II. (25) **Shifty Reactions.** The shift reaction \( \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \) is important in the commercial production of hydrogen. Use tabulated values of the free energy function given below to calculate \( K^\circ \) for this reaction at 1000 K.

\[
\Delta G^\circ = \Sigma n_i G^\circ_{T,i} = \Sigma n_i H^\circ_{i} - RT \Sigma n_i Z_i
\]

\[
\Delta H^\circ = R T \Sigma Z_i
\]

\[
\Delta H^\circ_0 = 10^3 R K [-47.29 + 0 + 13.69 + 28.736]
\]

\[
= -4.864 \times 10^3 K \text{R}
\]

\[
\Delta G^\circ = \Delta H^\circ - RT \Delta S^\circ
\]

\[
\Delta G^\circ_0 = 10^3 R [-47.29 + 0 + 13.69 + 28.736]
\]

\[
= -4.864 \times 10^3 K \text{R}
\]

\[
\Delta S^\circ = 1.43 \text{ J mol}^{-1} \text{ K}^{-1}
\]

\[
\Delta S^\circ_0 = 1.43 \text{ J mol}^{-1} \text{ K}^{-1}
\]

\[
K^\circ = \exp [-\frac{\Delta G^\circ}{RT}]
\]

\[
= 4.501 - 4.864 = 0.363
\]

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\]
III. (35) Upping the Pressure (vapor, that is). Consider the process, Br$_2$(l) \rightleftharpoons Br$_2$(g).
A. Use thermodynamic data tabulated below to calculate $\Delta H_{298}$, $\Delta S_{298}$, and $\Delta G_{298}$ for this process.
B. Specify precisely what states of reactants and products are implied for these calculated quantities. Then construct a $4$-step, constant-$T$ path that accomplishes the conversion from reactant to product and includes the equilibrium conversion of liquid to gas at the vapor pressure $P$ of Br$_2$(g) at 25.0°C.
C. Use your results from A (and B) to calculate $\Delta H_{vap}$ and the approximate vapor pressure of Br$_2$(g) at 25°C.
D. $V_m$ of Br$_2$(g) is 51.2 cm$^3$/mol. Calculate the activity of Br$_2$(g) under Ar gas at $P_{Ar} = 777$ atm.
E. Hence, what is the approximate vapor pressure of Br$_2$(g) at $P_{Ar} = 777$ atm? (Neglect the effect of the Ar on the fugacity of Br$_2$(g).)
F. In discussing the vapor/condensed-phase equilibrium processes of Br$_2$ in class, we illustrated with a figure showing two intersecting straight lines. What was plotted on the two axes, and why were there two lines?

**STANDARD-STATE THERMODYNAMIC PROPERTIES AT 25°C AND 1 BAR**

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_{298}^{\circ}$</th>
<th>$\Delta G_{298}^{\circ}$</th>
<th>$S_m^{\circ}$</th>
<th>$C_{P,m}^{\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$_2$(g)</td>
<td>111.884</td>
<td>82.396</td>
<td>175.022</td>
<td>20.786</td>
</tr>
<tr>
<td>Br$_2$(aq)</td>
<td>-121.55</td>
<td>-103.97</td>
<td>82.4</td>
<td>-141.8</td>
</tr>
<tr>
<td>Br$_2$(l)</td>
<td>0</td>
<td>0</td>
<td>152.231</td>
<td>75.689</td>
</tr>
<tr>
<td>Br$_2$(g)</td>
<td>30.907</td>
<td>3.110</td>
<td>245.463</td>
<td>36.02</td>
</tr>
</tbody>
</table>

A. $\Delta H_{298}^{\circ} = 30.907$ kJ/mol; $\Delta G_{298}^{\circ} = 3.110$ kJ/mol

$$\Delta S_{298}^{\circ} = \sum v_i S_{m,i}^{\circ} = 93.232 \text{ J/mol K}$$

B. $(l, g, \text{aq}, 25^\circ C, p^0)$ \rightleftharpoons $(\text{id} \text{al \ gas, 25}^\circ \text{C, } p^0)$

$(l, g, \text{aq}, 25^\circ C, p^0)$ \rightleftharpoons $(\text{gaseous, 25}^\circ \text{C, } p^0)$ \rightleftharpoons $(\text{gaseous, 25}^\circ \text{C, } p)$

C. $\Delta H_i = 0$; $\Delta H_1 \rightleftharpoons \Delta H_2 \rightleftharpoons 0 \Rightarrow \Delta H_{vap} = \Delta H^0_{vap} = 30.907$ kJ/mol

$$K_p = \exp \left[ \frac{\Delta H^0_{vap}}{RT} \right] = \frac{f_{B_r(g)}}{f_{B_r(l)}} \cdot \left( \frac{P}{P^0} \right)^{\alpha_{B_r(l)}} \approx \frac{P}{P^0}$$

$$K_p = e^{-1.255} = 0.2852 \Rightarrow P = 0.2852P^0 \approx 214 \text{ Torr}$$

D. $\ln a = \frac{\int_{p^0}^P V_m \, dp}{RT} = \frac{V_m \left( \rho - P^0 \right)}{RT} \approx \frac{51.2 \text{ cm}^3 \times 776 \text{ atm}}{RT}$

$$= 1.624 \Rightarrow a = 5.07$$

E. $K_p \approx \frac{p^0}{a_e} \Rightarrow P = P^0K_p \approx 1.447 P^0$

F. $\ln P \propto \frac{1}{T(K)}$. The steeper line represents the solid-vapor equilibrium, while the other is for liquid-vapor. The two intersect at the triple point.

IV. (45) Short Shots. Do JUST 3 of the following.
A. Consider the ideal gas dissociation equilibrium, $A(g) \rightleftharpoons B(g) + 2C(g)$.

1. Give the equilibrium expression for $K_p$ in terms of the partial pressures of reactants and products.
2. Obtain an equation which could be solved to yield the degree of dissociation $\alpha$ in terms of $K_p$ and the total pressure $P$. [Hint: Start with $n_0$ mol of $A$ and no $B$ or $C$.]

$$1. \quad K_p = \frac{(P_B/P^0)(P_C/P^0)^2}{(P_A/P^0)^3}$$

2. $A \rightleftharpoons B + 2C$

$n_0$ mol

$n_0(1-\alpha) = n_0 = 2\alpha n_0 \rightarrow \text{total} = n_0(1+2\alpha)$

$$X_i = \frac{1-\alpha}{1+2\alpha} \quad \frac{\alpha}{1+2\alpha} \quad \frac{3\alpha}{1+2\alpha}$$

$$P_i = \frac{P}{P^0} \quad \frac{4\alpha^3}{(1-\alpha)(1+2\alpha)^2}$$

Prob I

II

III

IV
B. Consider the virial 2 equation (i.e., the version that is a power series in P).
1. Give this equation through the term that includes the third virial coefficient.
2. Define the compressibility factor $Z$ for a gas that obeys this equation.
3. Obtain expressions for the fugacity coefficient $\phi$ and the fugacity $f$ for such a gas.

1. $PV_m = RT \left[ 1 + V'_1 \frac{P}{RT} + \frac{C'_1}{2} \frac{P^2}{RT^2} + \ldots \right]$

2. $Z \equiv \frac{PV_m}{RT} = \left[ 1 + V'_1 \frac{P}{RT} + \frac{C'_1}{2} \frac{P^2}{RT^2} + \ldots \right]$

3. $\ln \phi = \int_0^P \left[ \frac{V}{RT} - \frac{1}{P} \right] dP' = \int_0^P \left[ \frac{1}{P} - \frac{B}{P'} + C \frac{P^2}{2} \right] dP' = \int_0^P \left[ \frac{1}{P} \frac{B}{P'} + C \frac{P^2}{2} \right] dP'$

$\phi = e^{\int_0^P \left[ \frac{B}{P} \frac{1}{P'} + C \frac{P^2}{2} \right] dP'}$

$\phi = P_e^{B/P + C/P^2}$

C. Long ago we determined that the Joule-Thomson coefficient $\mu_{JT}$ is related to $C_p$ and $\frac{\partial^2 H}{\partial P^2}$ by $\mu_{JT} = -\frac{C_p}{(\partial^2 H/\partial P^2)}$. Use this result to evaluate $\Delta H$ for the isothermal $(T = 300 K)$ compression of 1.00 mol of CO$_2$ from 1.00 atm to 50.00 atm, given the following expressions for $C_p(T)$ and $\mu_{JT}(P)$:

$C_{p,m} = 26.00 + 0.0435 \times 10^{-5} \times T^2$ (units J mol$^{-1}$ K$^{-1}$; $T$ in K)

$\mu_{JT} = 1.107 - 0.0023 \times P$ (units K atm$^{-1}$; $P$ in atm, $T = 300$ K)

Compare your result with that which would be obtained for an ideal gas.

$\frac{\partial^2 H}{\partial P^2} = -C_p \mu_{JT} \Rightarrow \Delta H_T = -C_p \mu_{JT} dP_T$

$\Delta H = -C_p \int \mu_{JT} dP = -C_p \int [a - b P] dP'$

$\Delta H = -C_p \left[ \frac{49a}{2} - \frac{b}{2} (50^2 - 1) \right]$

$C_p \Delta H = 300 \times 1.00 \times 37.715 \times \frac{J}{K}$

$\Delta H_{\text{ideal gas}} = 0.$

D. Consider the reaction, (1) $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$. At 300°C this reaction has an equilibrium constant $K_1 = 2.73$.

1. Give the conditions for chemical reaction equilibrium in this reaction, in terms of chemical potentials.

2. Calculate $K^*$ (call it $K_2$) for the reaction, $2 \text{NOCl}(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2} \text{Cl}_2(g)$, at 300°C.

3. A reaction vessel is charged initially with 1.00 $P^*$ of NO, 2.00 $P^*$ of Cl$_2$, and 1.50 $P^*$ of NOCl at 300°C. Calculate the reaction quotient $Q$, and predict the direction in which Reaction 1 will proceed.

4. Suppose the volume of the vessel is such that it contains 0.60 mol NO under the conditions stated in 3. Calculate the amounts of the other two components.

5. Starting with the conditions in 4, what are the maximum and minimum possible values of the extent of reaction $\xi$: (i) for Reaction 1; and (ii) for Reaction 2?

1. $\Sigma u_i \mu_i = 0 \Rightarrow 2\mu_{\text{NO}} + \mu_{\text{Cl}_2} = 2\mu_{\text{NOCl}}$

2. $R \times 2 = \frac{1}{2} \times \text{reverse of (i)} \Rightarrow K_2^* = K_1^{* \frac{1}{2}} = 0.605$

3. $K_2^* = \frac{(P_{\text{NOCl}}/P)^2}{(P_{\text{NO}}/P)^2 (P_{\text{Cl}_2}/P)} \Rightarrow Q_1 = \frac{(1.50)^2}{100^2 \times 2.00} = 1.125$

$Q_1 < K_2^*$, so $R \times$ proceeds toward the right.

4. NO : $P = 1.00 P^*$; $n = 0.60$ mol

Cl$_2$ : $P = 2.00 P^*$; $n = 1.20$ mol

NOCl : $P = 1.50 P^*$; $n = 0.90$ mol

5. (1) $2 \text{NO} + \frac{1}{2} \text{Cl}_2 \rightleftharpoons 2 \text{NOCl}$

$\eta = \frac{n_{\text{NO}} + n_{\text{Cl}_2}}{2}$

$\eta = \min = 0.30$ mol

$\eta = \max = 0.45$ mol

(2) $\text{NOCl} \rightleftharpoons \text{NO} + \frac{1}{2} \text{Cl}_2$

$\eta = \frac{n_{\text{NO}} + \frac{1}{2} n_{\text{Cl}_2}}{2}$

$\eta = \max = 0.90$ mol

$\eta = \min = -0.60$ mol