CHEM 163B Prelim I, 11:00 – 12:10 AM, January 29, 2016

Name ___________________________ SID ___________________________ Section ___________________________

Constants

\[ R = 8.314 \text{ J/Kmol}; 1 \text{ bar} = 10^5 \text{ Pa}; 1 \text{ atm} = 1.0 \times 10^5 \text{ Pa}; \]

\[ \left( \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right)_y \right)_x = \left( \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)_x \right)_y \]

\[ \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1 \]

\[ \left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_z} \]

1. (20 pts) Please identify which of the following statements is (are) correct:

   - Density is an intensive variable and enthalpy is an extensive variable. (TRUE)(FALSE)
   - If neither heat nor matter can enter or leave a system, then the system must be isolated. (TRUE)(FALSE)
   - Doubling the volume of an ideal gas at fixed temperature and amount of gas will decrease the pressure by half. (TRUE)(FALSE)
   - The first law of thermodynamics is valid only for ideal gases. (TRUE)(FALSE)
   - Because \( H = U + PV \), the enthalpy change of a process at a constant volume is equal to the corresponding internal energy change, i.e., \( \Delta H_v = \Delta U_v \). (TRUE)(FALSE)

2. (20 pts) A 1.00 liter bulb of methane at a pressure of 10.0 kPa is connected to a 3.0 liter bulb of hydrogen at 20.00 kPa. Both bulbs are at the same temperature. (a) After the gases mix, what is the total pressure? (b) What is the molar fraction of each component in the mixture?

\[ n_{\text{total}} = \frac{1}{RT} \left( P_1 V_1 + P_2 V_2 \right) \]

\[ P_{\text{final}} = \frac{nRT}{V_1 + V_2} = \frac{P_1 V_1 + P_2 V_2}{V_1 + V_2} = \frac{1 \times 10 + 3 \times 20}{1 + 3} = 17.5 \text{ kPa} \]

\[ \chi_{\text{CH}_4} = \frac{P_1 V_1}{P_1 V_1 + P_2 V_2} = \frac{1 \times 10}{1 \times 10 + 3 \times 20} = \frac{1}{7} \]

\[ \chi_{\text{H}_2} = \frac{P_2 V_2}{P_1 V_1 + P_2 V_2} = \frac{6}{7} \]
3. (20 pts) Two moles of an ideal gas at 300 K and 10 atm pressure are expanded isothermally against a constant external pressure of 5 atm until the internal pressure reaches a value of 7 atm. At this point, the expansion is halted. Compute $\Delta U$, $\Delta H$, $q$ and $w$ for the process if possible.

\[
\text{Isothermal} \quad \Delta H = 0 = \Delta U
\]

\[
\begin{align*}
P_1 &= 10 \text{ atm} \\
T_1 &= 300 \text{ K} \\
\text{v} &= 2 \text{ mol}
\end{align*}
\]

\[
V_1 = \frac{nRT}{P_1} = \frac{2 \times 8.314 \times 300}{10 \times 1.01 \times 10^5} = 4.93 \times 10^{-3} \text{ m}^3
\]

\[
V_2 = \frac{nRT}{P_2} = \frac{2 \times 8.314 \times 300}{7 \times 1.01 \times 10^5} = 7.05 \times 10^{-3} \text{ m}^3
\]

\[
\Delta V = V_2 - V_1 = (7.05 - 4.93) \times 10^{-3} = 2.12 \times 10^{-3} \text{ m}^3
\]

\[
\Delta U = -P_{\text{ext}} \Delta V = -(5 \times 1.01 \times 10^5)(7.05 - 4.93) \times 10^{-3}
\]

\[
= -10.706 \times 10^2 \text{ J} = -1070.6 \text{ J}
\]

\[
\therefore \Delta U = -\Delta V = 1070.6 \text{ J}
\]

\[
\Delta H = \Delta U = 1070.6 \text{ J}
\]

\[
q = -w = 1070.6 \text{ J}
\]
4. (20 pts) At 298 K and 1 bar, the reaction enthalpy \( \Delta H^\circ_R \) of the following reactions have been determined to be:

\[
\begin{align*}
\text{C(s) + \( \frac{1}{2} \)O}_2(g) & \rightarrow \text{CO(g)} \quad \Delta H^\circ_R = -110.5 \text{ KJ/mol} \\
\text{CO(g) + \( \frac{1}{2} \)O}_2(g) & \rightarrow \text{CO}_2(g) \quad \Delta H^\circ_R = -283.0 \text{ KJ/mol} \\
\text{H}_2(g) + \( \frac{1}{2} \)O}_2(g) & \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ_R = -241.8 \text{ KJ/mol} \\
\text{NO(g) + \( \frac{1}{2} \)O}_2(g) & \rightarrow \text{NO}_2(g) \quad \Delta H^\circ_R = -57.1 \text{ KJ/mol} \\
\frac{1}{2}\text{N}_2(g) + \text{O}_2(g) & \rightarrow \text{NO}_2(g) \quad \Delta H^\circ_R = +33.2 \text{ KJ/mol}
\end{align*}
\]

At standard temp and pressure.

If the reaction enthalpy of aniline oxidation, \( 2\text{C}_6\text{H}_5\text{NH}_2(l) + 16.5\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 7\text{H}_2\text{O}(g) + 2\text{NO}(g) \), is \(-6296.6 \text{ KJ/mol} \), calculate the standard enthalpy of formation \( \Delta H^\circ_f \) of \( \text{C}_6\text{H}_5\text{NH}_2(l) \) at 298 K.

\[\Delta H^\circ_f (\text{CO}) = -110.5 \text{ KJ/mol}\]

\[\Delta H^\circ_f (\text{CO}_2) = -110.5 + (-283.0) = -393.5 \text{ KJ/mol}\]

\[\Delta H^\circ_f (\text{H}_2\text{O},g) = -241.8 \text{ KJ/mol}\]

\[\Delta H^\circ_f (\text{NO}_2, g) = +33.2 \text{ KJ/mol}\]

\[\Delta H^\circ_f (\text{NO}, g) = 33.2 + 57.1 = 90.3 \text{ KJ/mol}\]

For the reaction of aniline oxidation:

\[
\Delta H^\circ_R = 12\Delta H^\circ_f (\text{O}_2) + 7\Delta H^\circ_f (\text{H}_2\text{O}) + 2\Delta H^\circ_f (\text{NO}) - 2\Delta H^\circ_f (\text{aniline})
\]

\[-6296.6 = -12(393.5) - 7(241.8) + 2(90.3) - 2\Delta H^\circ_f (\text{aniline})\]

\[\Delta H^\circ_f (\text{aniline}) = +31.3 \text{ KJ/mol}\]
5. (20 pts) The exact differential of pressure \( P \) is expressed as 
\[
dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV.
\]
Please show that 
\[
dP = (\beta/\kappa) dT - (1/\kappa V) dV,
\]
where 
\[
\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \text{and} \quad \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P.
\]

\[
\frac{\partial P}{\partial T} = \frac{\partial P}{\partial V} \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial P}{\partial V} \right)_T
\]

\[
\kappa = \frac{1}{V} \frac{\partial V}{\partial P} \quad \Rightarrow \quad \left( \frac{\partial V}{\partial P} \right)_T = \frac{-1}{\kappa V} \quad \Rightarrow \quad \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial V}{\partial T} \right)_P = -1
\]

\[
\left( \frac{\partial P}{\partial P} \right)_V = - \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P
\]

\[
= - \frac{\beta V}{\left( \frac{\partial V}{\partial P} \right)_T} = - \frac{\beta V}{-\kappa V} = \frac{\beta}{\kappa}
\]

\[
\therefore dP = \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV
\]