(7) Jamieson, D. T.; Irving, J. B. "Advances in Thermal Conductivity"; Reisbig, R., Sauer, J., Eds.; University of Missouri—Rolla: Rolla, MO, 1974; p 185.
(8) Horrocks, J. K.; McLaughlin, E. *Proc. R. Soc. London, Ser. A* **1963**, *273*, 259.
(9) De Castro, C. A.; Calado, J. C. G.; Wakeham, W. A. *J. Phys. E.* **1976**, *9*, 1073.
(10) Weishaupt, J. *Forschung* **1940**, *11*, 20.
(11) De Groot, J. J.; Kestin, J.; Sooklazian, H. *Physica* **1974**, *75*, 454.
(12) Haarman, J. W. *Physica* **1971**, *52*, 605.
(13) Haarman, J. W.; Thesis, Technische Hogeschool, Delft, Holland, 1969.
(14) Kestin, J.; Ro, S. T.; Wakeham, W. A. *Physica* **1972**, *58*, 165.
(15) De Castro, C. A.; Wakeham, W. A. *Therm. Conduct.* **1978**, *15*.
(16) Grassmann, P. Doctoral thesis, no. 3078, Federal Institute of Technology, Zürich, Switzerland, 1960.
(17) Grassmann, P.; Straumann, W. *Int. J. Heat Mass Transfer* **1960**, *1*, 50.
(18) Grassmann, P.; Straumann, W.; Widmer, F.; Jobst, W. *Prog. Int. Res. Thermodyn. Transp. Prop., Pap. Symp. Thermophys. Prop., 2nd, 1962* **1962**, 447.
(19) Carslaw, H. A.; Jaeger, J. C. "Conduction of Heat in Solids", 2nd ed.; Oxford University Press: London, 1959.

(20) Healy, J. J.; de Groot, J. J.; Kestin, J. *Physica B & C (Amsterdam)* **1976**, *82*, 392.
(21) Shampine, L. F.; Allen, R. C. "Numerical Computing"; W. B. Saunders: Philadelphia, PA, 1973.
(22) Davis, P. J.; Rabinowitz, P. "Numerical Integration"; Blaisdell Publishing Co.: Waltham, MA, 1967.
(23) McLaughlin, E. *Chem. Rev.* **1964**, *64*, 389.
(24) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 56th ed.; CRC Press: Cleveland, OH, 1974.
(25) Jamieson, D. T.; Irving, J. B.; Tudhope, J. S. "Liquid Thermal Conductivity—A Data Survey to 1973"; HM Stationery Office: Edinburg, United Kingdom, 1975.
(26) Tufeu, R., et al., as given in ref 25.
(27) Vargaftik, N. B. "Tables on the Thermophysical Properties of Liquids and Gases", 2nd ed.; Hemisphere: Washington, DC, 1975 (also as given in ref 25).
(28) Abas-Zade, A. K., as given in ref 25.
(29) Takizawa, S.; Murata, H.; Nagashima, A. *Bull. JSME* **1978**, *21*, 273.
(30) Saklades, B. C.; Coates, J. *AIChE J.* **1955**, *1*, 275.

Enthalpies of Vaporization and Vapor Pressures of Triphenyl-, Tri(p-tolyl)-, and Tris(2-cyanoethyl)phosphines

Kees G. de Kruif*

Chemical Thermodynamics Group, State University of Utrecht, Utrecht, The Netherlands

Johan M. Herman and Pieter J. van den Berg

Department of Chemical Technology, Delft University of Technology, 2628 BL Delft, The Netherlands

Simultaneous torsion and mass loss effusion techniques were used to measure the vapor pressure as a function of temperature. The enthalpies of sublimation/vaporization were derived from the temperature dependence of vapor pressure. Overall mean values for both techniques are as follows: triphenylphosphine (liquid), $\Delta H_v^\circ(378.06\ \text{K}) = 91.4 \pm 2$ kJ mol^{-1}, $p(378.06\ \text{K}) = 4.0 \pm 0.1$ Pa; tri(p-tolyl)phosphine (liquid), $\Delta H_v^\circ(385.28\ \text{K}) = 126 \pm 5$ kJ mol^{-1}, $p(385.28\ \text{K}) = 0.40 \pm 0.01$ Pa; tris(2-cyanoethyl)phosphine (solid), $\Delta H_v^\circ(412.60\ \text{K}) = 105.7 \pm 2$ kJ mol^{-1}, $p(412.60\ \text{K}) = 0.40 \pm 0.01$ Pa.

Introduction

Lately hydridocarbonyltris(triphenylphosphine)rhodium(I), dissolved in triphenylphosphine (TPP) and capillarly condensed into the pores of a support, has been succesfully applied as a heterogenous catalyst in the industrially important hydroformylation of propylene, i.e., the conversion of propylene, hydrogen, and carbon monoxide to *n*- and isobutyraldehyde (*1, 2*). In order to calculate the maximum vaporization losses of TPP in a large-scale chemical reactor under reaction conditions, one must know its vapor pressure as a function of temperature. Since only few data could be found in the literature (*3*), it was decided to measure them. Because tri(p-tolyl)phosphine (TTP) and tris(2-cyanoethyl)phosphine (TCP) are also suitable solvents for hydridocarbonyltris(triphenylphosphine)rhodium(I), the vapor pressures of these materials were also measured. In this paper the results of this study are presented.

Experimental Section

Samples. TPP was obtained from Fluka (Switzerland). As preliminary measurements gave spurious results, we further purified TPP by zone refining.

TTP obtained from K & K laboratories Inc. appeared to contain brown impurities which were the cause of low vapor pressures and inconsistent enthalpies of sublimation. Also a sample kindly provided by the Van't Hoff Laboratory (University of Amsterdam) was insufficiently pure. Vacuum sublimation of this sample (400 → 300 K at 10^{-5} torr) improved results considerably (1 torr = 101325/760 Pa).

TCP was provided by Strem (USA) and could be used without additional purification.

Measuring Principle. Use was made of the simultaneous torsion and mass loss effusion technique. The apparatus described previously (*4*) is checked frequently on naphthalene of which very accurate vapor pressure data are given by Ambrose (*6*).

Treatment of Results. Vapor pressures obtained from simultaneous torsion effusion measurements (subscript t) and mass loss effusion measurements (subscript m) were fitted independently to the equation (*5*)

$$R \ln (p/p^\circ) = -\Delta G^\circ(\theta)/\theta + \Delta H^\circ(\theta)(1/\theta - 1/T) \quad (1)$$

in which θ is a reference temperature and p° a standard pressure (taken to be 1 Pa). In our measurements over a temperature range of 20 K, the plot of ln (p/p°) as a function of $1/T$ does not deviate significantly from a straight line. therefore, our results can be described adequately by two parameters, namely, $\Delta G^\circ(\theta)$ and $\Delta H^\circ(\theta)$.

Table I. Experimental Results[a]

			torsion effusion			mass loss effusion				mean values		
	T_1, K	T_2, K	θ_t, K	$\Delta G^\circ_t(\theta)$, J mol⁻¹	$\Delta H^\circ_t(\theta)$, kJ mol⁻¹	θ_m, K	$\Delta G^\circ_m(\theta)$, J mol⁻¹	$\Delta H^\circ_m(\theta)$, kJ mol⁻¹	$(p_m/p_t)(\theta_t)$	θ, K	$\Delta G^\circ(\theta)$, J mol⁻¹	$\Delta H^\circ(\theta)$, kJ mol⁻¹
triphenylphosphine (liquid)	364	392	378.37	-4361 ± 100	93.4 ± 1.5	377.75	-4354 ± 100	89.4 ± 1.5	1.05	378.06	-4358 ± 100	91.4 ± 2
tri(p-tolyl)phosphine (liquid)	372	398	385.20	2935 ± 100	126.0 ± 5	385.36	2936 ± 100	126.0 ± 5	0.98	385.28	2935 ± 100	126.0 ± 5
tris(2-cyanoethyl)phosphine (solid)	397	427	412.90	3146 ± 50	107.0 ± 2	412.29	3141 ± 50	104.4 ± 1	1.05	412.60	3143 ± 60	105.7 ± 2

[a] The $\Delta G^\circ(\theta)$ values are referred to a standard state of 1 Pa.

Table II. Pressure-Temperature Table

	T, K		
p, Pa	TPP	TTP	TCP
0.1		372.16	394.83
0.2		378.61	403.52
0.3		382.48	408.78
0.4		385.28	412.60
0.5		387.48	415.61
0.6		389.29	418.10
0.7		390.84	420.23
0.8		392.19	422.09
0.9		393.39	423.75
1.0	360.86	394.47	425.24
2	369.26		
3	374.36		
4	378.06		
5	380.98		
6	383.40		
7	385.48		
8	387.29		
9	388.90		
10	390.36		

For measurements made over a large temperature range, eq 1 may be extended with terms which contain as adjustable parameters $\Delta C_p^\circ(\theta)$ and the derivatives of $\Delta C_p^\circ(\theta)$ with respect to temperature. In practice it appears that only very accurate equilibrium data over a considerable temperature range allow the evaluation of a third parameter. This material has been discussed by Clarke and Glew (5). Nevertheless, if $\Delta C_p^\circ(\theta)$ is obtained by this or other means, eq 1 can be extended with the term

$$+\Delta C_p^\circ(\theta)\{\theta/T - 1 + \ln(T/\theta)\}$$

In that case, the vapor pressure can be extrapolated to other temperatures.

Results and Discussion

In Table I we present the experimental results expressed in terms of the parameters θ, $\Delta G^\circ(\theta)$, and $\Delta H^\circ(\theta)$ of eq 1. As the ratio p_m/p_t in Table I equals 1 within experimental error, we conclude that molecular mass of the vapor equals formula mass. In Table II we present a pressure–temperature table obtained by inserting the mean values of Table I into eq 1.

For TPP vapor pressure was measured at elevated temperatures by Forward et al. (3). Combination of their results with ours may lead to a vapor-pressure equation which allows for interpolation of experimental data and which may also be used for extrapolation. Now the data of Forward et al. (3) and ours may contain different systematic errors. Moreover, the result of fitting the combined data to an equation with three or more adjustable parameters will depend on the weight attributed to the respective data. It indeed appeared that the fitting results were not unambiguous. So we adopted the following procedure for calculating the third adjustable parameter, i.e., ΔC_p°. Fitting the data of Forward (3), which lie on a straight line in a Clapeyron plot, to eq 1, we find the following for TPP: $\Delta G^\circ(523.15$ K$) = 35677 \pm 25$ J mol⁻¹; $\Delta H_v^\circ(523.15$ K$) = 70.9 \pm 0.3$ kJ mol⁻¹. We now calculate

$$\Delta C_p^\circ = (91.4 - 70.9)/(378 - 523) =$$
$$-0.141 \pm 0.016 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

With this ΔC_p° value, the data presented here can be extrapolated with more confidence.

During the measurements on TTP, vapor pressure slowly decreased while ΔH_s° increased, for each successive run. This effect is probably caused by some impurities which remained after vacuum sublimation, but we do not exclude a slight decomposition of the sample. So the data presented in Table I were obtained by extrapolation of the experimental results to

the start of the measurement. We are not aware of literature values for either TTP or TCP.

Acknowledgment

Literature Cited

(1) Gerritsen, L. A.; Scholten, J. J. F. (Organisatie voor Zuiver Wetenschappelÿk Onderzoek) Netherlands Patent Applications 7 700 554 (1977), 7 712 648 (1977), and 7 902 964 (1979).

(2) Gerritsen, L. A.; Scholten, J. J. F. (Stamicarbon B.V.) German Patent Application 2 802 276 (1978) and British Patent Application 1 551 601 (1979).
(3) Forward, M. V.; Bowden, S. T.; Jones, W. J. J. Chem. Soc. 1949, 5, s121.
(4) de Kruif, C. G.; van Ginkel, C. H. D. J. Chem. Thermodyn. 1977, 9, 725.
(5) Clarke, E. C. W.; Glew, D. N. Trans. Faraday Soc. 1966, 62, 539.
(6) Ambrose, D.; Lawrenson, I. J.; Sprake, C. H. S. J. Chem. Thermodyn. 1975, 7, 1173.

Low-Pressure Compression Factors for R-12 Gas

Mithileshwar Prasad[†]

Department of Mechanical Engineering, Indian Institute of Technology, Kanpur 208016, India

Low-pressure compression factors of R-12 gas have been measured by using an improved Burnett apparatus from 298.15 to 373.15 K and from 0.3 to above 5 bar. R-12 is an abbreviation for dichlorodifluoromethane, a refrigerant. The uncertainties in the measurements of pressure, temperature, and compression factor are estimated to be $\pm 10^{-4}$ bar, ± 0.01 K, and $\pm 0.1\%$, respectively. The second virial coefficients for R-12 are reported.

The compression factor of a gas, defined as $Z = PV/(nRT)$, is a measure of its departure from ideality, and equation-of-state data are conveniently expressed in terms of Z values over a range of pressure and temperature.

The low-pressure compression factors of R-12 gas have been measured by using an improved Burnett apparatus. The details of the apparatus are described elsewhere (1, 2). R-12 is a refrigerant, dichlorodifluoromethane. The literature on the experimental determination of the pressure–volume–temperature relationship of R-12 gas is limited to pressures above 5 bar (3–7). The only published second virial coefficients for R-12 are those by Kunz and Kapner (8), who have used the input data from ref 4.

The objective of the present investigation was to obtain low-pressure compression factors for R-12 gas primarily to extend the range of existing $P-V-T$ data to the low-pressure region.

The Burnett apparatus (9) has been used repeatedly by several research workers for volumetric studies of various gases. A special feature of the apparatus lies in the fact that it dispenses with comparatively difficult measurements of mass and volume of the gas. Only pressure and temperature are needed to be measured, which can be done with relatively high accuracy. The basic design of the apparatus in most of the studies has been similar to that of Silberberg et al. (10). Eubank and Kerns (11) in their recent study have made salient recommendations to avoid adsorption and molecular association in the Burnett apparatus. All of the recommendations have been incorporated into the apparatus used for the present investigation (1, 2).

The apparatus was calibrated with high-purity helium for isotherms at 298.15 K and from 313.15 to 413.15 K at 20 K intervals. The second virial coefficients for helium were de-

termined and were compared with standard literature values (1). The agreement was found to be good. Pressure–volume–temperature relationships of Refrigerant 500 gas were measured with this apparatus (2).

The same apparatus as described above has been used for the compressibility study of R-12 gas at low pressures.

Results

Compression factors of R-12 gas were measured at 298.15 K and from 313.15 to 373.15 K at 20 K intervals for pressures from 0.3 to over 5 bar. Three runs were made at each isotherm to reduce the pressure gap between data points. The data reduction procedure described in ref 2 was used to obtain compression factors. These are reported in Table I. The uncertainties in the measurements were estimated to be ± 0.01 K, $\pm 10^{-4}$ bar, and $\pm 0.1\%$ for temperature, pressure, and compression factor, respectively.

The Berlin expansion of the virial equation of state was used to determine the second virial coefficient at each isotherm. This equation can be expressed as

$$(Z - 1)/P = B_p + C_p P + D_p P^2 + \ldots \qquad (1)$$

where Z is the compression factor, P is the pressure, and B_p, C_p, D_p, etc., are second, third, fourth, and so on, virial coefficients, respectively, and are functions of temperature alone.

From eq 1

$$\lim_{P \to 0} (Z - 1)/P = B_p \qquad (2)$$

The second virial coefficient, B_p, was determined graphically by extrapolating a large-scale, straight-line plot of $(Z - 1)/P$ vs. P to zero pressure at each temperature. Spurious points, if any, were ignored. Values of B_p are reported in Table II and are plotted in Figure 1 along with the results from Kunz and Kapner (8). The agreement between the two results is found to be good. The second virial coefficients computed in the present work are estimated to be accurate within $\pm 2\%$.

Conclusion

Low-pressure compression factors of R-12 gas have been measured at moderate temperatures by using an improved Burnett apparatus to extend equation-of-state data to the low-pressure region. Second virial coefficients determined from these data compare well with the published literature values.

[†] Present address: Heat Transfer Section, Central Mechanical Engineering Research Institute, Durgapur 713209, India.