obtain the functional form of the latent heat of vaporization of a pure fluid that is applicable throughout the entire domain of existence of latent heat. To illustrate the use of the latent-heat expression, we least-squares fit it to latent-heat data of water.

We apply the results of renormalization-group theory to obtain a functional form of the latent heat of vaporization L of a pure fluid that is applicable throughout the entire domain of existence of the latent heat, i.e., from the triple point to the critical point. The resulting formula for the latent heat contains system-dependent parameters which ultimately must be fitted to data.

The latent heat of a fluid may be written as a sum of two parts: one being the contribution to L describing the singular behavior near the critical point and the other being the analytic or regular contribution to L characterizing the behavior away from the critical region. Ley-Koo and Green¹ made use of the general form of the singular part of the thermodynamic potential proposed by

Wegner² for describing the critical region of fluids. Employing their expression in conjunction with the Clausius-Clapeyron equation, we are motivated to write

$$L = a_1 t^\beta + a_2 t^{\beta+\Delta} + a_3 t^{1-\alpha+\beta} + \sum_{n=1}^M b_n t^n \quad (1)$$

where the first three terms account for behavior in the vicinity of the critical point and the finite sum describes

(2) Wegner, F. J. *Phys. Rev. B* 1972, 5, 4529. The precise values of α and β are still open to some uncertainty. Our fractions, which fall well within the range of currently reasonable values, were chosen for their simplicity and convenience. In particular, for $\beta = 1/3$, the term constant $\times t^{3\beta}$, which is a singular term found in ref 1, coincides with our lowest-order regular term, $b_1 t$. The value of Δ is not well established either experimentally or theoretically; 1/2 from lowest-order theoretical calculations is the most commonly used value. We determine it here by a least-squares fit of data.

(1) Ley-Koo, M.; Green, M. S. *Phys. Rev. A* 1977, 16, 2483; 1981, 23, 2650.

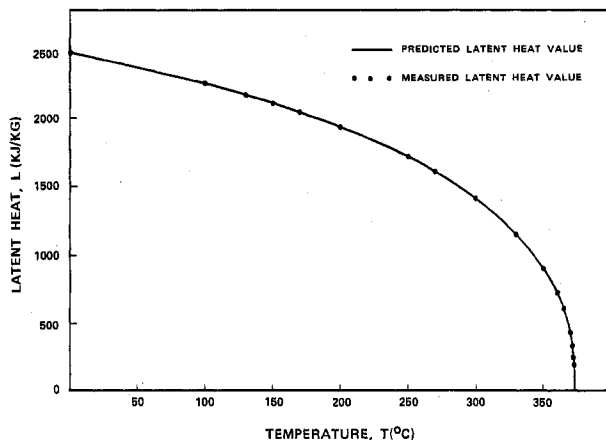


Figure 1. Comparison of measured latent heat of vaporization of water and eq 1 with $M = 3$ and parameters described in text.

L away from the critical point (M being the number of terms in the regular part of L). Here $t = (T_C - T)/T_C$, T is the temperature, T_C is the critical temperature, and the a_n and b_n are system-dependent parameters. The critical exponents describing the singularities associated with the specific heat α and the difference in coexisting densities β are taken to be $1/8$ and $1/3$, respectively, in our work below. The exponent Δ is Wegner's first gap exponent.² The singular part of eq 1 is based on retaining much of the symmetry of the Ising (lattice-gas) model to an extent that is in keeping with the conclusions of the most recent work that has focused upon this issue, which remains, however, a subtle one.³

As an example of the use of eq 1, we least-squares fit this formula to the highly accurate latent-heat data of water by Osborne, Stimson, and Ginnings (OSG)⁴ and Osborne, Stimson, and Fiock (OSF)⁵ which provide us with latent-heat data for $T_T \leq T \leq T_C$ (T_T is the triple point temperature). The optimum value of T_C and Δ (obtained by least-squares fitting the OSG data, using eq 1 with $M = 1$, for temperatures near T_C) is found to be 373.92 °C and $79/100 - \beta \approx 0.4567$, respectively.

We fit the aforementioned OSG and OSF data using eq 1 for various values of M . Subject to some uncertainty in our knowledge of the best error estimates to apply to the OSG and OSF data, we conclude that the cases $M \geq 3$

(3) See, e.g. Nicoll, J. F.; Zia, R. K. P. *Phys. Rev. B* 1980, 23, 6157, and references therein.

(4) Osborne, N. S.; Stimson, H. F.; Ginnings, D. C. *J. Res. Natl. Bur. Stand. (U.S.)* 1937, 18, 389.

(5) Osborne, N. S.; Stimson, H. F.; Fiock, E. F. *Trans. ASME* 1930, 52, 191.

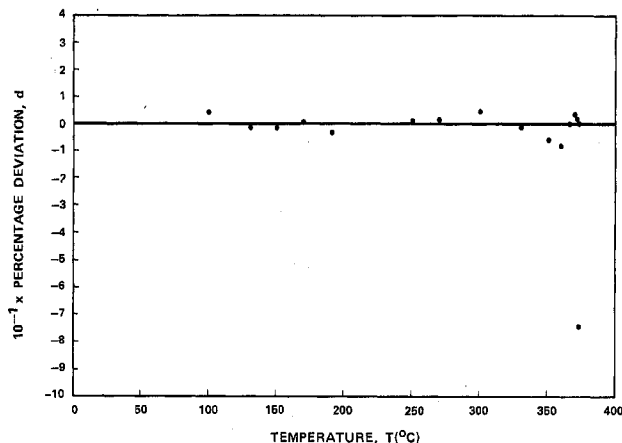


Figure 2. Percentage deviation associated with preceding figure.

should yield predicted L values within the experimental error. The predicted latent-heat values L_i for the case $M = 3$ are compared to the corresponding measured values L_i^* in Figure 1. The percentage deviations $d = 100(L_i^* - L_i)/L_i^*$, associated with the preceding figure, are given in Figure 2. The maximum deviation occurs at $T = 373.5$ °C (a temperature nearly equal to T_C) where the predicted L differs from the data by about one part in 100. In light of the enormous experimental difficulties one confronts in this region, 1% deviation is most likely within the experimental error. For $M = 3$, we find that the a_n and b_n (in kJ/kg) are given by

$$\begin{aligned} a_1 &= 2059.1061 & a_2 &= 6604.5410 & a_3 &= 7694.3132 \\ b_1 &= -11318.0281 & b_2 &= -4284.4296 & b_3 &= 2598.6025 \end{aligned}$$

The standard error $\sigma = [\sum_{i=1}^N (L_i^* - L_i)^2 / N]^{1/2}$ (N being the number of values) for the aforementioned case is equal to 0.63 kJ/kg. For $M > 5$, very little accuracy is gained by increasing M .

In summary, we are able to formulate a highly accurate and relatively simple expression for the latent heat of a fluid over its entire domain of its existence. The latent-heat formulae obtained here may be applied to fluids which are in the same universality class as water.^{6,7}

Acknowledgment. Acknowledgment is made by S. Torquato to General Motors Institute and to the National Science Foundation, and by G. Stell to the Office of Basic Energy Sciences, U.S. Department of Energy, for support of this research.

(6) Stell, G. *Phys. Rev. Lett.* 1974, 32, 286.

(7) Sengers, J. V.; Sengers, J. M. H. NASA Contract Report, 1977.