critical solution temperatures are determined visually from the drawn solubility curves. They range from −36.8° C for 1,4-diethylbenzene to −50.2° C for 1-methyl-4-ethylbenzene. The standard deviation of these temperatures is probably equivalent to the standard deviation of the observed data points—i.e., 0.13° C (*2*).

The transition from a clear solution to two immiscible liquids can be observed very clearly if the temperature of the bath is slowly decreased. At this transition point, the well-stirred mixture is no longer optically uniform; and because of the amount of light scattered, the result is a clearly observable opalescence (*1, 4*).

If the temperature is maintained just below the transition point, the mixture will separate into two phases in a few minutes after stirring is discontinued. The lower CO_2-rich phase is usually clear, but the lighter hydrocarbon-rich phase is often opaque. For practical reasons, temperature and volume observations are taken with rise in temperatures just before the point where the cloudy emulsion changes into a clear solution. The rate of change of the temperature is maintained at 0.5° C a minute or less during these transitions. Further cooling of the mixture will result in an intersection with the solidus line. At this point the solids formed can usually be observed in the form of platelets. In many cases there are only a few degrees difference between these two transitions. Solidus lines are not reported in this communication. The accurate determination of these curves by the present method is not feasible, because the liquid-solid transition is masked by the opalescence of the two immiscible liquid phases.

The region where the hydrocarbon solidifies in equilibrium with liquid CO_2 without going through a liquid-liquid region is very small in some and virtually nonexistent in the majority of the systems studied. The crystal forms of the hydrocarbons are markedly different from that of CO_2. The solid-liquid equilibrium lines are shown dashed in Figures 1 and 2. In the region of high hydrocarbon concentration, the solid which crystallizes out should contain considerable amounts of the hydrocarbon (as in 1-methyl-3-ethyl- and in 1-methyl-4-ethylbenzene). In the region of low hydrocarbon concentration, where the solid-liquid phase equilibrium lines originate at −56.6°C, the melting point of pure CO_2, the crystalline phase consists mainly of CO_2.

The only hydrocarbon which could be observed to crystallize at low concentrations without being obscured by the region of two immiscible liquid phases is 1,2,3-trimethylbenzene. This solid-liquid curve is shown dashed in the region of −49° to −57° C and 0.05 to 0.2 gram per ml of solution. From the slope of the curve and the crystal form, which was markedly different from that of CO_2, it appears that the solid which crystallizes in this region should contain appreciable amounts of 1,2,3-trimethylbenzene. At still lower hydrocarbon concentrations, below the eutectic, the crystallizing solid is, of course, predominantly CO_2.

Table I lists the results of these measurements. The melting points given in the second column are those reported in the literature, included to indicate the relative position of the equilibrium lines in respect to the melting point of the constituents of the mixtures.

LITERATURE CITED

(1) Einstein, A., *Ann. Physik.* **33**, 1275 (1910).
(2) Gouw, T.H., J. CHEM. ENG. DATA **14**, 473 (1969).
(3) "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44, April 30, 1965.
(4) Zimm, Bruno H., *J. Phys. Colloid Chem.* **54**, 1306 (1950).

RECEIVED for review September 25, 1969. Accepted February 6, 1970.

Vapor Pressures of Liquid Alkaline Earth Bromides and Iodides

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The vapor pressures of the bromides and iodides of calcium, strontium, and barium in the liquid range were measured by a Knudsen effusion method. Equations for the vapor pressures as a function of temperature were determined and the enthalpies of vaporization at temperature were calculated from these equations.

THE VAPOR PRESSURE and heats of vaporization of the alkaline earth bromides and iodides have been estimated by a number of authors (*2, 3, 4, 7, 8*). However, there have been very few experimental measurements of these vapor pressures on which to base and confirm the estimates. The anhydrous salts were prepared by direct union of the elements and purified by vacuum sublimation. The vapor pressures were measured by observing the rate of weight loss from a Knudsen diffusion cell.

EXPERIMENTAL PROCEDURE

The salts were prepared by direct union because alkaline earth metals of high purity with respect to other metals were available and because the hydrated salts are difficult to dehydrate without hydrolysis. The method was similar to one described in the literature (*1*).

Five to 10 grams of the pure metal crystals were placed in a quartz boat in a quartz reaction tube. An amount of iodine or bromine greater than stoichiometric was placed in a sidearm and cooled to liquid nitrogen temperature. The apparatus was then evacuated and closed off by a vacuum stopcock; the sidearm was allowed to warm to room temperature. The reaction tube was heated slowly to 650° C and held at temperature for 2 to 4 days, at which time the reaction was complete. The heating rate was slower for strontium because its higher vapor pressure allowed rapid and uncontrolled reaction in some cases. The holding temperatures for the strontium salts were below the respective melting points. The tube was cooled, the excess halogen removed by a vacuum pump, and the product removed in an inert atmosphere glove box. The salts were further purified by vacuum sublimation in an Inconel retort onto an air-cooled condenser. X-ray diffraction patterns of the resulting compounds corresponded to the reported structures and showed no metal or oxide lines. All salts were handled in a glove box which was evacuated and filled with argon.

The vapor pressures were measured by observing the time necessary for 1 mg of the metal halide to escape from the effusion cell. Each vapor pressure data point was the mean of at least four measurements at a given temperature. The effusion cell was suspended from an Ainsworth microbalance mounted in the vacuum system. The keyboard weights could be manipulated by a lever through the vacuum wall. The sensitivity of the balance allowed an unbalance of 5 μg to be easily detected and the period was short compared to the elapsed times, so the time of escape could be determined to 0.5 relative %. The effusion cells were 20 mm in outside diameter, 19 mm in inside diameter, and 30 mm long. They were made of 304 stainless steel and showed no evidence of corrosion or attack by the molten halides. The orifices were cylindrical holes from 0.15 to 0.4 mm in diameter and 0.75 to 3 mm in length. The orifice area was determined from optical photomicrographs by a planimeter and was remeasured after use. In no case was a change in area observed. The Clausing factors for the orifices were graphically interpolated from values computed by Demarcus (*5*).

The effusion cell was heated by a furnace with three independently controlled windings that provided a temperature constant to within 2° C in the center 10 cm of the furnace. The temperature of an experiment was measured by a Chromel-Alumel thermocouple outside the vacuum system at a point 5 mm below the bottom of the effusion cell. The temperature difference between the thermocouple and the bottom of the effusion cell was less than 0.5° C. The temperature gradient in the furnace was adjusted so that the top of the effusion cell was 1° to 2° C hotter than the bottom, to avoid condensation of the salt at the top and plugging of the orifice.

The principal vapor species was assumed to be the metal dihalide monomer. A spectroscopic study of BaI_2 vapor by Winchell (*10*) indicated that $BaI_2(g)$ was the primary species in the vapor and study of the vaporization of CaF_2 by Schulz and Searcy (*9*) showed negligible concentrations of polymeric species. Brewer, Brackett, and Somoyajula (*4*) predicted that for the alkaline earth dihalides the dihalide monomer would be the dominant vapor species.

RESULTS AND DISCUSSION

The observed vapor pressures of the liquid halides as a function of temperature are shown in Figures 1 to 6. A two-parameter equation of the type, $\log P_{\mathrm{mm}} = -A/T + B$, for the vapor pressure of each halide was obtained

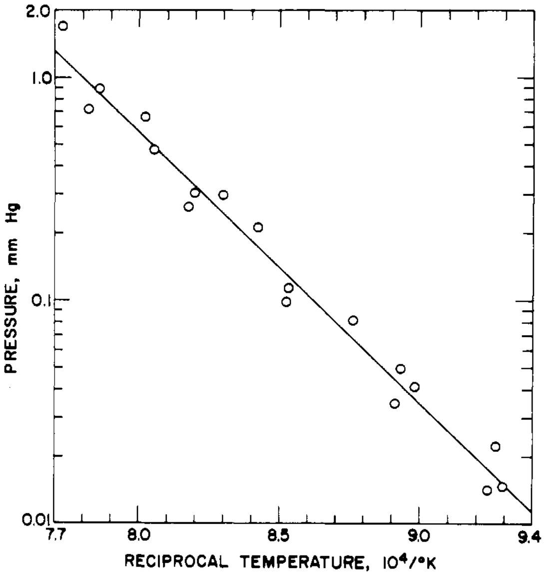

Figure 2. Vapor pressure of calcium iodide

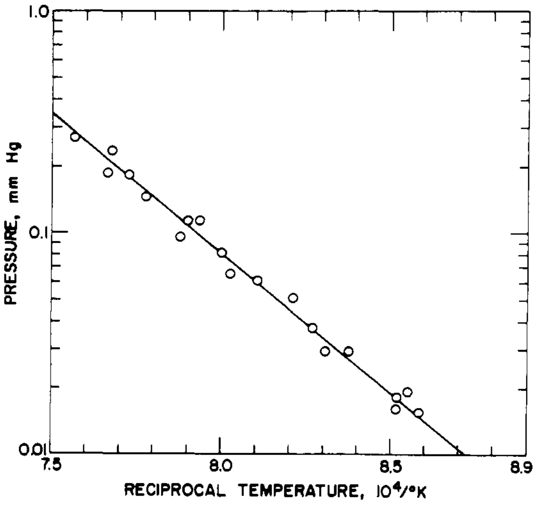

Figure 1. Vapor pressure of calcium bromide

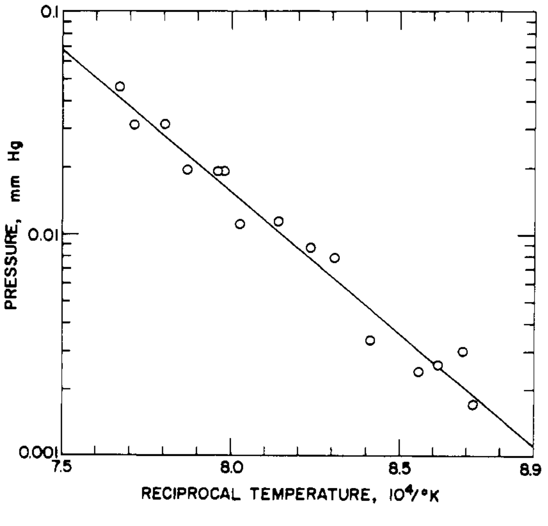

Figure 3. Vapor pressure of strontium bromide

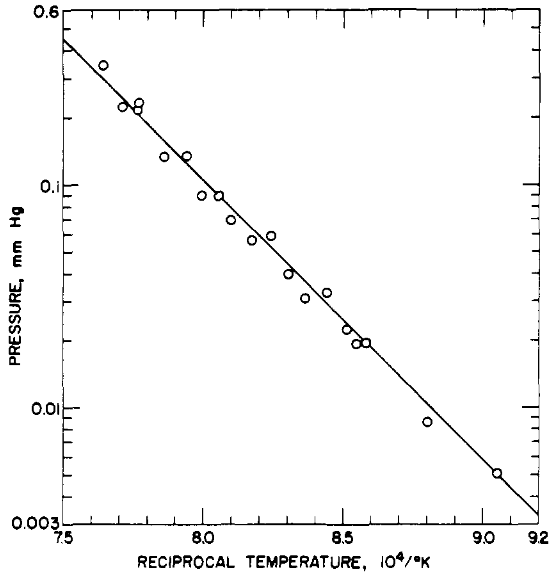

Figure 4. Vapor pressure of strontium iodide

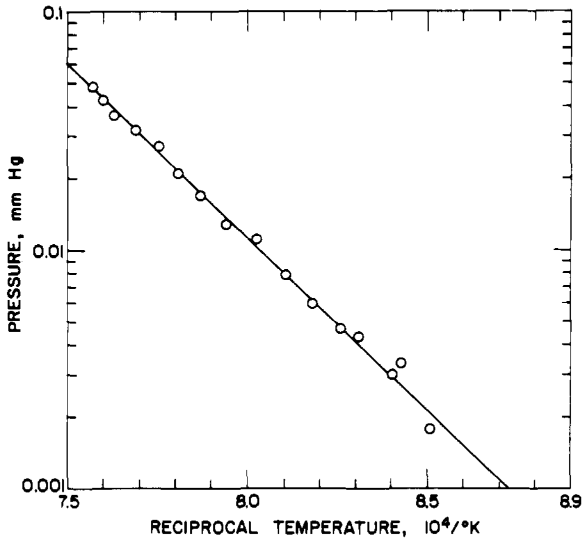

Figure 5. Vapor pressure of barium bromide

from the observed data by a least-squares treatment of all the measurements for each compound. The appropriate constants for each metal dihalide are given in Table I, along with the calculated boiling points and entropies of vaporization at the mean temperature of measurement. The uncertainties given in Table I represent the standard deviations of the calculated constants as given by the least-squares treatment. The largest source of error in the measurement of the vapor pressure is believed to be the error in measuring the orifice area. This includes deviations of the orifice from the assumed cylindrical shape, such as noncircular cross section and variation in diametric area along the axis, particularly at the ends. The error in effective orifice area is constant for a given orifice and it was observed that sets of data from a given cell usually fell close to a straight line on the plot of log P against reciprocal temperature but were uniformly displaced from the data from other orifices. Each run with a given orifice usually covered nearly the entire temperature range, so any errors in measuring the orifice area should not introduce a systematic error in the determination of the slope and intercept of the vapor pressure relationship. The results of this investigation agree closely with the estimated values for the enthalpies of vaporization at 298° K of Brewer *et al.* (*4*), if a constant value of 10 cal per mole for ΔC_p is assumed. For calcium bromide, Kubaschewski, Evans, and Alcock (*8*) report a boiling point 2073° K, which is in good agreement with the value of 2088° K calculated from the results of this investigation. Winchell (*10*) measured the temperature dependence of the vapor pressure of barium iodide and found an enthalphy of vaporization of 54 ± 4 kcal per mole, which agrees very well with the value of 53.6 kcal per mole found in this investigation.

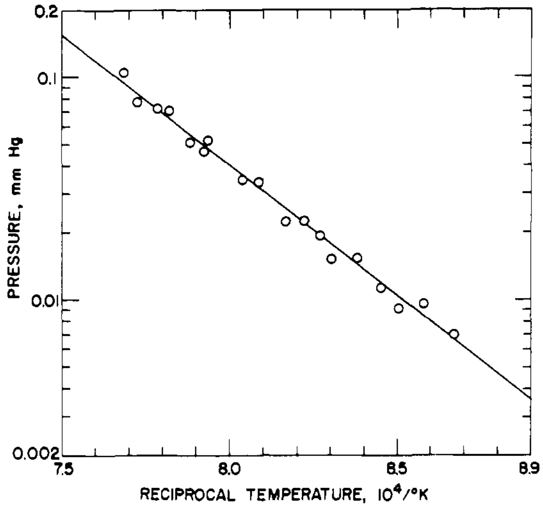

Figure 6. Vapor pressure of barium iodide

Table I. Vapor Pressure Equation Constants, Boiling Points, and Heats of Vaporization

Halides	A	B	Boiling Point	ΔH_{vap}
$CaBr_2$	12,380 ± 190	8.804 ± 0.159	2088	56.5 ± 0.9
CaI_2	12,220 ± 180	9.583 ± 0.157	1831	56.1 ± 0.8
$SrBr_2$	12,710 ± 330	8.362 ± 0.247	2318	58.2 ± 1.5
SrI_2	12,410 ± 150	8.947 ± 0.130	2046	56.8 ± 0.7
$BaBr_2$	14,670 ± 350	9.793 ± 0.281	2122	67.1 ± 1.8
BaI_2	11,710 ± 280	7.974 ± 0.225	2300	53.6 ± 1.3

The plots of log P *vs.* $1/T$ do not show the slight curvature which should result from the difference in the heat capacities of the vapor and the liquid. The magnitude of this curvature is small enough to be hidden by the scatter of the data and a sigma plot was not used. Dworkin and Bredig (*6*) have reported the heat capacities of both the solid and liquid halides and heats of fusion and transformation. However, since no experimental data are available for the heat capacities of the gaseous alkaline earth dihalides, only the enthalpy of vaporization at temperature was calculated.

The vaporization behavior of the alkaline earth bromides and iodides shows certain general characteristics. The vapor pressures of the iodides decrease from calcium iodide to strontium iodide to barium iodide. The vapor pressures of the bromides also decrease in the same order and in nearly the same increments. The iodide of each alkaline earth had a higher vapor pressure than the corresponding bromide. The enthalpies of vaporization were all similar, with the exception of barium bromide. There is no obvious reason for the higher enthalpy of vaporization of barium bromide and this compound might well be the subject of further study.

LITERATURE CITED

(1) Bailor, J.C., editor-in-chief, "Inorganic Synthesis," Vol. 4, McGraw-Hill, New York, 1953.
(2) Bichowsky, F., Rossini, F., "Thermochemistry of Chemical Substances," Reinhold, New York, 1936.
(3) Brewer, L., "Fusion and Vaporization Data of the Halides," in "Chemistry and Metallurgy of Miscellaneous Materials," L. Quill, Ed., pp. 193-275, McGraw-Hill, New York, 1950.
(4) Brewer, L., Brackett, E., Somoyajula, G.R., *Chem. Rev.* **63**, 111 (1963).
(5) Demarcus, W., Oak Ridge Gaseous Diffusion Plant, Tenn. U.S. Atomic Energy Commission Rept. **K-1302** Part 3 (1956).
(6) Dworkin, A.S., Bredig, M.A., *J. Phys. Chem.* **67**, 697 (1963).
(7) Kelley, K.K., U.S. Bur. Mines Bull. **584**, 1 (1960).
(8) Kubaschewski, O., Evans, E.L.L., Alcock, C.B., "Metallurgical Thermochemistry," Pergamon Press, London, 1967.
(9) Schulz, D.A., Searcy, A.N., *J. Phys. Chem.* **67**, 106 (1963).
(10) Winchell, P., *Nature* **206**, 1252 (1965).

RECEIVED for review September 26, 1969. Accepted February 9, 1970. Work performed in the Ames Laboratory, U.S. Atomic Energy Commission. Contribution 2620. Based on M.S. thesis of J.F. Hutchison, Iowa State University, November 1965. For supplementary material, order NAPS Document 00840 from ASIS National Auxiliary Publications Service, ℅ CCM Information Sciences, Inc., 22 West 34th St., New York, N.Y., 10001, remitting $1.00 for microfiche or $3.00 for photocopies.

Excess Enthalpy, Volume, and Gibbs Free Energy of Cyclopentane-Tetrachloroethylene Mixtures at 25° C

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Molar excess enthalpies and volumes of the system cyclopentane-tetrachloroethylene at 25° C were determined by direct calorimetric and dilatometric measurements. Excess Gibbs free energies (also at 25° C) were obtained from a study of the vapor-liquid equilibrium in a circulation still. The values of the excess thermodynamic properties are compared with the results of a previous similar investigation of the system cyclopentane–carbon tetrachloride.

THE RESULTS of an investigation of the interactions of carbon tetrachloride and tetrachloroethylene with the polar material pyridine were published recently by Fried, Franceschetti, and Schneier (*9*), who studied vapor-liquid equilibria in the systems pyridine-carbon tetrachloride and pyridine-tetrachloroethylene. Assuming that the factors affecting the nonideal behavior of these systems are separable into nonspecific and specific (polar-double bond) contributions, it appears that the polar-double bond interaction contributes about 182 J mole^{-1} to the excess Gibbs free energy of an equimolar mixture of pyridine and tetrachloroethylene at 50° C.

In a previous investigation (*3*) we reported values of the excess enthalpy, volume, and Gibbs free energy of the system cyclopentane–carbon tetrachloride at 25° C. The present study was undertaken to provide similar information for the system cyclopentane-tetrachloroethylene and to make possible a comparison of the interaction of the carbon tetrachloride and tetrachloroethylene molecules with the nonpolar (and approximately spherical) cyclopentane molecule. Such a comparison should be helpful in assessing the validity of the assumption that the difference between the excess free energies of the two pyridine systems of Fried *et al.* (*9*) can be attributed to a specific polar–double bond interaction.

EXPERIMENTAL

The methods used in our laboratory for studying the excess thermodynamic properties of binary mixtures have been described (*2, 16, 18*). Reference can be made to these earlier publications for details of the apparatus and techniques. The outlines given below are intended only to indicate the nature of the various measurements and any changes which have been made for the present investigation.

Calorimetric Measurements. The dilution calorimeter described by Murakami and Benson (*16*) was used for determining the molar excess enthalpies. In this calorimeter, successive portions of one component contained over mercury can be added to a weighed amount (about 0.8 mole) of the other component in the absence of any vapor space. In the present application the cooling effect of the mixing process was compensated by Joule heating, and the amount of electrical energy needed to maintain a set value of the temperature (nominally 25.00° ± 0.01° C) in the mixing vessel was determined. During a dilution, temperature variations as large as ±0.003° C sometimes occurred for short periods of time, but usually there was close compensation between positive and negative deviations. In general, the temperature in the vessel was restored after each dilution to within ±0.0003° C of the set value. The errors of the enthalpy values for the present system are estimated to be less than ±1 J mole^{-1}.

Volumetric Measurements. A successive dilution technique (*18*) was also used in measuring the volumes of mixing. At the start of an experiment the mixing chamber of the

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