*Honor Code Pledge and Signature:*

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**Fundamental Constants:**    $R = 8.31451$ J mol$^{-1}$ K$^{-1}$ = 0.0820578 L atm mol$^{-1}$ K$^{-1}$ = 1.9872 cal mol$^{-1}$ K$^{-1}$

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I.  (35)  **The Third Degree.**  The molar heat capacity of a solid substance at $P = P°$ can be represented over a certain range of temperatures as a polynomial in $T$, $C°_{P,\mathrm{m}} = a + bT + cT^2$.

A.  Obtain expressions for $\Delta H_\mathrm{m}°$ and $\Delta S_\mathrm{m}°$ for heating this substance from $T_1$ to $T_2$.

B.  For $CS_2(s)$ in the range 15 K – 60 K, $a = -11.53$ J mol$^{-1}$ K$^{-1}$, $b = 1.365$ J mol$^{-1}$ K$^{-2}$, and $c = -0.0095$ J mol$^{-1}$ K$^{-3}$.  Calculate $\Delta H_\mathrm{m}°$ and $\Delta S_\mathrm{m}°$ for heating $CS_2(s)$ from 15.0 K to 60.0 K.

C.  Use the Debye theory for the heat capacity at low temperatures to estimate $S_\mathrm{m}°$ for $CS_2(s)$ at 15.0 K; then calculate $S_\mathrm{m}°$ at 60.0 K.

D.  Can this information be used to evaluate $\Delta G_\mathrm{m}°$ for the heating of $CS_2(s)$ from 15.0 K to 60.0 K?  Explain very briefly.

II. (25) **Shifty Reactions.** The <u>shift reaction</u> — $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ — 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.

**Gaseous elements and compounds with values referenced to $H_0^\bullet$**

|  | $-(G_T - H_0^\bullet)/RT$ | | | | | $(H^\bullet_{298} - H_0^\bullet)/R$ | $H^\bullet_{f,0}/R$ |
|---|---|---|---|---|---|---|---|
|  | 298.15 K | 500 K | 1000 K | 1500 K | 2000 K | (K) | $(10^3 K)$ |
| $H_2$ | 12.301 | 14.076 | 16.485 | 17.921 | 18.968 | 1018.5 | – |
| $O_2$ | 21.173 | 22.992 | 25.521 | 27.088 | 28.243 | 1044.0 | – |
| CO | 20.275 | 22.086 | 24.558 | 26.069 | 27.183 | 1042.9 | $-13.69 \pm 0.02$ |
| $CO_2$ | 21.934 | 24.001 | 27.246 | 29.445 | 31.138 | 1126.4 | $-47.29 \pm 0.01$ |
| $H_2O$ | 18.716 | 20.802 | 23.674 | 25.493 | 26.881 | 1191.3 | $-28.736 \pm 0.005$ |
| $CH_4$ | 18.376 | 20.531 | 24.00 | 26.63 | 28.82 | 1204.7 | $-7.999$ |

III. (35) **Upping the Pressure (vapor, that is).** Consider the process, $Br_2(l) \quad Br_2(g)$.

   A. Use thermodynamic data tabulated below to calculate $H°_{298}$, $S°_{298}$, and $G°_{298}$ for this process.

   B. Specify <u>precisely</u> what states of reactants and products are implied for these calculated quantities. Then construct a <u>4-step</u>, 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 $Br_2(l)$ at 25.0°C.

   C. Use your results from A (and B) to calculate $H_{vap}$ and the approximate vapor pressure of $Br_2(l)$ at 25°C.

   D. $V_m$ of $Br_2(l)$ is 51.2 cm$^3$/mol. Calculate the activity of $Br_2(l)$ under Ar gas at $P_{Ar} = 777$ atm.

   E. Hence, what is the approximate vapor pressure of $Br_2(l)$ 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 <u>two</u> lines?

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

| Substance | $H^{\bullet}_{f,298}$ (kJ/mol) | $G^{\bullet}_{f,298}$ (kJ/mol) | $S^{\bullet}_{m,298}$ $\dfrac{J}{mol\ K}$ | $C^{\bullet}_{P,m,298}$ $\dfrac{J}{mol\ K}$ |
|---|---|---|---|---|
| Br(g) | 111.884 | 82.396 | 175.022 | 20.786 |
| Br$^-$(aq) | −121.55 | −103.97 | 82.4 | −141.8 |
| Br$_2$(l) | 0 | 0 | 152.231 | 75.689 |
| Br$_2$(g) | 30.907 | 3.110 | 245.463 | 36.02 |

## IV. (45)  Short Shots.  Do JUST 3 of the following.

A.  Consider the <u>ideal gas</u> dissociation equilibrium,  $A(g) \rightleftharpoons B(g) + 2\,C(g)$.

    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 $\quad$ in terms of $K°_P$ and the total pressure $P$.  [<u>Hint</u>:  Start with $n_0$ mols of A and no B or C.]

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**Prob  I** _____

**II** _____

**III** _____

**IV** _____

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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 <u>third virial coefficient</u>.

    2. Define the <u>compressibility factor</u> $Z$ for a gas that obeys this equation.

    3. Obtain expressions for the <u>fugacity coefficient</u> and the <u>fugacity</u> $f$ for such a gas.

C. Long ago we determined that the Joule-Thomson coefficient $\mu_{JT}$ is related to $C_P$ and $(\partial H/\partial P)_T$ by $(\partial H/\partial P)_T = -C_P \, \mu_{JT}$. 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 $\mu_{JT}(P)$:

$$C_{P,m} = 26.00 + 0.0435\,T - 1.483 \times 10^{-5}\,T^2 \quad \text{(units J mol}^{-1}\,\text{K}^{-1}; T \text{ in K)}$$

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

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

D. Consider the reaction, (1) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$. 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. Be specific.

2. Calculate $K°$ (call it $K_2°$) for the reaction, (2) $NOCl(g) \rightleftharpoons NO(g) + \frac{1}{2}\,Cl_2(g)$, 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 $Q_1$, 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?