Name: __________________________
Section: __________________________

Chemistry 383
Final Examination
December 14, 1995

This examination consists of 16 questions each worth 10 points. Your total score will be multiplied by 1.25 to obtain your grade on the examination. Tables of data are attached to the equation sheets.

1. Determine the amount of heat given off when 500 mol of H\(_2\) (\(\sim\) 1 kg) is burned in O\(_2\) (g) to produce H\(_2\)O(l) at 25 °C in a constant pressure process.

\[
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{H}_2\text{O}(l)
\]

\[
\Delta H = \Delta H^0_f (\text{H}_2\text{O}(l)) = -28583 \text{ kJ mol}^{-1}
\]

For one mole H\(_2\) burned, 285.83 kJ given off.

For 500 mol H\(_2\), \((500)(285.83) = 142,915 \text{ kJ given off.}\)

2. Determine the amount of heat given off for the same amount of H\(_2\) (g) in the reaction in Problem 1 if it is carried out in a constant volume container at 25 °C.

\[
\Delta U = q_V = \Delta H - \Delta n RT
\]

\[
\Delta n = -1.5 \text{ mol}
\]

\[
\Delta U = -28583 \text{ kJ} - \frac{-(15 \text{ mol})(8315 \text{ J mol}^{-1} \text{ K}^{-1})(29815 \text{ K})}{1000 \text{ J kJ}^{-1}} = -282.11 \text{ kJ}
\]

For 500 mol, \((500)(282.11) = 141,056 \text{ kJ}\).
3. The weight of 0.500 L of a gas measured at 0.400 atm pressure and 300 K is 0.812 g. What is the molecular weight of the gas.

\[ pV = nRT \]

\[ n = \frac{pV}{RT} = \frac{(0.400 \text{ atm})(0.500 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{K}^{-1})(300 \text{ K})} \]

n = 0.00812 mol

mass = 0.812 g

\[ \frac{0.812 \text{ g}}{0.00812 \text{ mol}} = 100 \text{ g mol}^{-1} \]

4. The van der Waals constants \( a \) and \( b \) take into account the two main differences between an ideal gas and a real gas. State the two differences and identify the van der Waals constant that accounts for each of them.

\( a \): Real gas molecules attract one another; ideal gas molecules do not

\( b \): Real gas molecules occupy finite volume; ideal gas molecules are assumed to be mass points
5. The enthalpy change for the reaction

\[ 2 \text{C(g)} + 4 \text{H(g)} = \text{H}_2\text{C=CH}_2(\text{g}) \]

is \(-2253 \text{ kJ}\). If the C–H bond energy is 412 \text{ kJ mol}^{-1}, estimate the C=C bond energy in \text{ kJ mol}^{-1}.

For \( \text{H}_2\text{C=CH}_2(\text{g}) = 2 \text{C(g)} + 4 \text{H}_2(\text{g}) \)

\[ \Delta H = +2253 \text{ kJ} \]

Also, \( \Delta H = 4 \text{B(C-H)} + \text{B(C=C)} \)

\[ \text{B(C=C)} = 2253 - 4 \times 412 = 605 \text{ kJ mol}^{-1} \]

6. One (1.00) mole of solid water (i.e., ice) is heated from \(-10 \, ^\circ\text{C}\) to \(0 \, ^\circ\text{C}\) at 1 atm pressure and then melted. The heat capacity of ice at constant pressure is 36.6 \text{ J K}^{-1} \text{ mol}^{-1} and the enthalpy of fusion of water is 6.01 \text{ kJ mol}^{-1} at \(0 \, ^\circ\text{C}\). Evaluate the entropy change for the process.

For \( \text{H}_2\text{O(s)(-10 \, ^\circ\text{C})} \rightarrow \text{H}_2\text{O(s)(0 \, ^\circ\text{C})} \)

\[ \Delta S_1 = C_p \ln \frac{T_2}{T_1} = (1 \text{ mol})(366 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{273.15}{263.15} \right) = 1365 \text{ J K}^{-1} \]

For \( \text{H}_2\text{O(s)(0 \, ^\circ\text{C})} \rightarrow \text{H}_2\text{O(l)(0 \, ^\circ\text{C})} \)

\[ \Delta S_2 = \frac{\Delta H_{\text{fus}}}{T} = \frac{(1 \text{ mol})(6010 \text{ J mol}^{-1})}{273.15 \text{ K}} = 2200 \text{ J K}^{-1} \]

Total \( \Delta S = \Delta S_1 + \Delta S_2 = 1365 + 22.00 = 23.37 \text{ J K}^{-1} \)
7. The equilibrium constant for the reaction

\[ \text{Br}_2(\text{g}) \leftrightarrow 2 \text{Br}(\text{g}) \]

is \( 3.35 \times 10^{-5} \) at 1000 K. The enthalpy change at this temperature is 196.2 kJ. What is the pressure of Br(\text{g}) in equilibrium with Br\(_2\) at 1 bar pressure at 1000 K?

\[
K = \frac{(p_{\text{Br}} / 1 \text{bar})^2}{(p_{\text{Br}_2} / 1 \text{bar})}
\]

\[
\frac{p_{\text{Br}}}{1 \text{bar}} = \sqrt{(p_{\text{Br}_2} / 1 \text{bar})(K)} = \sqrt{(1)(335 \times 10^{-5})} = 580 \times 10^{-3}
\]

\[
p_{\text{Br}} = 5.80 \times 10^{-3} \text{ bar}
\]

8. What is \( \Delta S^\circ \) at 1000 K for the reaction in Problem 7?

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

\[
\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}
\]

\[
\Delta G^\circ = -(1 \text{ mol}) \text{RT} \ln K = -(1 \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1})(1000 \text{ K}) \ln(3.35 \times 10^{-5}) = 85,680 \text{ J}
\]

\[
\Delta S^\circ = \frac{196200 \text{ J} - 85680 \text{ J}}{1000 \text{ K}} = 1105 \text{ JK}^{-1}
\]
9. At 30 °C the equilibrium vapor pressure of pure acetone is 283 Torr and the Henry’s Law constant for dilute solutions of acetone in ether is 588 Torr. The vapor pressure of acetone over a solution in ether is 90 Torr when the mole fraction of acetone is 0.200. Determine the activity coefficient of acetone in this solution based on a solute (not solvent) standard state.

\[ a_B = \frac{P_B}{K_B} = \gamma_B x_B \]

\[ \frac{90 \text{ Torr}}{588 \text{ Torr}} = \gamma_B(0.200) \]

\[ \gamma_B = 0.765 \]

10. The freezing point of naphthalene measured with a selected laboratory thermometer is found to be 80.52 °C. The freezing point of a 0.400 molal solution of benzene in naphthalene is measured to be 77.74 °C. Estimate the freezing-point depression constant (i.e., cryoscopic constant) for naphthalene.

\[ \Delta T_f = T_f^o - T_f = K_f m \]

\[ 80.52 - 77.74 = K_f(0.4) \]

\[ K_f = 6.95 \text{ K m}^{-1} \]
11. Determine the pOH of 0.015 M NaCN solution. You may assume that $\gamma_{\pm} = 1$.

$$\text{CN}^- + \text{H}_2\text{O} = \text{HCN} + \text{OH}^-$$

$$K = K_b = \frac{([\text{HCN}]/1\text{mol L}^{-1})([\text{OH}^-]/1\text{mol L}^{-1})}{([\text{CN}^-]/1\text{mol L}^{-1})}$$

$$2 \times 10^{-5} = \frac{x^2}{0.015 - x}$$

$$x = 5.38 \times 10^{-4} \quad [\text{OH}^-] = 5.38 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}(5.38 \times 10^{-4}) = 3.27$$

12. The solubility of CaF$_2$ in 0.005 molar NaF solution is $1.6 \times 10^{-6} \text{ mol L}^{-1}$. Estimate the solubility product constant for CaF$_2$. You may assume that $\gamma_{\pm} = 1$.

$$\text{CaF}_2(s) = \text{Ca}^{2+}(aq) + 2 \text{F}^-(aq)$$

$$K_s = a_{\text{Ca}^{2+}}a_{\text{F}^-}^2 = (1.6 \times 10^{-6})(0.005)^2$$

$$K_s = 4 \times 10^{-11}$$
13. Identify the Brønsted-Lowry acids and bases and write the value of the equilibrium constant for the following equation.

\[ \text{CN}^- (aq) + \text{H}_2\text{O}(\ell) = \text{HCN}(aq) + \text{OH}^- (\ell) \]

- **Brønsted-Lowry acids**: H₂O, HCN
- **Brønsted-Lowry bases**: CN⁻, OH⁻

**Equilibrium constant** = \(2 \times 10^{-5}\)

14. It is desired to oxidize \(\text{Fe}^{2+}(aq)\) to \(\text{Fe}^{3+}(aq)\) without oxidizing \(\text{H}_2\text{O}\) to \(\text{O}_2(g)\) (assume an acid solution).

**a.)** Use the table of reduction half reactions attached to the equation sheet to choose a reagent that will perform the desired oxidation (assume all concentrations near 1 M) and write a balanced chemical equation for the reaction.

Left electrode: \(\text{Fe}^{3+} + e^- = \text{Fe}^{2+}\)

Right electrode: \(\text{Br}_2 + 2 \text{e}^- = 2 \text{Br}^-\)

Right - 2 x Left: \(\text{Br}_2 + 2 \text{Fe}^{2+} = 2 \text{Br}^- + 2\text{Fe}^{3+}\)

**b.)** Diagram a galvanic cell that has the \(\text{Fe}^{2+}/\text{Fe}^{3+}\) oxidation as the left electrode and your other reagent as the right electrode and give the value of \(E^o\) for your cell.

\[ \text{Pt} | \text{Fe}^{3+}, \text{Fe}^{2+}, \text{Br}^- | \text{Br}_2(g) | \text{Pt} \]

\[ E^o = E^o_{right} - E^o_{left} \]

\[ E_o = 1.09 - 0.77 = 0.32 \text{ V} \]
15. The time required for one-half of a sample of cyclopropane to isomerize to propylene does not depend on the initial pressure of cyclopropane. In an experiment at 1000 K the time required for the initial partial pressure of 0.40 atm for cyclopropane to decay to 0.20 atm is 0.075 s. What is the order of the reaction and what is the rate constant for the reaction (give your reasoning and give units for the rate constant).

The half-life is independent of the concentration only for a first order reaction.

Then,
\[ k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{0.075\text{s}} = 9.24\text{s}^{-1} \]

16. The reaction \( 2 \text{NO}_2\text{Cl}(g) \rightarrow 2 \text{NO}_2(g) + \text{Cl}_2(g) \)

follows the rate law
\[ -\frac{d[\text{NO}_2\text{Cl}]}{dt} = k[\text{NO}_2\text{Cl}] \]

The mechanism seems to be
\[ \begin{align*}
    &k_1 \\
    \text{NO}_2\text{Cl} &\rightarrow \text{NO}_2 + \text{Cl} \\
    &k_2 \\
    \text{NO}_2\text{Cl} + \text{Cl} &\rightarrow \text{NO}_2 + \text{Cl}_2
\end{align*} \]

Assume the steady state approximation for the Cl atom intermediate, solve for \([\text{Cl}]\), and show that the reaction is first order in \(\text{NO}_2\text{Cl}\).

\[ \frac{d[\text{Cl}]}{dt} = k_1[\text{NO}_2\text{Cl}] - k_2[\text{NO}_2\text{Cl}][\text{Cl}] = 0 \]

\[ [\text{Cl}] = \frac{k_1[\text{NO}_2\text{Cl}]}{k_2[\text{NO}_2\text{Cl}]} = \frac{k_1}{k_2} \]

\[ -\frac{d[\text{NO}_2\text{Cl}]}{dt} = k_1[\text{NO}_2\text{Cl}] + k_2[\text{NO}_2\text{Cl}][\text{Cl}] \]

\[ -\frac{d[\text{NO}_2\text{Cl}]}{dt} = k_1[\text{NO}_2\text{Cl}] + k_2[\text{NO}_2\text{Cl}][k_1/k_2] \]

\[ -\frac{d[\text{NO}_2\text{Cl}]}{dt} = 2k_1[\text{NO}_2\text{Cl}] = k[\text{NO}_2\text{Cl}] \quad \text{where} \quad k = 2k_1 \]