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# Semiempirical equation of state of solid hydrogen iodide

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We derive a semiempirical Birch-Murnaghan equation of state (EOS) for solid hydrogen iodide using those of HCl and HBr and a relation between the Debye temperature $\Theta_D$ and the bulk moduli of the hydrogen halides. This EOS is compared at high pressures with one derived treating HI as iodine hydride.

In another paper[1] we presented measurements of the Raman-active vibrational mode frequencies and the optical band gap of HI as a function of pressure to 25 GPa. To compare these data with models in which the mode frequencies and optical band gap are expressed as a function of the intermolecular distances, the equation of state (EOS) of solid HI, which has not been measured, must be known. Stewart[2] measured the EOS of solid HCl and HBr at 130 and 150 K, respectively, and fitted his data to a Birch-Murnaghan equation.[3] This equation contains two parameters, $B_0$, the bulk modulus at zero pressure and $\xi$, a parameter related to the volume derivative of the bulk modulus, and can be written

$$P=\tfrac{3}{2}B_0(y^7-y^5)[1-\xi(y^2-1)]\ ,$$

where $y^3=V_0/V$ with $V_0$ the volume at zero pressure, and $V$ the molar volume at pressure $P$. For HCl the values for $B_0$ and $\xi$ are 2.78 GPa and $-2.8$; for HBr, 2.74 GPa and $-2.4$.[2] The similarity between the EOS of HCl and HBr is striking; the values of $B_0$ and $\xi$ differ only by a few percent. Because of this and the similarities of the phase diagrams of HCl, HBr, and HI,[1] we expect that the EOS of HI will also be similar. To determine a semiempirical EOS of HI we estimate the value of $B_0$ for HI from those of HCl and HBr by relating them to the Debye temperature $\Theta_D$, which has been measured for all three. Further, we determine $\xi$ from a relation between $\xi$ and the Gruneisen constant $\gamma$.

Different relations have been proposed between $\Theta_D$ and $B$. The two most commonly cited are those of Slater[4] and of Dugdale and MacDonald,[5] who give as the functional relation between $\Theta_D$, $B_0$, and $V_0$, $m\Theta_D^2 \propto V_0^{1/3}B_0$. We use this form with

$$m\Theta_D^2=CV_0^{1/3}B_0\ ,$$

where $C$ is a constant having the same value for all of the hydrogen halides.

Table I gives experimental values for $\Theta_D$, $V_0$, and $B_0$, as well as $m\Theta_D^2/V_0^{1/3}$ normalized to the value for HCl. This table demonstrates that the bulk moduli of HCl and HBr are nearly equal and scale, to within a few percent, as $m\Theta_D^2/V^{1/3}$. We also see that $m\Theta_D/V^{1/3}$ is nearly equal to HCl and HBr, which is reassuring for our intention of determining the EOS of HI by interpolation. For HI we give $B_0$ the value of 2.765 GPa, the average of the bulk moduli derived from scaling to HCl and HBr. This makes the first variable $B_0$ of the Birch-Murnaghan equations equal for all hydrogen halides to within 2%.

We find a value for the second parameter $\xi$ of the Birch-Murnaghan relation for HI from the measured values for HCl and HBr by using a relation between $\xi$ and the Grüneisen constant $\gamma$. For both models the Grüneisen constant $\gamma$ can be expressed as

$$\gamma=a-\frac{V}{2}\frac{\partial^2P}{\partial V^2}\left[\frac{\partial P}{\partial V}\right]^{-1}\ ,$$

where $a$ is $-\frac{2}{3}$ and $-1$ for Slater's and Dugdale's theory, respectively.[5]

Using the Birch-Murnaghan relation, we express $\partial^2P/\partial V^2$ and $\partial P/\partial V$ at $P=0$ in terms of the variables $B_0$ and $\xi$:

$$\frac{\partial P}{\partial V}=-\frac{B_0}{V_0}\ ,$$

$$\frac{\partial^2P}{\partial V^2}=\frac{B_0}{(3V_0^2)(7-4\xi)}\ ,$$

$$\frac{V_0(\partial^2P/\partial V^2)}{(\partial P/\partial V)}=-\tfrac{7}{3}+\tfrac{4}{3}\xi\ ,$$

TABLE I. Some thermodynamic quantities of HCl, HBr, and HI at the indicated temperature.

| | $T$ (K) | $V_0$ (cm$^3$/mol) | $B_0$ (GPa) | $\xi_D$ (K) | $m$ (g/mol) | $m\xi_D^2/V_0^{1/3}$ | Ref. |
|---|---|---|---|---|---|---|---|
| HCl | 130 | 25.3 | 2.78 | 144.2 | 36.5 | 1 | 2,10 |
| HBr | 150 | 31.7 | 2.74 | 101.5 | 80.9 | 1.018 | 2,10 |
| HI | 150 | 37.1 | ? | 82.5 | 127.9 | 1.010 | 10,11 |

TABLE II. Some thermodynamic quantities of HCl, HBr, and HI.

| | $B_0$ (GPa) | $c_v$ (J/mol K) | $\alpha$ ($10^{-4}$ $K^{-1}$) | $\gamma$ | $\xi_{calc}$ | $\xi_{expt}$ | Ref. |
|---|---|---|---|---|---|---|---|
| HCl | 2.78 | 24 | 6.42 | 1.88 | −2.57 | −2.8(2) | 2,7 |
| HBr | 2.74 | 24 | 6.17 | 2.23 | −3.09 | −2.4(2) | 2,7 |
| HI | 2.765 | 24 | 5.0 | 2.13 | −2.96 | ? | 7,8<br>this work |

and thus,

$$-2\gamma = 2 - \tfrac{7}{3} + \tfrac{4}{3}\xi$$

or

$$\xi = -\tfrac{3}{2}\gamma + \tfrac{1}{4} \quad (\text{Slater } \xi = -\tfrac{3}{2}\gamma + \tfrac{3}{4}) .$$

The Grüneisen constant $\gamma$ has not been measured for the hydrogen halides; however, the volume expansion coefficients $\alpha$, the lattice contribution to the heat capacities, and the bulk moduli have been, and from these quantities we can estimate $\gamma$, using[6] $\gamma = B\alpha/c_v$. Table II gives $B_0$, $c_v$, and $\alpha$ at 130, 150, and 150 K for HCl, HBr, and HI, and the calculated $\xi$ as well as the experimental $\xi$. In view of the irregularities in comparing the values of $\xi$ in this table, it may be that the equations only approximately describe the relation between $B$, $\alpha$, and $c_v$.

Given the spread in both the experimental $\xi$ and calculated $\xi$, the estimate of $\xi$ for HI from these values can be expected to have a relatively large error. We expect $\xi$ to be in the interval −2.0 to −3.0. We have chosen a value of −2.4 for solid HI, equal to the value for solid HBr, making the equations of state for the hydrogen halides very similar. Moreover, this value gives good agreement with a model for the EOS of HI when considered as a metal hydride, discussed below. We feel that the possible error in the EOS is acceptable, considering the lack of any high-pressure data for HI. Table III gives some selected values of the EOS at 77 K. The molar volume of HI at this temperature is 36.0 $cm^3$/mol.[8] For this evaluation we used the 150-K values of $B_0$ and $\xi$ which we believe to be justified, given the estimated error in $\xi$.

At high pressure ($P > 20$ GPa), a different approach to derive an EOS for solid HI is possible. At these pressures, HI will at first resemble and eventually become an atomic solid. We then use Bouten and Miedema's model[9] for alloys and more specifically for metal hydrides to approximate the EOS of iodine hydride. The volume of a metal hydride H$X$ at $P = 0$ is[9]

$$V_{HX} = V_H + V_X + \Delta ,$$

where $\Delta$ is the molar volume change due to charge transfer,[9] $V_X$ is the molar volume of the metal, and $V_H$ is the molar volume of hydrogen as a metal. The volume of a metal hydride under pressure is

$$V_{HX}(P) = V_I(P) + V_H(P) + \Delta(P) .$$

The EOS of metallic I has been measured to 30 GPa at room temperature.[10] The volume of H as a metal has not been measured. Bouten and Miedema[9] take the volume to be 1.70 $cm^3$/mol at $P = 0$, which gives the best results for most metal hydrides. The volume at the metallization pressure (approximately 300 GPa) is estimated to be 1.06 $cm^3$/mol. We have taken $V_H = 1.7$ $cm^3$/mol for all pressures which most likely gives a small over-estimate at high pressures. The volume of metallic I is 14 $cm^3$/mol at 20 GPa, and 12.2 $cm^3$/mol at 50 GPa, the last value being an extrapolation.[10] These

TABLE III. Molar volume vs pressure of HI at 77 K, $B_0 = 2.765$, $\xi = -2.4$.

| $V$ ($cm^3$/mol) | $P$ (GPa) |
|---|---|
| 36.0 | 0 |
| 34.2 | 0.171 |
| 32.4 | 0.424 |
| 30.6 | 0.795 |
| 28.8 | 1.34 |
| 27.0 | 2.14 |
| 25.2 | 3.33 |
| 23.4 | 5.10 |
| 21.6 | 7.80 |
| 19.8 | 11.99 |
| 18.0 | 18.68 |
| 16.2 | 29.71 |
| 14.4 | 48.70 |
| 12.6 | 83.17 |

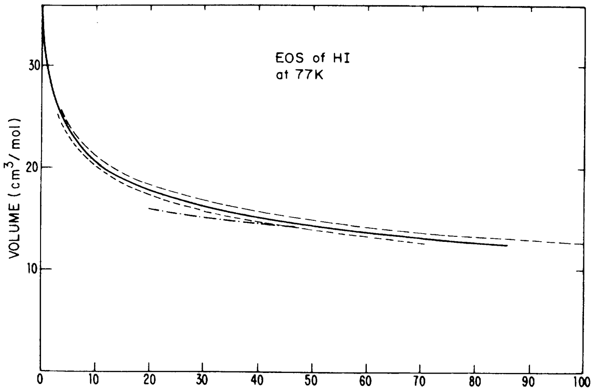

FIG. 1. Solid line: equation of state of HI. Dashed lines are estimated upper and lower bounds. The dash-dotted line is the EOS calculated using the hydride model.

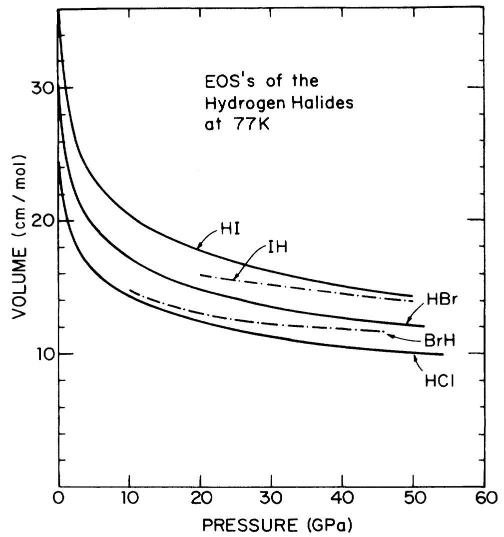

FIG. 2. Equations of state of HCl, HBr, and HI.

volumes give molar volumes for HI of 15.7 and 13.9 $cm^3/mol$ at 20 and 50 GPa, respectively; including small corrections[9] for charge transfer ($\Delta$), these volumes become 15.91 and 14.09 $cm^3/mol$.

Figure 1 shows the EOS of HI for $B_0=2.765$ and $\xi=-2.4$ (solid line) at 77 K as well as lower and upper limits (dashed lines), corresponding to $B_0=2.72$ and $\xi=-2.4$, and $B_0=2.81$ and $\xi=-3.0$, respectively. We believe the true EOS to lie within these limits. The volume of iodine hydride derived from Bouten and Miedema's model is represented by the dash-dotted line. The two equations give the same volume at approximately 50 GPa, in rough agreement with the metallization pressure of HI.[11] Figure 2 compares the EOS's of HI, HBr, and HCl at 77 K. We have also drawn the EOS's for iodine hydride and of bromine hydride, which was calculated using the EOS of solid molecular $Br_2$.[12] Since $Br_2$ is not a metal at these pressures, this latter EOS overestimates the volume of bromine hydride. The two EOS's for HBr seem to reach a common value as they do for HI, albeit at a higher pressure. This can be expected since HBr becomes a metal at a higher pressure than HI.

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