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Vapor Pressure, Iodine Solubility, and Hydrogen Solubility of Hydrogen Iodide–Iodine Solutions

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Vapor pressure, iodine solubility, and hydrogen solubility data have been obtained for hydrogen iodide–iodine solutions. The vapor pressure and the iodine solubility of such mixtures have been measured over the temperature range 298–363 K and found to display nearly ideal behavior. The iodine solubility data fit the normal eutectic-type phase behavior of a two-component system. The hydrogen solubility in pure liquid hydrogen iodide and iodine was found to obey Henry's law.

Introduction

The data reported in this paper resulted from the need for such data in defining the conditions for a liquid hydrogen iodide decomposition step in a thermochemical water-splitting cycle for hydrogen production (*1*). Through employment of equipment specifically designed to perform proof of concept catalysis studies, it has been possible to obtain useful data for a chemical system for which data appear to be nonexistent under the conditions studied.

Experimental Apparatus

The basic apparatus used for the present studies is sketched in Figure 1. A glass vial serves as a 3.4-MPa (500-psia) rated pressure vessel. It is sealed to the metal parts of the system by a stainless-steel adapter that has an elastomer O-ring seal to the glass. The O-ring is a high-temperature perfluorocarbon "Kalrez" elastomer made by Du Pont. The other metal parts (pipes, valves, etc.) are made of stainless steel. The pressure gauge is a Bourdon type, with all wetted parts of stainless steel. Its range is from 100 kPa (15 psia) to 2.1 MPa (300 psia). The zone above the pressure vessel is heated (as shown in Figure 1) to a temperature above that of the constant-temperature bath. This is done to prevent condensation of HI in the metal parts of the system. The gauge was calibrated at a given temperature (~410 K) and maintained at this temperature for all runs. The gauge calibration held well over the entire measurement range. The gauge was calibrated against a National Bureau of Standards calibrated gauge. The error associated with the pressure measurements is estimated to be about ±1%.

The procedure employed to make up the HI–I_2 solutions for study was as follows: (1) The glass vessel, loaded with a selected amount of I_2, was evacuated to about 1 Pa (0.01 torr). (2) The vessel was cooled to liquid-N_2 temperature. (3) HI was transferred into the vessel. (4) The source of HI was removed when the desired amount of frozen HI was introduced. (5) The system was then pumped down again to about 1 Pa to remove any hydrogen that may have accompanied the HI. (6) The system was allowed to warm up to the temperature desired for performing the experiment. (7) The mixtures were stirred well to assure good mixing of the components. The particular procedures used in obtaining each of the specific measurements reported herein are contained in the individual discussions of the results below.

Results and Discussion

Vapor Pressure of HI–I_2 Solutions. The vapor pressures of different HI–I_2 solutions at different temperatures were measured by employing the apparatus in Figure 1 and the general procedure for making up solutions as indicated above.

Figure 2 illustrates the measured vapor pressure behavior of HI–I_2 mixtures compared to ideality. Following standard procedures, ideal curves (dotted lines in Figure 2) are obtained by superposing the expected ideal behavior of each separate pure component according to its mole fraction. The vapor pressure for I_2 is so much les than for HI at the experimental temperatures ($T \leq 363$ K) that the ideal pure HI component curve nearly passes through (0,0) as shown in Figure 2. Pure HI vapor pressure values were obtained from the literature (*2*). Measurements of pure HI vapor pressures using the present apparatus correlated with the literature values to within ±5%.

The most fruitful determination of HI–I_2 mixture ideality was by measurement of the vapor pressure at saturation levels of I_2. This approach also supplied the information on I_2 solubility in HI discussed later. Figure 2 locates individual points between 297.5 and 363 K. Aside from one point at 342 K, all data are for I_2 saturation and represent end points of the vapor pressure change.

The measurements at 318 K and below produced data which could not be distinguished from ideal behavior. Data taken for 342 and 363 K are somewhat removed from the ideal curves in the positive direction. These deviations would, for regular solutions, indicate endothermic heats of solution of 460 J/mol (110 cal/mol) for 342 K and 268 J/mol (64 cal/mol) for 363 K and would represent, on this basis, only a small deviation from ideality. The heat of solution values have been estimated by assuming ideal entropies of solution.

I_2 Solubility in HI Liquid. As part of the study of vapor pressure behavior discussed above, the I_2 solubility in HI was obtained. These measurements were made by utilizing a magnetically actuated glass dipper as depicted in Figure 1. The procedure was as follows: (1) Good mixing of the I_2 and HI was assured. This was most effectively done by stirring the mixture of I_2 and HI well at a higher-than-run temperature at which there was no iodine saturation. (2) The solution was cooled until I_2 solid was visually evident in the bottom of the vessel. (3) The mixture was allowed to stabilize at temperature. (4) The magnetically actuated glass dipper of known volume (2.55 cm^3) was used to remove a sample of the main pressure vessel mixture. (5) Once a sample was obtained, the HI vapor was removed to a water trap outside the pressure vessel, with the I_2 remaining behind. This operation was done carefully to prevent loss of I_2 from the dipper. (6) Once the HI was removed to atmospheric pressure, the dipper was removed and the I_2 dissolved in KI solution and titrated for I_2 and HI content. In all cases, negligible amounts of HI were present in the I_2 residue. When the I_2 weight was obtained, the initial HI weight present in the dipper was calculated from known (*2*) densities of HI and I_2 and an assumption of molar volume additivity. This assumption expects that the HI–I_2 interaction is not strong (i.e., ΔV of solubility = 0 which is true for ideal solutions).

The results are shown in Figure 3, where I_2 solubility, in terms of the number of grams of I_2 in 100 g of HI–I_2 solution, is plotted vs. temperature. This diagram includes all the points measured in the HI vapor pressure experiments plus the pure molten iodine point, which is based on the literature value. Also shown in Figure 3 is a data point for the lowest I_2 content

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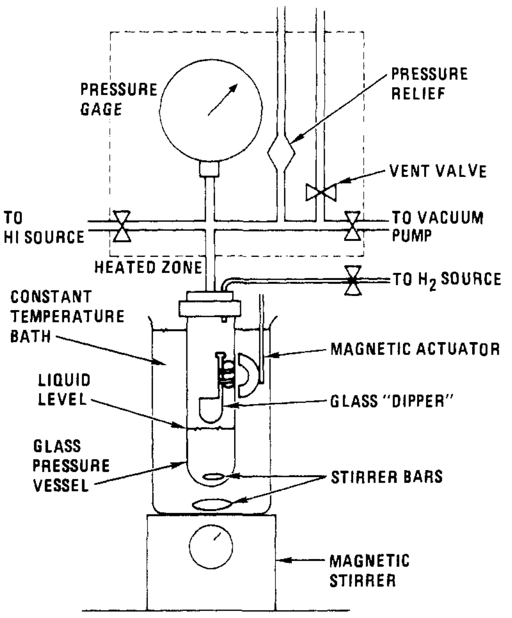

Figure 1. Apparatus used to measure vapor pressure, I_2 solubility, and H_2 solubility of $HI-I_2$ solutions.

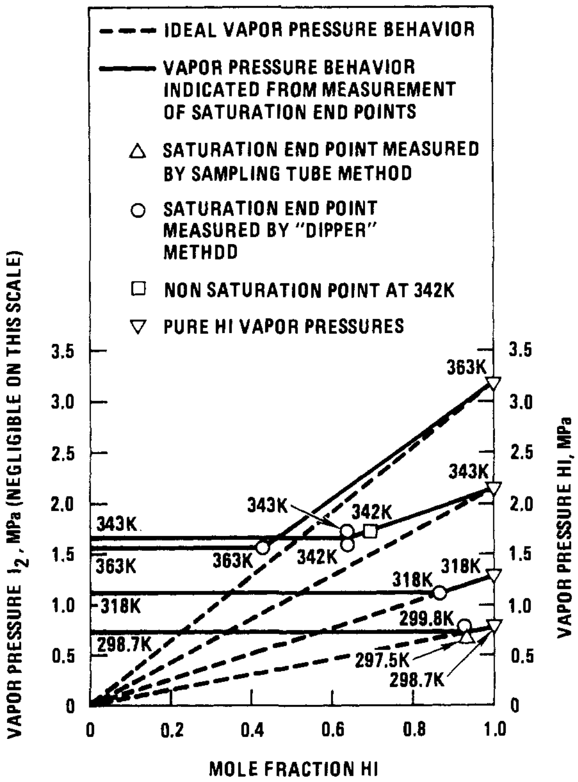

Figure 2. Vapor pressure behavior of HI/I_2 mixtures and comparison with ideality.

mixture using a sampling tube method. This measurement helps to provide credence for the dipper method. The curved line fitted to the points is actually one section of a standard eutectic curve designating the phase behavior of two-component systems. In Figure 3, the curve represents the interface between a liquid-solid region and a single-liquid region for $HI-I_2$ mixtures. Since Figure 3 does not proceed to temperatures lower than 298 K, the eutectic point is not yet reached. This point would be below the melting point of HI (~222 K).

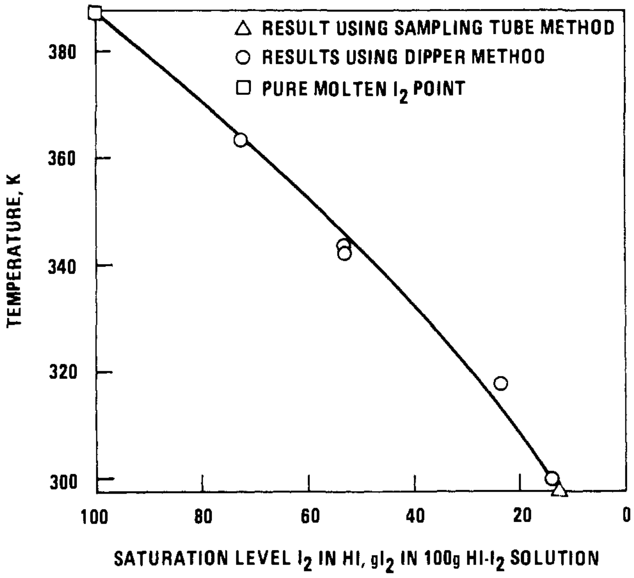

Figure 3. Solubility of I_2 in HI.

H_2 Gas Solubility in HI and I_2 Liquids. The apparatus employed in studying the H_2-gas solubility in various process mixtures was also that shown in Figure 1. A side tube was simply used to admit the H_2 gas. The method which was employed (1) supplied the system with regulated H_2 gas, (2) maintained a constant partial pressure of H_2 and HI at constant temperature until equilibrium was achieved, and (3) measured the amount of H_2 dissolved in HI in the fashion outlined below. The run duration chosen was conveniently the time elapsed overnight (typically 15–17 h). The shortest time required to achieve equilibrium was found to be ~2 h by observing the kinetic effects of stirring.

Assuming a gas pressure vessel in which there are η regions of different volumes V_i, at different temperatures T_i but with the same pressure P, for an ideal gas

$$\frac{R\sum_{i=1}^{\eta}\eta_i}{P} = \sum_{i=1}^{\eta}\left(\frac{V_i}{T_i}\right) = C \qquad (1)$$

where R = the gas constant in appropriate units, and η_i = the number of moles of gas (H_2 in this case) in region i. The assumption of a constant pressure P between regions is made because negligible thermal transpiration effects result for the high pressures and, consequently, for small mean free paths used in these studies.

The parameter V_i/T_i is without direct physical meaning, but it tags the different regions involved. In reality, C is a constant if the temperatures in the different regions are kept constant.

Equation 1 an be rewritten as

$$\frac{R\sum_{i=2}^{\eta}\eta_i}{P} = C - \left(\frac{V_1}{T_1}\right) \qquad (2)$$

where the factor V_1/T_1 is subtracted from both sides of eq 1. Note that the summation for η_i now proceeds from $i = 2$ only.

The quantity C was measured in a side experiment in which the volume of gas at ambient conditions was obtained for various pressures at system temperature (T_1, T_2, ..., T_i, ..., T_η). This value was then transformed to represent the number of moles of gas. The average value of C was found to be 0.3402 cm^3/K for a 303 K bath temperature. This quantity was measured without any liquid in the system.

Using eq 2

$$\sum_{i=2}^{\eta}\eta_i = (P/R)[0.3402 - (V_L/T_L)] \qquad (3)$$

where V_L and T_L equal the equivalent volume and the tem-

Table I. H_2/HI(l) Solubility Data for 303 K

run no.	temp, K	H_2 press., MPa	Henry's constant,[a] MPa	solubility[b]
1	303.0	0.734 ± 0.007	275^{+17}_{-15}	17.9 ± 1.0
2	302.2	1.145 ± 0.011	368^{+16}_{-14}	18.3 ± 1.0
3	302.2	0.793 ± 0.008	248^{+13}_{-12}	19.8 ± 1.0
4	303.0	0.496 ± 0.005	254^{+15}_{-13}	19.3 ± 1.0
5	303.1	0.261 ± 0.003	227^{+12}_{-10}	21.6 ± 1.0
6	302.8	0.883 ± 0.009	263^{+15}_{-14}	18.7 ± 1.0
7	302.8	0.993 ± 0.010	236^{+12}_{-11}	20.8 ± 1.0

[a] $K = P_{H_2}/X_{H_2}$. [b] (cm^3 of H_2)/(100 cm^3 of HI(l)).

Table II. H_2/HI(l) Solubility Data for 273 K

run no.	temp, K	H_2 press., MPa	Henry's constant,[a] MPa	solubility[b]
1	273	1.620 ± 0.016	294^{+21}_{-19}	16.1 ± 1.0
2	273	1.200 ± 0.012	334^{+25}_{-22}	14.1 ± 1.0
3	273	0.752 ± 0.007	302^{+20}_{-19}	15.6 ± 1.0
4	273	0.393 ± 0.004	296^{+30}_{-8}	15.4 ± 1.0

[a] $K = P_{H_2}/X_{H_2}$. [b] (cm^3 of H_2)/(100 cm^3 of HI(l)).

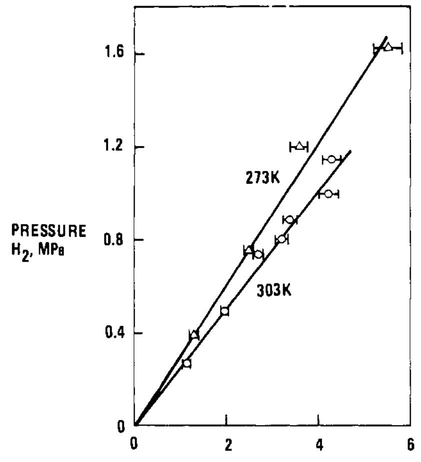

Figure 4. Henry's law for solubility of H_2 in liquid HI.

Table III. H_2/I_2(l) Solubility Data for 394 K

run no.	temp, K	H_2 press., MPa	Henry's constant,[a] MPa	solubility[b]
1	394.5	0.794 ± 0.007	806^{+282}_{-168}	6.4 ± 1.7
2	394.9	1.367 ± 0.012	1579^{+1740}_{-550}	3.3 ± 1.7
3	393.4	1.905 ± 0.018	1091^{+566}_{-282}	4.7 ± 1.7

[a] $K = P_{H_2}/X_{H_2}$. [b] (cm^3 of H_2)/(100 cm^3 of I_2(l)).

perature of the region, respectively, that the liquid occupies.

Equation 3 provides the number of moles that exist in the gas phase above the liquid. The total number of moles (including those in the liquid at equilibrium) is obtained by exhausting all gas (H_2 and HI) to atmosphere and measuring the resulting volume of H_2. The number of moles of H_2 in the liquid at equilibrium is the difference between the total moles of H_2 and the moles of H_2 in the gas phase. This quantity (moles in liquid HI) is put into a form which is directly comparable with literature values. In this case, a modified Ostwald absorption coefficient, which states the cm^3 of gas dissolved per 100 cm^3 of liquid, was chosen. For noninteractive mixtures, this coefficient is independent of the pressure.

The most sensitive of the measured quantities leading to error in the determination of H_2 solubility appears to be pressure. Calibration of the system consists of obtaining the *C* value described above, which in turn consists of relying on an accurate measurement of the change in pressure resulting from the removal of a given volume of gas at various temperatures from the apparatus. The error associated with pressure measurement is believed to be about ±1%. Consequently, the error associated with the measurements of H_2 solubility reflects this magnitude of error in pressure measurement.

The H_2-gas-volume measurements were obtained by water displacement. The H_2 solubility in water at room temperature is, according to the literature (ref *3*), about 1.89 cm^3 of H_2 per 100 cm^3 of H_2O at 303 K. Thus, negligible error is expected from this effect. However, corrections to the volume measurements due to the presence of H_2O vapor in the H_2 gas volume above the displaced water had to be taken into account.

The solubility of H_2 gas in pure liquid HI at about 303 K was measured. The results are recorded in Table I. The solubility value, based on the modified Ostwald definition, is 19.5 ± 1.4 cm^3 of H_2 per 100 cm^3 of HI, and the Henry's law constant ($K = P_{H_2}/X_{H_2}$) is 253 ± 18 MPa. In both cases, the measurement error is quoted in terms of standard deviations. P_{H_2} is the partial pressure of H_2, and X_{H_2} is the mole fraction of H_2 in the liquid. The correlation with Henry's law (column 4 of Table I and Figure 4) indicates that a strong interaction between the H_2 solute molecules does not exist.

The solubility of H_2 in HI measured at 273 K is recorded in Table II and in Figure 4. This solubility value is 15.3 ± 0.8 cm^3 of H_2 per 100 cm^3 of HI and the Henry's law constant is 306 ± 19 MPa. The solubility within the study temperature range is relatively insensitive to temperature. There may be a small increase in solubility with increasing temperature, although the experimental error associated with the measurement method does not allow this conclusion with certainty. Such gas solubility behavior is generally accepted as abnormal, but there are many cases where this effect is reported (ref *4*). Applying the correct thermodynamic arguments leads to a heat of solution for H_2 in liquid HI that is endothermic by about 4.31 ± 1.05 kJ/mol (1.03 ± 0.25 kcal/mol). The total pressure limitations of the present apparatus limit the studies to temperatures less than room temperature.

The HI quantity was measured by titration and from the known volume and the literature value for density. Both determinations correlated well.

The solubility of H_2 in liquid I_2 was measured at 394 K and three different pressures; the results are recorded in Table III and Figure 5. It is immediately obvious that the error associated with this measurement is much higher than that for the case for pure HI. This increased error results from the fact that the solubility of H_2 in liquid I_2 is significantly lower than that for H_2 in HI (about $^1/_4$ that in HI) and approaches the lower level of detectability of the apparatus. In the present apparatus the total gas volume above the liquid is about 40 cm^3, and discerning the disappearance of 5 cm^3 into the liquid requires the detection of a change of about 10% in the total volume of H_2 removed from the system at the end of the experiment. This is at the limit of detection of the present experimental setup. To provide more accurate results for such low solubilities, an apparatus possessing a much larger liquid volume to gas volume ratio is required.

The significant difference in the method of measurement of H_2 solubility in liquid I_2 compared with that of the liquid HI results from the fact that it was not possible to stir the liquid I_2 by using a magnetic stirrer because of the unavailability of a dense enough magnetic stir bar. Instead, the following procedure was followed. The charge of crystalline I_2 placed in the pressure vessel at room temperature was pressurized to the desired

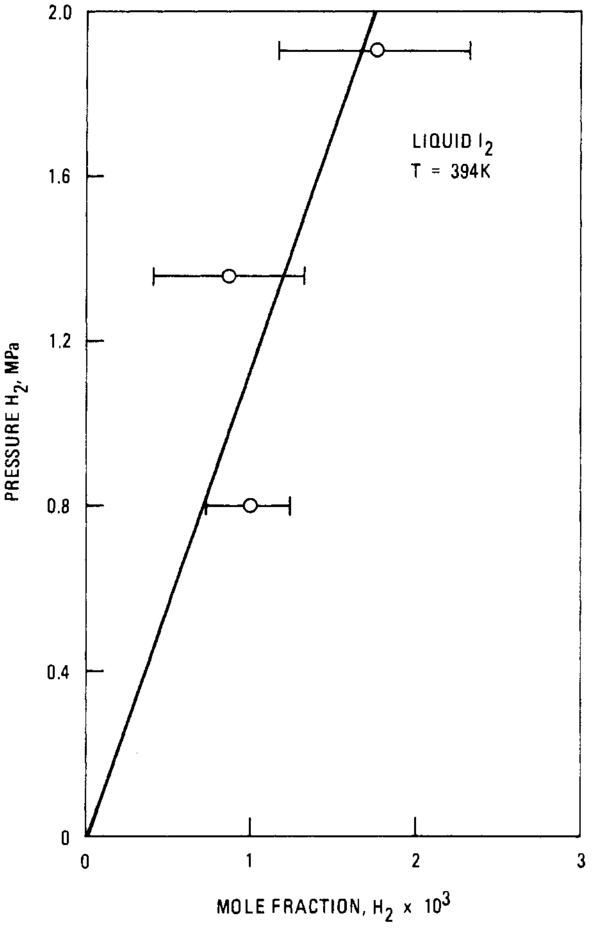

Figure 5. Henry's law for solubility of H_2 in liquid I_2.

pressure before raising the temperature and melting the I_2. This minimized the long-term waiting period of H_2 diffusion into the liquid I_2 and assured the achievement of virtual equilibrium conditions over much shorter times.

Although the amount of data obtained was limited, the $H_2/I_2(l)$ solubility data appear to exhibit Henrian behavior, as do the H_2/HI results. More accurate data obtained by using a better-designed apparatus would be required to verify this fact.

No detectable HI formation from the reaction of H_2 and I_2 at 394 K was observed even though this reaction would seem to be favorable because of the existence of a sink for HI by way of dissolution into the liquid I_2. There was no detectable pressure increase due to the formation of HI, nor was there any experimental evidence of HI gas dissolution in the water collection system for the H_2. This observation is borne out by the experiments performed in decomposing liquid HI (ref *1*). In such a case, a catalyst is found to be required in order to obtain a measurable reaction rate, despite the fact that again the reaction is favored, in this instance, by the dissolution of I_2 into the HI liquid. On the basis of this evidence, not much HI would be expected to be formed during the exposure time of H_2 to $I_2(l)$ in these solubility measurements.

Table IV. H_2/H_2O Solubility Data for 303 K

run no.	temp, K	H_2 press., MPa	Henry's constant,[a] MPa	solubility[b]
1	302.9	1.978 ± 0.018	-1.2×10^5 $+1.0 \times 10^5$ -1.3×10^5	−0.12 ± 1
2	302.3	1.103 ± 0.010	4.3×10^3 $+1.8 \times 10^3$ -1.0×10^3	3.3 ± 1

[a] $K = P_{H_2}/X_{H_2}$. [b] (cm^3 of H_2)/(100 cm^3 of H_2O).

A few attempts were made at measuring the solubility of H_2 in H_2O for the purpose of checking out the behavior of the equipment. Table IV presents the results of these attempts. Again, because of the small value expected according to the literature (ref *3*), i.e., 1.89 cm^3 of H_2 per 100 cm^3 of H_2O at 303 K, and the problems with the apparatus in measuring these small quantitites, there is a large variation between the measurements. Nevertheless, the measurements indicate a low value for H_2/H_2O solubility in the correct range and thus indicate that the higher values obtained for I_2 and HI are valid measurements.

Conclusion

The vapor pressure of HI–I_2 solutions is shown to follow ideal behavior quite closely. This has been established by graphically comparing the experimental data and the theoretically expected behavior for ideal solutions. As well an indication of the endothermic heats of solution for those data showing some deviation are estimated by assuming regular solution behavior. The values of the heats of solution are small.

The solubility of I_2 in HI liquid falls on a curve which is one section of a standard curve designating the phase behavior of two-component eutectic systems.

The hydrogen solubility in liquid HI exhibits Henrian behavior at 273 and 303 K. The solubility within this study temperature range is relatively insensitive to temperature having an estimated heat of solution which is endothermic by about 4.31 ± 0.25 kJ/mol. The solubility of hydrogen in liquid I_2 at 394 K also appears to display Henrian behavior although, in this case, the limitations of the measuring method introduce a great degree of uncertainty in the data.

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