Final Exam
CHM 3410, Dr. Mebel, Fall 2005

1. At -31.2°C, pure propane and *n*-butane have vapor pressures of 1200 and 200 Torr, respectively. (a) Calculate the mole fraction of propane in the liquid mixture that boils at -31.2°C at a pressure of 760 Torr. (b) Calculate the mole fraction of propane in the vapor that is in equilibrium with the liquid of part (a).

2. What is the equilibrium constant, *K*, for the reaction $I_2(g) \leftrightarrows 2\ I(g)$ at 1000 K? Calculate the degree of dissociation of iodine molecules in this reaction at 1 bar and at 0.1 bar.

3. For the following electrochemical cells write electrode reduction half-reactions, cell reactions, Nernst equations, and determine the standard emf's, standard reaction Gibbs energies, and equilibrium constants. Specify the spontaneous direction for each reaction.

(a) $Pt(s)|Cl_2(g)|HCl(aq)||K_2CrO_4(aq)|Ag_2CrO_4(s)|Ag(s)$

(b) $Cu(s)|Cu^{2+}(aq)||Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$

4. The gas phase decomposition of ethyl bromide is a first-order reaction, occurring with a rate constant that demonstrates the following dependence on temperature:

Trial Number	**Temperature (K)**	***k* (s^{-1})**
1	800	0.036
2	900	1.410

(a) Determine the Arrhenius parameters for this reaction. (b) Using these parameters, determine the enthalpy, entropy, and Gibbs energy of activation.

5. Compounds *A* and *B* react to produce product *P* via intermediate *C* by the following reaction mechanism:

$A + B \rightarrow C$ with rate constant k_1

$C \rightarrow A + B$ with rate constant k_2

$C \rightarrow P$ with rate constant k_3

Derive an expression for the rate of production of *P* provided that a steady-state approximation is accurate for compound *C*. What is the order of the reaction with respect to *A*, *B* and overall? What is the reaction rate constant in terms of k_1, k_2, and k_3? What are the units of this rate constant?

Final Exam
CHM 3410, Dr. Mebel, Fall 2006

There are 8 problems + 2 bonus problems. Each problem is 12.5 pts.

1. A balloon filled with 10.50 L of Ar at 18.0°C and 1 atm rises to a height in the atmosphere where the pressure is 248 Torr and the temperature is –30.5°C. What is the final volume of the balloon?

2. One mole of a perfect gas, for which $C_{V,\mathrm{m}} = 3/2\, R$ initially at 20.0°C and 1.00×10^6 Pa undergoes a two-stage transformation. For each of the stages described in the following list, calculate the final pressure, as well as q, w, ΔU, and ΔH. Also calculate q, w, ΔU, and ΔH for the complete process.

   a) The gas is expanded isothermally and reversibly until the volume doubles.
   b) Beginning at the end of the first stage, the temperature is raised to 80.0°C at constant volume.

3. Consider the following reaction: $\nu_1\mathrm{NH_3(g)} + \nu_2\mathrm{NO(g)} \rightarrow \nu_3\mathrm{N_2(g)} + \nu_4\mathrm{H_2O(g)}$

   a) Balance the reaction making all stoichiometric coefficients integer numbers.
   b) Calculate $\Delta_r H^\varnothing$, $\Delta_r U^\varnothing$, $\Delta_r S^\varnothing$, $\Delta_r G^\varnothing$, and equilibrium constant K for this reaction at 298 K.
   c) Calculate $\Delta_r H^\varnothing$ at 500 K.
   d) Assuming that the change in $\Delta_r H^\varnothing$ from 298 K to 500 K is not significant, calculate $\Delta_r G^\varnothing$ and K at 500 K.
   e) Compare your results for $\Delta_r G^\varnothing$ and K at 298 and 500 K and explain them in terms of Le Chatelier's principle.

4. Sketch the phase diagram of the system A/B given that the two substances do not form a compound with each other, that A freezes at -56°C and B freezes at +5°C, and that a eutectic is formed when the mole fraction of B is 0.15 and that the eutectic melts at -65°C.

5. You place 2.00 mol of NOCl(g) in a reaction vessel. Equilibrium is established with respect to the decomposition reaction $\mathrm{NOCl(g)} \rightarrow \mathrm{NO(g)} + 1/2\ \mathrm{Cl_2(g)}$.

   a) Derive an expression for the equilibrium constant K in terms of the extent of reaction ξ.
   b) Simplify your expression for part (a) in the limit that ξ is very small.
   c) Calculate ξ in the limit that ξ is very small at 375 K and a pressure of 0.500 bar given that $K(375\ \mathrm{K}) = 4.535\times10^{-3}$.

6. Determine the half-reactions and the overall cell reaction, calculate the cell potential and determine the equilibrium constant at 298.15 K for the cell

$$|\mathrm{Cd(s)}|\mathrm{Cd^{2+}}(\mathrm{aq}, a_{\mathrm{Cd(2+)}} = 0.100)||\mathrm{Cl^-}(\mathrm{aq}, a_{\mathrm{Cl-}} = 0.005)|\mathrm{AgCl(s)}|\mathrm{Ag(s)}|$$

Is the cell reaction spontaneous as written for the given activities of Cl^- and Cd^{2+}?

7. Consider the following mechanism, which results in the formation of product P:

$A \to B$	with rate constant k_1
$B \to A$	with rate constant k_{-1}
$B \to C$	with rate constant k_2
$C \to B$	with rate constant k_{-2}
$C \to P$	with rate constant k_3

Derive an expression for the rate of production of P provided that a steady-state approximation is accurate for compounds B and C. What is the order of the reaction? What is the reaction rate constant in terms of k_1, k_2, k_{-1}, k_{-2}, and k_3? What are the units of this rate constant? If only A species is present at $t = 0$, what is the expression for the concentration of P as a function of time?

8. Describe briefly different experimental approaches considered in this course, which can be used to measure thermodynamical properties, such as enthalpy, entropy, and Gibbs energy.

Bonus problems

9. Derive an expression for the internal pressure π_T for a Dieterici gas described by the following equation of state,

$$p = \frac{RTe^{-a/RTV_m}}{V_m - b}$$

Express your result in terms of variables p, T, and V_m, and constants a and R and simplify it as much as possible.

10. Liquid A is in equilibrium with its vapor at 300 K, at which temperature the equilibrium vapor pressure is 40 Torr. The enthalpy of vaporization at 300 K is 8.0 kJ mol^{-1}. The heat capacities of A(l) and A(g) are 67.0 J mol^{-1} K^{-1} and 35 J mol^{-1} K^{-1}, respectively. Compute the equilibrium vapor pressure over liquid A at 350 K. **Do not assume $\Delta_{\mathrm{vap}}H$ to be independent of temperature!** (*Hint*: To derive an expression to solve this problem, follow the derivation of the Clausius-Clapeyron equation, but take into account that $\Delta_{\mathrm{vap}}H$ is a function of T). Compare your result with the result obtained with temperature-independent $\Delta_{\mathrm{vap}}H$ and calculate the percentage of error in the latter.

Final Exam
CHM 3410, Dr. Mebel, Fall 2013 (Part I)

There are 8 problems + 2 bonus problems in two parts. Each problem is 12.5 pts.

1. A simplest aromatic molecule benzene was recently detected in the stratosphere of Titan, a Saturn moon. The mole fraction of C_6H_6 in the stratosphere is 1×10^{-6} in the region where the pressure is 0.1 mbar and the temperature is 150 K. Given that calculate how many C_6H_6 molecules can be found in a volume of 1 m^3.

2. One mole of CO_2 in a state defined by $T_i = 300$ K and $V_i = 2.50$ L undergoes an isothermal reversible expansion until $V_f = 23.0$ L. Calculate the work of expansion assuming

a) that the gas is perfect;
b) that the gas is described by the van der Waals equation of state.

What is the percent error in the calculated work when you use the perfect gas law instead of the van der Waals equation? The van der Waals parameters for CO_2 are listed in Table 1.6.

3. Consider the following reaction: $\nu_1 C_6H_6(l) + \nu_2 O_2(g) \rightarrow \nu_3 CO_2(g) + \nu_4 H_2O(l)$

a) Balance the equation (all stoichiometric coefficients do not have to be integer numbers).
b) Calculate $\Delta_r H^\varnothing$, $\Delta_r U^\varnothing$, $\Delta_r S^\varnothing$, $\Delta_r G^\varnothing$, and equilibrium constant K for this reaction at 298.15 K.
c) Calculate $\Delta_r H^\varnothing$ at 600 K.
d) Assuming that the change in $\Delta_r H^\varnothing$ from 298.15 K to 600 K is not significant, calculate $\Delta_r G^\varnothing$ and K at 600 K.
e) Compare your results for $\Delta_r G^\varnothing$ and K at 298.15 and 600 K and explain them in terms of Le Chatelier's principle.
f) How will an increase in pressure (by compressing the reaction mixture) affect the equilibrium composition?

4. The surface of Titan, a Saturn's moon, is covered with lakes made from a mixture of liquid methane and liquid ethane. The pressure at the surface level is 1.5 bar and the temperature is 94 K. Using the fact that standard boiling temperatures of methane and ethane are 111.65 K and 184.55 K and their enthalpies of vaporization are 8.19 kJ/mol 14.69 kJ/mol, respectively, determine the following:

a) What are the boiling temperatures of methane and ethane at Titan's surface?
b) To what values pressure should decrease to make methane boil at 94 K?
c) To what values pressure should decrease to make ethane boil at 94 K?
d) Assume that a lake consists of 70% of methane and 30% of ethane and their liquid mixture behaves as an ideal solution. What is the total vapor pressure of methane and ethane above the lake at 94 K?

5. Calculate the degree of dissociation of N_2O_4 in the reaction $N_2O_4(g) \rightarrow 2NO_2(g)$ at 250 K and a total pressure of 0.500 bar. Do you expect the degree of dissociation to increase or decrease as the temperature is increased to 550 K? Assume that $\Delta_r H^\varnothing$ is independent of temperature.

6. Consider the following electrochemical cell:

$Pt(s)|H_2(g,p)|HCl(aq,b)|Hg_2Cl_2(s)|Hg(l)$

Write electrode half-reactions and the cell reaction. Determine the standard emf $E^{\varnothing}$ for this cell from standard potential data in the Data Section of your textbook. Calculate the standard Gibbs energy and the equilibrium constant for the cell reaction at 25°C. Write the Nernst equation for the cell and calculate its emf E given that the pressure of $H_2(g)$ $p = 1$ bar, the molality of HCl(aq) $b = 1.6077$ mmol kg^{-1}, and the mean activity coefficient of H^+ and Cl^- in the electrolyte solution follows the Debye-Hückel law.

7. Hydrogen iodide can be synthesized from its elements in a gas-phase reaction $I_2 + H_2 \rightarrow 2HI$. One proposed mechanism for the process is

$I_2 \xrightarrow{k_1} 2I$ (first order)

$2I \xrightarrow{k_2} I_2$ (second order)

$H_2 + 2I \xrightarrow{k_3} 2HI$ (first order in H_2, second order in I, third order overall)

Derive a rate law for the rate of production of HI if

a) I_2 and I are in equilibrium throughout the reaction.
b) Steady-state approximation can be applied to I atoms and $k_3[H_2] >> k_2$.

How could you determine experimentally which of these two assumptions, a) or b), is correct?

8. Discuss the features, advantages, and limitations of the Michaelis-Menten mechanism of enzyme action. Distinguish between competitive and uncompetitive inhibition of enzymes. Discuss how these modes of inhibition may be detected experimentally.

Bonus problems

9. Derive an expression for the internal pressure π_T for a Redlich-Kwong gas described by the following equation of state,

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}}\frac{1}{V_m\left(V_m + b\right)}$$

Express your result in terms of variables p, T, and V_m, and constants a, b, and R and simplify it as much as possible.

10. The dissociation of 5.25 g of a non-volatile substance in 565 g of benzene raises the boiling point by 0.625°C. Note that the ebullioscopic constant $K_b = 2.53$ K kg mol^{-1} and the cryoscopic constant $K_f = 5.12$ K kg mol^{-1}, and the density of benzene is 876.6 kg m^{-3}. Calculate the freezing point depression, the molar mass of the solute, the osmotic pressure at 298 K, and the vapor pressure above the solution at 298 K taking that $p^*_{\text{benzene}} = 103$ Torr at this temperature.

Final Exam
CHM 3410, Dr. Mebel, Fall 2017 (Part I)

There are 8 problems + 2 bonus problems in two parts. Each problem is 12.5 pts.

1. A balloon filled with 13.25 L of He at 15.4ºC and 1.0 atm rises to a height where the pressure is 248 Torr and the temperature is -30.5ºC. What is the final volume of the balloon? Assume that the pressure inside and outside the balloon is the same.

2. A 67.0 g piece of gold at 725 K is dropped into 165 g of $H_2O(l)$ at 298 K in an insulated container at 1 bar pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that $C_{p,\mathrm{m}}$ for Au and H_2O is constant at its value for 298 K throughout the temperature range of interest. Calculate ΔS for this process.

3. Consider the following reaction of oxidation of solid urea:

$$\nu_1 CO(NH_2)_2(s) + \nu_2 O_2(g) \rightarrow \nu_3 CO_2(g) + \nu_4 H_2O(l) + \nu_5 N_2(g)$$

a) Balance the equation.
b) Calculate $\Delta_r H^\varnothing$, $\Delta_r U^\varnothing$, $\Delta_r S^\varnothing$, $\Delta_r G^\varnothing$, and equilibrium constant K for this reaction at 298.15 K.
c) Calculate $\Delta_r H^\varnothing$ at 450 K.
d) Assuming that the change in $\Delta_r H^\varnothing$ from 298.15 K to 450 K is not significant, calculate $\Delta_r G^\varnothing$ and K at 450 K.
e) Compare your results for $\Delta_r G^\varnothing$ and K at 298.15 and 450 K and explain them in terms of Le Chatelier's principle.
f) How will an increase in pressure (by compressing the reaction mixture) affect the equilibrium composition?

4. One of the effects of climate change related to global warming caused by combustion of fossil fuels is the increase of concentration of CO_2 dissolved in water (in the oceans, seas, lakes, etc.). Considering that the partial pressure of CO_2 in the air increased from 2.8×10^{-4} atm in pre-industrial times to 3.6×10^{-4} atm now, calculate the increase of molality of CO_2 in the water solution.

Bonus 1. One mole of an alkane C_nH_{2n+2} is burned in excess of oxygen to form $CO_2(g)$ and $H_2O(l)$ at 298.15 K and 1 bar of pressure. At constant pressure, the heat released in the process is found to be 4816.8 kJ. If the products of the combustion at 298.15 K and 1 bar of pressure are $CO_2(g)$ and $H_2O(g)$, the heat released is 4464.7 kJ. Determine the molecular formula of the alkane and its standard enthalpy of formation.

Final Exam

CHM 3410, Dr. Mebel, Fall 2017 (Part II)

There are 8 problems + 2 bonus problems in two parts. Each problem is 12.5 pts.

5. Consider the equilibrium $NO_2(g) \leftrightarrows NO(g) + (1/2)O_2(g)$. 1 mole of $NO_2(g)$ is placed in a vessel and allowed to come to equilibrium at a total pressure of 1 bar. An analysis of the content of the vessel gives the following results:

T	600 K	900 K
$p(NO)/p(NO_2)$	0.224	5.12

a) Calculate the equilibrium constant K at 600 and 900 K.
b) Calculate $\Delta_r G^{\varnothing}$ and $\Delta_r H^{\varnothing}$ for this reaction at 298.15 K, using only the data in the problem. Assume that $\Delta_r H^{\varnothing}$ is independent of temperature.
c) Calculate $\Delta_r G^{\varnothing}$ and $\Delta_r H^{\varnothing}$ at 298.15 K using thermochemical data tables and compare your answer with that obtained in part b).

6. Consider the following electrochemical cell:

$Pt(s)|H_2(g,p)|HCl(aq,b)|AgCl(s)|Ag(s)$

Write electrode half-reactions and the cell reaction. Determine the standard emf $E^{\varnothing}$ for this cell from standard potential data in the Data Section of your textbook. Calculate the standard Gibbs energy and the equilibrium constant for the cell reaction at 25°C. Write the Nernst equation for the cell and calculate its emf E given that the pressure of $H_2(g)$ $p = 1$ bar, the molality of HCl(aq) $b = 0.01$ mol kg^{-1}, and the mean activity coefficient of H^+ and Cl^- in the electrolyte solution follows the Debye-Hückel limiting law.

7. Consider the following mechanism of ozone thermal decomposition:

$$O_3 \xrightarrow{k_1} O_2 + O$$
$$O_2 + O \xrightarrow{k_{-1}} O_3$$
$$O_3 + O \xrightarrow{k_2} 2O_2$$

a) Derive the rate law expression for the loss of O_3.
b) Under what conditions will the rate law expression for O_3 decomposition be first order with respect to O_3? What is the overall rate constant for O_3 decomposition in this case? What is the reaction rate-determining step then? Give a qualitative explanation of your result for the overall rate constant for O_3 decomposition in this case.

8. A certain reaction is first order, and 540 s after initiation of the reaction, 32.5% of the reactant remains.

(a) What is the rate constant for this reaction?
(b) At what time after initiation of the reaction will 10% of the reactant remain?

Bonus 2. Show that the ratio of the half-life to the one-quarter-life, $t_{1/2}/t_{1/4}$, for a reaction that is nth order ($n > 1$) in reactant A can be written as a function of n alone (that is, there is no concentration and rate constant dependence in the ratio). To achieve this, derive the expression for $t_{1/2}/t_{1/4}$. What is $t_{1/2}/t_{1/4}$ for a second-order reaction? How your result compares with $t_{1/2}/t_{1/4}$ for a first-order reaction? (Note: the one-quarter-life is defined as the time at which the concentration falls to ¼ of the initial concentration.)

Final Exam
CHM 3410, Dr. Mebel, Fall 2005

1. At -31.2°C, pure propane and *n*-butane have vapor pressures of 1200 and 200 Torr, respectively. (a) Calculate the mole fraction of propane in the liquid mixture that boils at -31.2°C at a pressure of 760 Torr. (b) Calculate the mole fraction of propane in the vapor that is in equilibrium with the liquid of part (a).

(a) x(propane) = 0.56 (b) y(propane) = 0.88

2. What is the equilibrium constant, K, for the reaction $I_2(g) \rightleftarrows 2\,I(g)$ at 1000 K? Calculate the degree of dissociation of iodine molecules in this reaction at 1 bar and at 0.1 bar.

$\Delta_r H^{\varnothing} = 151.24$ kJ mol^{-1} $K = 2.33\times10^{-3}$ (for 1000 K)

$\xi(1\text{ bar}) = 2.41\times10^{-2}$ $\xi(0.1\text{ bar}) = 7.61\times10^{-2}$

3. For the following electrochemical cells write electrode reduction half-reactions, cell reactions, Nernst equations, and determine the standard emf's, standard reaction Gibbs energies, and equilibrium constants. Specify the spontaneous direction for each reaction.

(a) $Pt(s)|Cl_2(g)|HCl(aq)||K_2CrO_4(aq)|Ag_2CrO_4(s)|Ag(s)$
(b) $Cu(s)|Cu^{2+}(aq)||Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$

(a) $E^{\varnothing} = -0.91$ V $\Delta_r G^{\varnothing} = 175.59$ kJ mol^{-1} $K = 1.66\times10^{-31}$
(b) $E^{\varnothing} = 0.89$ V $\Delta_r G^{\varnothing} = -171.73$ kJ mol^{-1} $K = 1.22\times10^{30}$

4. The gas phase decomposition of ethyl bromide is a first-order reaction, occurring with a rate constant that demonstrates the following dependence on temperature:

Trial Number	**Temperature (K)**	***k* (s^{-1})**
1	800	0.036
2	900	1.410

(a) Determine the Arrhenius parameters for this reaction. (b) Using these parameters, determine the enthalpy, entropy, and Gibbs energy of activation.

(a) $E_a = 219.6$ kJ mol^{-1} $A = 7.84\times10^{12}$ s^{-1}
(b) $\Delta^{\#}H = 219.6$ kJ mol^{-1} $\Delta^{\#}S = -6.8$ J K^{-1} mol^{-1} $\Delta^{\#}G = 225.4$ kJ mol^{-1}

5. Compounds A and B react to produce product P via intermediate C by the following reaction mechanism:

$A + B \rightarrow C$	with rate constant k_1
$C \rightarrow A + B$	with rate constant k_2
$C \rightarrow P$	with rate constant k_3

Derive an expression for the rate of production of P provided that a steady-state approximation is accurate for compound C. What is the order of the reaction with respect to A, B and overall? What is the reaction rate constant in terms of k_1, k_2, and k_3? What are the units of this rate constant?

$$\frac{d[P]}{dt} = \frac{k_1 k_3}{(k_2 + k_3)}[A][B]$$

$$k = \frac{k_1 k_3}{(k_2 + k_3)} \qquad \text{L mol}^{-1}\ \text{s}^{-1}$$

Final Exam
CHM 3410, Dr. Mebel, Fall 2006

There are 8 problems + 2 bonus problems. Each problem is 12.5 pts.

1. A balloon filled with 10.50 L of Ar at 18.0°C and 1 atm rises to a height in the atmosphere where the pressure is 248 Torr and the temperature is –30.5°C. What is the final volume of the balloon?

V_2 = 26.82 L

2. One mole of a perfect gas, for which $C_{V,\mathrm{m}} = 3/2\ R$ initially at 20.0°C and 1.00×10^6 Pa undergoes a two-stage transformation. For each of the stages described in the following list, calculate the final pressure, as well as q, w, ΔU, and ΔH. Also calculate q, w, ΔU, and ΔH for the complete process.

a) The gas is expanded isothermally and reversibly until the volume doubles.
b) Beginning at the end of the first stage, the temperature is raised to 80.0°C at constant volume.

a) w = -1689.4 J q = +1689.4 J $\Delta U = \Delta H = 0$ $p_f = 5.0\times10^5$ Pa

b) w = 0 q = +748.3 J ΔU = +748.3 J ΔH = 1247.1 J $p_f = 6.02\times10^5$ Pa

Total: w = -1689.4 J q = +2437.7 J ΔU = +748.3 J ΔH = 1247.1 J

3. Consider the following reaction: $\nu_1 NH_3(g) + \nu_2 NO(g) \rightarrow \nu_3 N_2(g) + \nu_4 H_2O(g)$

a) Balance the reaction making all stoichiometric coefficients integer numbers.

b) Calculate $\Delta_r H^\varnothing$, $\Delta_r U^\varnothing$, $\Delta_r S^\varnothing$, $\Delta_r G^\varnothing$, and equilibrium constant K for this reaction at 298 K.

c) Calculate $\Delta_r H^\varnothing$ at 500 K.

d) Assuming that the change in $\Delta_r H^\varnothing$ from 298 K to 500 K is not significant, calculate $\Delta_r G^\varnothing$ and K at 500 K.

e) Compare your results for $\Delta_r G^\varnothing$ and K at 298 and 500 K and explain them in terms of Le Chatelier's principle.

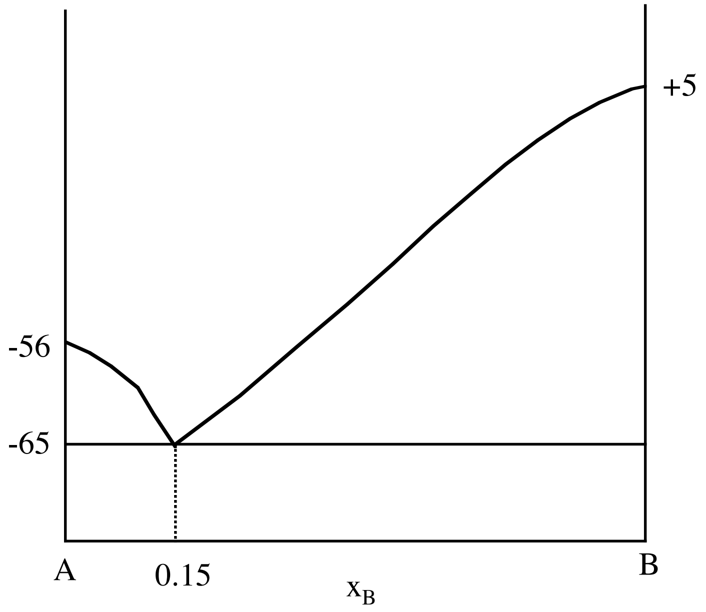
a) $4\ NH_3(g) + 6\ NO(g) \rightarrow 5\ N_2(g) + 6\ H_2O(g)$

b) $\Delta_r H^\varnothing = -1808$ kJ $\Delta_r U^\varnothing = -1810.5$ kJ $\Delta_r S^\varnothing = 56.57\ J\ K^{-1}$ $\Delta_r C_p = 27.80\ J\ K^{-1}$
$\Delta_r G^\varnothing = -1824.92$ kJ ln K = 736.6

c) $\Delta_r H^\varnothing$ (500 K) = -1802.38 kJ

d) ln K'(500 K) =441.8 $\Delta_r G^\varnothing$ (500 K) = -1836.5 kJ

4. Sketch the phase diagram of the system A/B given that the two substances do not form a compound with each other, that A freezes at -56°C and B freezes at +5°C, and that a eutectic is formed when the mole fraction of B is 0.15 and that the eutectic melts at -65°C.



5. You place 2.00 mol of NOCl(g) in a reaction vessel. Equilibrium is established with respect to the decomposition reaction $NOCl(g) \rightarrow NO(g) + 1/2\ Cl_2(g)$.

a) Derive an expression for the equilibrium constant K in terms of the extent of reaction ξ.

b) Simplify your expression for part (a) in the limit that ξ is very small.

c) Calculate ξ in the limit that ξ is very small at 375 K and a pressure of 0.500 bar given that $K(375\ K) = 4.535\times10^{-3}$.

a) $$K = \frac{\xi^{3/2}}{2^{1/2}(2-\xi)(2+0.5\xi)^{1/2}}\left(\frac{p}{p^{\Theta}}\right)^{1/2}$$

b) $$K = \frac{\xi^{3/2}}{4}\left(\frac{p}{p^{\Theta}}\right)^{1/2}$$

c) $\xi = 0.087$ mol

6. Determine the half-reactions and the overall cell reaction, calculate the cell potential and determine the equilibrium constant at 298.15 K for the cell

$$|\mathrm{Cd(s)}|\mathrm{Cd^{2+}}(\mathrm{aq},\ a_{\mathrm{Cd(2+)}} = 0.100)||\mathrm{Cl^-}(\mathrm{aq},\ a_{\mathrm{Cl-}} = 0.005)|\mathrm{AgCl(s)}|\mathrm{Ag(s)}|$$

Is the cell reaction spontaneous as written for the given activities of Cl^- and Cd^{2+}?

R: $AgCl(s) + e \rightarrow Ag(s) + Cl^-$ ×2 $E_L^{\varnothing} = +0.22$ V

L: $Cd^{2+} + 2e \rightarrow Cd(s)$ $E_R^{\varnothing} = -0.40$ V

R-L: $Cd(s) + 2\ AgCl(s) \rightarrow Cd^{2+} + 2\ Ag(s) + 2\ Cl^-$ $E^{\varnothing} = +0.62$ V

$\ln K = +48.265$ $K = 9.15 \times 10^{20}$ $Q = 2.5 \times 10^{-6}$ $E = 0.79$ V spontaneous

7. Consider the following mechanism, which results in the formation of product P:

$A \rightarrow B$	with rate constant k_1
$B \rightarrow A$	with rate constant k_{-1}
$B \rightarrow C$	with rate constant k_2
$C \rightarrow B$	with rate constant k_{-2}
$C \rightarrow P$	with rate constant k_3

Derive an expression for the rate of production of P provided that a steady-state approximation is accurate for compounds B and C. What is the order of the reaction? What is the reaction rate constant in terms of k_1, k_2, k_{-1}, k_{-2}, and k_3? What are the units of this rate constant? If only A species is present at $t = 0$, what is the expression for the concentration of P as a function of time?

$$\frac{d[P]}{dt} = \frac{k_1 k_2 k_3}{k_{-1}k_{-2} + k_{-1}k_3 + k_2 k_3}[A]$$

$$[P] = [A_0]\left(1 - e^{-kt}\right) \quad \mathrm{s}^{-1}$$

8. Describe briefly different experimental approaches considered in this course, which can be used to measure thermodynamical properties, such as enthalpy, entropy, and Gibbs energy.

1) calorimetry
2) measurements of equilibrium constants
3) $\ln p \sim 1/T$ (for $\Delta_{\text{trans}}H$)
4) measurements of cell potentials
5) forward and reverse rate constants

Bonus problems

9. Derive an expression for the internal pressure π_T for a Dieterici gas described by the following equation of state,

$$p = \frac{RTe^{-a/RTV_m}}{V_m - b}$$

Express your result in terms of variables p, T, and V_m, and constants a and R and simplify it as much as possible.

$$\pi_T = \frac{ap}{V_m RT}$$

10. Liquid A is in equilibrium with its vapor at 300 K, at which temperature the equilibrium vapor pressure is 40 Torr. The enthalpy of vaporization at 300 K is 8.0 kJ mol^{-1}. The heat capacities of A(l) and A(g) are 67.0 J mol^{-1} K^{-1} and 35 J mol^{-1} K^{-1}, respectively. Compute the equilibrium vapor pressure over liquid A at 350 K. **Do not assume $\Delta_{\text{vap}}H$ to be independent of temperature!** (*Hint*: To derive an expression to solve this problem, follow the derivation of the Clausius-Clapeyron equation, but take into account that $\Delta_{\text{vap}}H$ is a function of T). Compare your result with the result obtained with temperature-independent $\Delta_{\text{vap}}H$ and calculate the percentage of error in the latter.

$$\ln\frac{p_2}{p_1} = \frac{\Delta_{vap}H_1 - \Delta C_p T_1}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{\Delta C_p}{R}\ln\frac{T_2}{T_1}$$

$p_2 = 60.56$ Torr

With the Clausius-Clapeyron equation $p_2 = 63.25$ Torr

% error = 4.44%

1. A simplest aromatic molecule benzene was recently detected in the stratosphere of Titan, a Saturn moon. The mole fraction of C_6H_6 in the stratosphere is 1×10^{-6} in the region where the pressure is 0.1 mbar and the temperature is 150 K. Given that calculate how many C_6H_6 molecules can be found in a volume of 1 m^3.

(11.5)

$1\ bar = 10^5\ Pa$

$x_{C_6H_6} = 1\times10^{-6}$

$P_{Total} = .1 \times 10^{-3}\ bar = 10\cancel{0}\ Pa$

10 Pa

$PV = nRT$

$T = 150\ K$

The total Pressure is 100 Pa, we want to know the pressure of Benzene so

$(1\times10^{-6})(100\ Pa) = 1\times10^{-4}\ Pa$

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{\text{mole Benzene}}{1\ m^3} = \frac{(1\times10^{-4,5}\ Pa)}{(8.314)(150K)}$$

$$\frac{\text{mole Benzene}}{1\ m^3} = \frac{8.018\times10^{-8}\ mol\ C_6H_6}{1\ m^3}$$

$$\left(\frac{6.022\times10^{23}\ \text{molecule Benzene}}{1\ mol\ \cancel{\text{Benzene}}}\right) \cdot \frac{8.018\times10^{-8}\ mol\ \cancel{\text{Benzene}}}{1\ m^3}$$

$$\boxed{4.82\times10^{1\cancel{6}5}\ \frac{\text{molecule Benzene}}{m^3}}$$

2. One mole of CO_2 in a state defined by $T_i = 300$ K and $V_i = 2.50$ L undergoes an isothermal reversible expansion until $V_f = 23.0$ L. Calculate the work of expansion assuming

a) that the gas is perfect;

b) that the gas is described by the van der Waals equation of state.

What is the percent error in the calculated work when you use the perfect gas law instead of the van der Waals equation? The van der Waals parameters for CO_2 are listed in Table 1.6.

$\boxed{12.5}$

Isothermal Reversible expansion

Part A

For a perfect gas, the work done during an isothermal Reversible expansion is, $w = -nRT\ln\left(\frac{V_f}{V_i}\right)$

$n = 1$ $T = 300K$ $V_f = 23L$ $V_i = 2.50L$

$$W = -(1)(8.314)(300)\ln\left(\frac{23\cancel{L}}{2.50\cancel{L}}\right) = \boxed{-5.53 \times 10^3 J}$$

✓

Part B

$$W = -\int_{V_i}^{V_f} p\, dV$$

, For a Van der waals gas

$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}, \quad n = 1$$

$a = 3.61\ atm\ \frac{dm^6}{mol^2}$

$b = 4.29\ \frac{dm^3}{100\,mol}$

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

Plugging in P to the work equation

$$W = \int_{V_i}^{V_f} -\left(\frac{RT}{V-b} - \frac{a}{V^2}\right) d\underset{2}{V} \qquad W = \int_{V_i}^{V_f} -\frac{RT}{V-b}\, dV + \int_{V_i}^{V_f} \frac{a}{V^2}\, dV$$

✓

$$W = -RT\int_{V_i}^{V_f} \frac{1}{V-b}\,dV + a\int_{V_i}^{V_f}\frac{dV}{V^2}$$

W = ~~$-RT\ln(V-b)$~~ $\Big]_{V_i}^{V_f} - \frac{a}{V}\Big]_{V_i}^{V_f}$

$$W = -RT\left[\ln\left(\frac{V_f - b}{V_i - b}\right)\right] - a\left[\frac{1}{V_f} - \frac{1}{V_i}\right]$$

$$W = -(8.314)(300K)\ln\left(\frac{23 - 4.29\times10^{-2}}{2.50 - 4.29\times10^{-2}}\right) - (3.61)\left[\frac{1}{23L} - \frac{1}{2.50L}\right]$$

$$W = -5.57\times10^{3}J + 1.28\,atm\cdot dm^3$$

The term on the right is in different units so I am going to convert it from $atm\cdot dm^3$ to $Pa\cdot m^3 = 1$

$$W = -5.57\times10^{3}J + 129.69\,J = \boxed{-5.44\times10^{3}\,J}$$

The percent error is $\frac{|5.44\times10^{3}J - 5.53\times10^{3}J|}{5.44\times10^{3}J}\times100$ ✓

$= \boxed{1.65\%}$ ✓

$6 - \frac{15}{2}$ $\frac{12}{2} - \frac{15}{2}$

3. Consider the following reaction: $\nu_1C_6H_6(l) + \nu_2O_2(g) \rightarrow \nu_3CO_2(g) + \nu_4H_2O(l)$
   a) Balance the equation (all stoichiometric coefficients do not have to be integer numbers).
   b) Calculate $\Delta_rH^\varnothing$, $\Delta_rU^\varnothing$, $\Delta_rS^\varnothing$, $\Delta_rG^\varnothing$, and equilibrium constant K for this reaction at ~~298.15 K.~~
   c) Calculate $\Delta_rH^\varnothing$ at 600 K.
   d) Assuming that the change in $\Delta_rH^\varnothing$ from 298.15 K to 600 K is not significant, calculate $\Delta_rG^\varnothing$ and K at 600 K.
   e) Compare your results for $\Delta_rG^\varnothing$ and K at 298.15 and 600 K and explain them in terms of Le Chatelier's principle.
   f) How will an increase in pressure (by compressing the reaction mixture) affect the equilibrium composition?

12.5

Part A

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

Part B

$$\Delta_r H^\ominus = \left[3(-285.83\times10^3) + 6(-393.51\times10^3\,\mathrm{J})\right] - \left[(49\times10^3) + \frac{15}{2}(0\right.$$

$$\boxed{\Delta_r H^\ominus = -3267\ \mathrm{kJ/mol}}\ ✓$$

$$\Delta_r H^\ominus = \Delta_r U^\ominus + RT\Delta n_g \qquad \Delta n_g = -\frac{3}{2}$$

$$\Delta_r H^\ominus - RT\Delta n_g = \Delta_r U^\ominus \qquad -3267\times10^3 - (8.314)(298)\left(-\frac{3}{2}\right) = \Delta_r U^\ominus$$

$$\boxed{\Delta_r U^\ominus = -3263.28\ \mathrm{kJ/mol}}\ ✓$$

$$\Delta_r S^\ominus = \left[6(213.74\ \mathrm{K^{-1}mol^{-1}}) + 3(69.91\ \mathrm{J\,K^{-1}mol^{-1}})\right] - \left[\frac{15}{2}(205.138) + (173.3\ \mathrm{J\,K^{-1}}\right]$$

$$\boxed{\Delta_r S^\ominus = -219.66\ \mathrm{J\,K^{-1}mol^{-1}}}\ ✓$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus \qquad \boxed{\Delta_r G^\ominus = -3201.53\ \mathrm{kJ}}\ ✓$$

$$\Delta_r G^\ominus = -3267\times10^3 - (298)(-219.66)$$

The eq const $K = e^{-\frac{\Delta_r G^\circ}{RT}}$

$\boxed{\ln(K) = 1.29 \times 10^3}$ = my Calculator can't solve this number (Over flow error, too big) ✓

Part C

$$\Delta_r H^\circ(600K) = \Delta_r H^\circ(298K) + \int_{T_1}^{T_2} \Delta_r C_p^\circ \, dT$$

$$\Delta_r C_p^\circ = \left[3(75.29 J) + 6(37.11 J)\right] - \left[\tfrac{15}{2}(29.355 J) + (136.1 JK^{-1})\right]$$

$$\Delta_r C_p^\circ = 448.53 - 356.26$$

$$\Delta_r C_p^\circ = 92.264$$

$$\Delta_r H^\circ(600K) = -3267 \times 10^3 + (92.264)(600 - 298)$$

$$\boxed{\Delta_r H^\circ(600K) = -3239.13 \, kJ}$$ ✓

Part D

Find $\Delta_r G^\circ$ and K @ 600 (K)

$$\partial\left(\frac{\Delta_r G^\circ}{T}\right) = -\frac{\Delta_r H^\circ}{T^2} dT$$

$$\frac{\Delta_r G^\circ_2}{T_2} - \frac{\Delta_r G^\circ_1}{T_1} = \Delta_r H^\circ\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{\Delta_r G^\circ_2}{T_2} = -3267 \times 10^3 \left(\frac{1}{600} - \frac{1}{298}\right) - \frac{3201 \times 10^3}{298K}$$

$$= 5.518 \times 10^3 J - 1.07416 \times 10^4 J$$

$$\boxed{\Delta_r G^\circ(600K) = -3134.11 \, kJ} \quad \boxed{\ln(K) = 628.27}$$ ✓ Cont on Scratc Paper →

Continuation of Problems

Part E

The reaction is exothermic, meaning that heat is a product $A + B \longrightarrow P + \text{heat}$

When we raise the temperature we are adding products and According to Le'Chateliers principle the system will act to minimize the change (Shifting to the left in this case). This is observed in the Gibb's energy because it becomes less negative and in the value of K (becomes smaller meaning products went to reactants to minimize change) ✓

Part F

$$C_6H_{6(l)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$$

An increase in pressure will shift the reaction to the side with the least mols of gas (in this case, the Products side) to the right so the composition will increase in products after pressure is applied for this reaction. ✓

4. The surface of Titan, a Saturn's moon, is covered with lakes made from a mixture of liquid methane and liquid ethane. The pressure at the surface level is 1.5 bar and the temperature is 94 K. Using the fact that standard boiling temperatures of methane and ethane are 111.65 K and 184.55 K and their enthalpies of vaporization are 8.19 kJ/mol 14.69 kJ/mol, respectively, determine the following:

a) What are the boiling temperatures of methane and ethane at Titan's surface?
b) To what values pressure should decrease to make methane boil at 94 K?
c) To what values pressure should decrease to make ethane boil at 94 K?
d) Assume that a lake consists of 70% of methane and 30% of ethane and their liquid mixture behaves as an ideal solution. What is the total vapor pressure of methane and ethane above the lake at 94 K?

95

$T_B = 111.65\,K$ (methane)

$P = 1.5 \times 10^6\,Pa$ $T = 94\,K$ $\Delta_{vap}H = 8.19 \times 10^3\,J\,mol^{-1}$

(Ethane)

$\Delta_{vap}H = 14.69 \times 10^3\,J\,mol^{-1}$

$T_B = 184.55\,K$

Part A

$$\int d\ln p = \int \frac{\Delta_{vap}H}{RT^2}\,dT \;, \quad \ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{1.5 \times 10^6\,Pa}{101325\,Pa}\right) = -\frac{(8.19 \times 10^3)}{R}\left(\frac{1}{T_B} - \frac{1}{111.65\,K}\right)$$

$$-2.7356 \times 10^{-3} = \frac{1}{T_B} - \frac{1}{111.65} \qquad \boxed{T_B = \overset{117.0}{\cancel{160.75}}\,K} \text{ Methane}$$

$$\ln\left(\frac{1.5 \times 10^6\,Pa}{101325}\right) = -\frac{(14.69 \times 10^3)}{8.314}\left(\frac{1}{T_B} - \frac{1}{184.55}\right)$$

$$-1.525 \times 10^{-3} = \frac{1}{T_B} - \frac{1}{184.55} \qquad \boxed{T_B = \overset{192.7}{\cancel{256.84\,K}}\,K} \text{ Ethane}$$

Part B

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{P_2}{101325\,Pa}\right) = -\left(\frac{8.19\times10^3}{8.314}\right)\left(\frac{1}{94K} - \frac{1}{111.65K}\right)$$

$$\boxed{P_2 = 101325\,e^{-1.656} = 1.93\times10^4\,Pa}$$ methane

✓

Part C

We do the same for ethane

$$\ln\left(\frac{P_2}{101325\,Pa}\right) = \frac{-14.69\times10^3\,Pa}{8.314}\left(\frac{1}{94} - \frac{1}{184.55}\right)$$

$$\boxed{P_2 = 101325\,e^{-9.22} = 10.007\,Pa}$$ Ethane

✓

Part D

For this we use Raoult's law

mol fraction of methane = .70   mol fraction Ethane = .30

$P_A = x_A P_A^*$

On titans moon $P_{meth}^* = 1.93\times10^4\,Pa$ $x_{meth} = .70$

$P_{meth} = (.70)(1.93\times10^4\,Pa) = 1.351\times10^4\,Pa$

$P_{Eth} = (.30)(10.007\,Pa) = 3.002\,Pa$

$$\boxed{P_{meth} + P_{Eth} = 1.3513\times10^4\,Pa}$$

✓

There are 8 problems + 2 bonus problems in two parts. Each problem is 12.5 pts.

12.5

5. Calculate the degree of dissociation of N_2O_4 in the reaction $N_2O_4(g) \rightarrow 2NO_2(g)$ at 250 K and a total pressure of 0.500 bar. Do you expect the degree of dissociation to increase or decrease as the temperature is increased to 550 K? Assume that $\Delta_r H^{\circ}$ is independent of temperature.

$T = 250 K$

$P_{tot} = .5 bar$

	$N_2O_{4(g)} \rightleftharpoons$	$2NO_{2(g)}$
I	n	0
C	$-n\alpha$	$+2n\alpha$
E	$(1-\alpha)n$	$2n\alpha$
e fraction	$\frac{(1-\alpha)\cancel{n}}{(1+\alpha)\cancel{n}}$	$\frac{2\cancel{n}\alpha}{(1+\alpha)\cancel{n}}$
=	$\frac{(1-\alpha)P_{tot}}{(1+\alpha)}$	$\frac{2\alpha P_{tot}}{(1+\alpha)}$

$n - \alpha n + 2\alpha n$

$n + \alpha n$

$$K = \frac{(P_{NO_2}/p^{\circ})^2}{(P_{N_2O_4}/p^{\circ})} = \frac{(2\alpha)^2}{(1+\alpha)^2} \cdot \frac{(1+\alpha)}{(1-\alpha)} \left(\frac{P_{tot}}{p^{\circ}}\right)$$

In order to find α (Degree of dissociation we must ind K. We can do this using the gibb's energy of e reaction

$$\Delta_r G^\circ = 2\left[51.31 \times 10^3\right] - \left[97.89 \times 10^3\right]$$

$\Delta_r G^\circ = 4.73 \times 10^3$ J , From this we can find

~~K using $RT\ln(K) = -\Delta_r G^\circ$~~

$$\ln(K) = \frac{-4.73\times10^3}{(8.314)(298\text{K})} = -1.909$$

$K = .1482$, but this is K @ 298K we need K @ 250K. We use the Vant' Hoff equation. First we find

$$\Delta_r H^\circ = 2\left[33.18\times10^3\right] - \left[9.16\times10^3\right]$$

$\Delta_r H^\circ = 57.2\times10^3$ J (constant over temperature range)

$$\ln\left(\frac{K_2}{.1482}\right) = \frac{-57.2\times10^3}{8.314}\left(\frac{1}{250} - \frac{1}{298}\right)$$

$$\ln\left(\frac{K_2}{.1482}\right) = -6.879\times10^3\left(6.44\times10^{-4}\right)$$

$K = 1.76\times10^{-3}$ @ 250K , Now we can find α

$$1.76\times10^{-3} = \frac{4\alpha^2}{(1+\alpha)(1-\alpha)}\left(\frac{P_{tot}}{P^\circ}\right)$$

✓

$$4.40\times10^{-4}(1-\alpha^2) = \alpha^2(.5/1)$$

$$4.40\times10^{-4} - 4.40\times10^{-4}\alpha^2 = .5\alpha^2$$

$$\boxed{\alpha = 2.96\times10^{-2}}$$

From $\Delta_r H^\circ$, we see that this is an endothermic reaction, if we add heat (Temp increase) then according to Le chatelier's Principle the Equilibrium will shift to the right. hence $\boxed{\text{Degree of dissociation will increase @ 25}}$

6. Consider the following electrochemical cell:

$Pt(s)|H_2(g,p)|HCl(aq,b)|Hg_2Cl_2(s)|Hg(l)$

Write electrode half-reactions and the cell reaction. Determine the standard emf $E^{\varnothing}$ for this cell from standard potential data in the Data Section of your textbook. Calculate the standard Gibbs energy and the equilibrium constant for the cell reaction at 25°C. Write the Nernst equation for the cell and calculate its emf E given that the pressure of $H_2(g)$ p = 1 bar, the molality of HCl(aq) b = 1.6077 mmol kg^{-1}, and the mean activity coefficient of H^+ and Cl^- in the electrolyte solution follows the Debye-Hückel law.

12.5

Left: $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ $E^{\ominus} = 0$

Right: $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$ $E^{\ominus} = .27V$

CEll Reaction: R − L

$$\boxed{Hg_2Cl_{2(s)} + H_{2(g)} \longrightarrow 2HCl_{(aq)} + 2Hg_{(l)}}$$

$$\boxed{E^{\ominus} = (.27V - 0) = .27 \text{ Volts}}$$ ↙ $E^{\ominus}_{CEll}$

$$E^{\ominus}_{CEll} = -\frac{\Delta_r G^{\ominus}}{\nu F}, \quad \Delta_r G^{\ominus} = -\nu F E^{\ominus}_{CEll}$$

$\Delta_r G^{\ominus}$ ↙

$$\Delta_r G^{\ominus} = -(2)(9.64\times10^4)(.27V) = \boxed{-5.21\times10^4 \text{ J mol}^{-1}}$$

$$\ln(K) = \frac{(2)(9.64\times10^4)(.27V)}{(8.314)(298K)} = 21.029$$

$$\boxed{K = 1.358\times10^9}$$

✓

NErnst eq

$$E_{CEll} = E^{\ominus}_{CEll} - \frac{RT}{\nu F}\ln(Q), \quad \text{For this Cell } Q = \frac{a_{H^+}^2 a_{Cl^-}^2}{P_{H_2}}$$

$* P_{H_2} = 1$ bar

✓

$$E_{CEll} = E^{\ominus} - \frac{RT}{2F} \ln\left(a_{H+}^{2} \, a_{Cl^-}^{2} \right)$$

$$E_{CEll} = E^{\ominus} - \frac{RT}{2F} \ln\left[\left(b_{H+} \, \gamma_{\pm}(HCl)\right)^{2} \left(b_{Cl^-} \, \gamma_{\pm}(HCl)\right)^{2} \right]$$

To find $\gamma_{\pm}$ we use Debye Huckel limiting law

$$\log \gamma_{\pm} = -|z_{+} z_{-}| A I^{1/2} \qquad A = .509$$

$$I = \frac{1}{2}\left[(1.6077\times10^{-3})(1)^{2} + (1.6077\times10^{-3})(-1)^{2} \right] / b^{\ominus}$$

$$I = 1.6077\times10^{-3} \qquad \log \gamma_{\pm} = -2.04089\times10^{-2}$$

$\gamma_{\pm} = .954$ ✓

$$E_{CEll} = .27 - \frac{(8.314)(298K)}{2(9.64\times10^{4})} \, 2 \ln\left[b_{H+} \gamma_{\pm} \right]^{2}$$

$$E_{CE\,ll} = .27 - \frac{(8.314)(298)(-12.96)}{(9.64\times10^{4})}$$

$$\boxed{E_{CEll} = .603 \text{ Volts}}$$ ✓

7. Hydrogen iodide can be synthesized from its elements in a gas-phase reaction $I_2 + H_2 \rightarrow 2HI$. One proposed mechanism for the process is

step 1 $I_2 \xrightarrow{k_1} 2I$ (first order)
step 2 $2I \xrightarrow{k_2} I_2$ (second order)
step 3 $H_2 + 2I \xrightarrow{k_3} 2HI$ (first order in H_2, second order in I, third order overall)

12.5

Derive a rate law for the rate of production of HI if

a) I_2 and I are in equilibrium throughout the reaction.
b) Steady-state approximation can be applied to I atoms and $k_3[H_2] >> k_2$.

How could you determine experimentally which of these two assumptions, a) or b), is correct?

Part A

If I_2 and I are in equilibrium throughout the reaction we can use Pre-equilibrium and assume step 3 is very slow

$$V_1 = k_1[I_2] \qquad V_2 = k_2[I]^2$$

at equilibrium the rate of formation into products is equal to the rate of formation into reactants for the forward and reverse reactions

$$k_1[I_2] = k_2[I]^2 \qquad [I]^2 = \frac{k_1}{k_2}[I_2]$$

The last step happens very slowly and is critical to the formation of products, hence it is the rate determining step

$$Rate = k_3[H_2][I]^2$$, using the expression above

$$\boxed{Rate = \frac{k_1 k_3 [H_2][I_2]}{k_2}}$$ ✓

Once again

$Rate = k_3[H_2][I]^2$, I is an intermediate so we try to remove it ~~from the rate law~~

Net Rate of formation of I is

$$\frac{d[I]}{dt} = k_1[I_2] - k_2[I]^2 - k_3[H_2][I]^2$$

Using the steady state approximation we assume $\frac{d[I]}{dt} \approx 0$

$$[I]^2 = \frac{k_1[I_2]}{k_2 + k_3[H_2]}$$

, the problem also states that $k_3[H_2] >>> k_2$

this simplifies to

$$[I]^2 = \frac{k_1[I_2]}{k_3[H_2]}$$

, plugging in to the rate law

$$Rate = \frac{\cancel{k_3[H_2]}\, k_1[I_2]}{\cancel{k_3[H_2]}}$$

$$\boxed{Rate = k_1[I_2]}$$

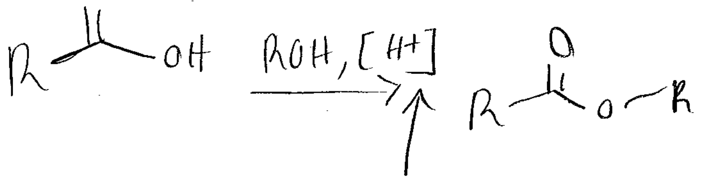
✓

One rate states that the rate is dependant only on $[I_2]$ while the other states that the rate is dependant on $[H_2]$ and $[I_2]$. This can be determined experimentally by varying the concentration of $[I_2]$ and $[H_2]$ and observing the rate. If assumption ⓑ is correct then we should be able to hold $[I_2]$ constant and change $[H_2]$ without observing a change in the rate. If this is true then ⓑ holds, if not then it must be ⓐ

8. How is a catalyst defined, and how does such a species increase the reaction rate? Can a catalyst affect the equilibrium constant? What is the difference between a homogeneous and a heterogeneous catalyst? Give some examples of homogeneous and heterogeneous catalyses.

12.5

A catalyst is a species that increases the reaction rate but is not itself consumed in the reaction. A catalyst increases the reaction rate by providing the substrate with an alternative reaction path with a lower Activation energy. A catalyst cannot affect the eq. Constant. A homogenoes catalyst is in the same phase as the reactants unlike heterogenous catalyst Which is in a different phase from the reactants. An example of heterogenous catalysis is the palladium used in the hydrogenation of Alkenes. A good example of a homogenous catalyst is acid in reactions such as the esterification of a carboxylic Acid.



Homogenous catalyst.

$T^{-1/2}$ $-\frac{1}{2} T^{-3/2}$

Bonus problems

9. Derive an expression for the internal pressure π_T for a Redlich-Kwong gas described by the following equation of state,

$$p=\frac{RT}{V_m-b}-\frac{a}{\sqrt{T}}\frac{1}{V_m(V_m+b)}$$

12.5

Express your result in terms of variables p, T, and V_m, and constants a, b, and R and simplify it as much as possible.

$$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\pi_T = T\left(\cancel{\frac{R}{V_m-b}} + \frac{a}{2(T)^{3/2}\,V_m(V_m+b)}\right)$$

$$-\cancel{\frac{RT}{V_m-b}} + \frac{a}{\sqrt{T}\,V_m(V_m+b)}$$

$$\pi_T = a\left(\frac{T}{2(T)^{3/2}\,V_m(V_m+b)} + \frac{1}{\sqrt{T}\,V_m(V_m+b)}\right)$$

$T^{2/2} \cdot T^{-\frac{3}{2}}$

$$\pi_T = \frac{a}{V_m(V_m+b)}\left(\frac{1}{2\sqrt{T}} + \frac{1}{\sqrt{T}}\right)$$

$$\pi_T = \frac{a}{V_m(V_m+b)}\left(\frac{1+2}{2\sqrt{T}}\right)$$

$$\boxed{\pi_T = \frac{3a}{2\sqrt{T}\,V_m(V_m+b)}}$$ ✓

10. The dissociation of 5.25 g of a non-volatile substance in 565 g of benzene raises the boiling point by 0.625 °C. Note that the ebullioscopic constant $K_b = 2.53$ K kg mol^{-1} and the cryoscopic constant $K_f = 5.12$ K kg mol^{-1}, and the density of benzene is 876.6 kg m^{-3}. Calculate the freezing point depression, the molar mass of the solute, the osmotic pressure at 298 K, and the vapor pressure above the solution at 298 K taking that $p^*_{\text{benzene}} = 103$ Torr at this temperature.

12.5

$\Delta T = K_f b$

b = molality of solute
ΔT is freezing point depression

$$b = \frac{\Delta T_{bp}}{k_b} = \frac{0.625\ \cancel{K}}{2.53\ \cancel{K}\,kg/mol} = 0.247\ mol/kg$$

$$\Delta T = (5.12\ K\,\cancel{kg/mol})(0.247\ \cancel{mol}/\cancel{kg}) = \boxed{1.265\ K}$$ ✓

$$\cancel{mw_{solute}} = \quad b = \frac{n_{solute}}{(n_{solv}/m_{solv})/1000}$$

$$X_{solute} = \frac{n_{solv}}{n_{solute}} =$$

$$\frac{0.247\ mol\ solute}{1\ \cancel{kg}}\ \frac{1\ \cancel{kg}}{1000\ g}\ 565\ g = 0.13956\ mol\ \cancel{solute}$$

5.25 g solute

0.8766 g/mL

$$\frac{5.25\ g\ solute}{0.13956\ mol\ solute} = \boxed{37.62\ g/mol}$$ ✓

$$\frac{\cancel{565\ g}\ Benzene}{0.8766\ g/mL}$$

$$\Pi = [B]RT \qquad [B] = \frac{n_{solute}}{V} = \frac{0.13956\ mol}{0.64454\ L}$$

$[B] = 0.217$ ✓

$$\Pi = (0.217)(0.08206)(298) = \boxed{5.295\ atm}$$

$\cancel{P_{Benz} =}$

$$x_{Benz} = \frac{n_{Benz}}{n_{total}} = 0.981$$

$$565\ g \,\Big|\, \frac{1\ mol}{78.11\ g} = 7.233\ mol$$

$x_{solute} = 0.0189$

$$5.25\ g \,\Big|\, \frac{1\ mol}{37.62\ g} = 0.13955$$

~~$P_{Benz} = 0.981(103)$~~
~~$= 101.053$~~

$$\Delta P_{Benze} = -X_{solute}(P^*_{Benze})$$

$n_{tot} = 7.373\ mol$

$$(-0.0189)(10.3)$$

$\Delta P_{Benze} = 1.9467$ ✓

$$P_{total} = 103\ Torr - 1.9467 = \boxed{101.053\ Torr}$$

1. A balloon filled with $\overset{V_1}{\text{13.25 L}}$ of He at $\overset{T_1}{\text{15.4°C}}$ and $\overset{P_1}{\text{1.0 atm}}$ rises to a height where the pressure is $\overset{P_2}{\text{248}}$ Torr and the temperature is $\overset{T_2}{\text{-30.5°C}}$. What is the final volume of the balloon? Assume that the pressure inside and outside the balloon is the same.

$PV = nRT$

$V_1 = 13.25\text{ L}$

$T_1 = (15.4 + 273.15)\text{ K} = 288.55\text{ K}$

$P_1 = 1\text{ atm} \cdot \frac{760\text{ Torr}}{1\text{ atm}} = 760\text{ Torr}$

$V_2 = ?$

$T_2 = (-30.5 + 273.15)\text{ K} = 242.65$

$P_2 = 248\text{ Torr}$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\Downarrow$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$= \frac{(760\text{ Torr})(13.25\text{ L})(242.65\text{ K})}{(288.55\text{ K})(248\text{ Torr})}$$

$$= \boxed{34.15\text{ L}}$$ ✓

12.5

2. A 67.0 g piece of gold at 725 K is dropped into 165 g of $H_2O(l)$ at 298 K in an insulated container at 1 bar pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that $C_{p,m}$ for Au and H_2O is constant at its value for 298 K throughout the temperature range of interest. Calculate ΔS for this process.

$\text{Au} = 67\text{ g} \quad C_p = 0.129\ \text{J/gC}$

$T_A = 725\text{ K}$

$\boxed{10.5}$

$H_2O = 165\text{ g} \quad C_p = 4.184\ \text{J/g}\cdot\text{C}$

$T_W = 298$

$$-m_A C_{pA}(T_{eq} - T_A) = m_W C_{pW}(T_{eq} - T_W)$$

$$67 \times 0.129(725 - T_{eq}) = 165 \times 4.184(T_{eq} - 298)$$

➡ $T_{eq} = 303.28$ ✓

$Q = 3645\text{ J}$

$$\Delta S_{\text{gold}} = m\int \frac{C_p}{T}dT = C_{pA}\ln\frac{T_2}{T_1} = -0.1124\ \text{J/g°C} \times 67\text{g} = \cancel{-7.53}\ \text{J/°C}$$

calc. errors

$$\Delta S_{\text{water}} = m\int \frac{C_p}{T}dT = C_{pw}\ln\frac{T_2}{T_1} = 0.44\ \text{J/g°C} \times 165\text{ g} = \cancel{72.61}\ \text{J/°C}$$

$$\Delta S = \Delta S_{Au} + \Delta S_{H_2O}$$ – should be $+4.606\ \frac{\text{J}}{\text{K}}$

3. Consider the following reaction of oxidation of solid urea:

$\nu_1 CO(NH_2)_2(s) + \nu_2 O_2(g) \rightarrow \nu_3 CO_2(g) + \nu_4 H_2O(l) + \nu_5 N_2(g)$

a) Balance the equation.
b) Calculate $\Delta_r H^\varnothing$, $\Delta_r U^\varnothing$, $\Delta_r S^\varnothing$, $\Delta_r G^\varnothing$, and equilibrium constant K for this reaction at 298.15 K.
c) Calculate $\Delta_r H^\varnothing$ at 450 K.
d) Assuming that the change in $\Delta_r H^\varnothing$ from 298.15 K to 450 K is not significant, calculate $\Delta_r G^\varnothing$ and K at 450 K.
e) Compare your results for $\Delta_r G^\varnothing$ and K at 298.15 and 450 K and explain them in terms of Le Chatelier's principle.
f) How will an increase in pressure (by compressing the reaction mixture) affect the equilibrium composition?

$\boxed{10.5}$

a) $2CO(NH_2)_2 + 3O_2 \rightarrow 2CO_2 + 4H_2O + 2N_2$

b) $\Delta_r H^\varnothing = \sum_{\text{products}} \Delta_f H^\circ - \sum_{\text{reactants}} \Delta_f H^\circ$

$\Delta_r H^\varnothing = (2 \times -393.51 \text{ kJ/mol} + 4 \times -285.83 \text{ kJ/mol}) - (2 \times -333.51 \text{ kJ/mol})$

$\boxed{\Delta_r H^\varnothing = -1263.32 \text{ kJ/mol}}$ ✓

$\Delta_r S^\varnothing = (2 \cdot 213.74 \text{ J/mol K} + 4 \cdot 69.91 \text{ J/mol K} + 2 \cdot 191.61 \text{ J/mol K}) - (2 \times 104.60 \text{ J/mol K} + 3 \cdot 205.138 \text{ J/mol K})$

$\boxed{\Delta_r S^\varnothing = 265.73 \text{ J/mol K}}$ ✓

$\Delta_r G^\varnothing = \Delta_r H^\circ - T\Delta_r S^\circ$

$\Delta_r G^\varnothing = -1263.32 \text{ kJ/mol} - 298.15\text{K} \times 0.26573 \text{ kJ/mol}$

$\boxed{\Delta_r G^\circ = -1342.55 \text{ kJ/mol}}$ ✓

$$\Delta_r U^\circ = \underline{\qquad} \qquad \Delta_r H^\circ - \Delta n_g RT$$

$\Delta_r G^\varnothing = -RT\ln K$

$-1342550 \text{ J/mol} = -R \times 298.15\text{K} \cdot \ln K$

$\boxed{K = 1.6462 \times 10^{235}}$ ✓

c) $\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p (T_2 - T_1)$

$\Delta H_{450K} = -1263320 \text{ J/mol} + ((2 \cdot 37.11 \text{ J/mol K} + 4 \cdot 75.291 \text{ J/mol K} + 2 \cdot 29.125 \text{ J/mol K}) - (2 \cdot 93.14 \text{ J/mol K} + 3 \cdot 29.355 \text{ J/mol K}) \times (450\text{K} - 298.15\text{K})$

$\Delta H_{450K} = -1239 \text{ kJ/mol K}$ ✓

d) $\frac{\Delta_r G_2}{T_2} - \frac{\Delta_r G_1}{T_1} = \Delta_R H \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$\frac{\Delta_r G_{450K}}{450K} - \frac{-1342.55 \text{ kJ/mol}}{298.15K} = -1263.32 \text{ kJ/mol} \left(\frac{\overset{3}{1}}{450K} - \frac{1}{298.15K} \right)$ $\boxed{\Delta_r G_{450K} = -1383 \text{ kJ/mol}}$ ✓

Continue on back →

$-1363000\ \text{J/mol} = -R \cdot 950\text{K} \cdot \ln K_{950K}$

$$\boxed{K_{950K} = 3.38 \cdot 10^{260}}$$ ✓

e) K is smaller at 950K. This makes sense because the reaction is exothermic, so adding heat will shift the equilibrium toward the reactants ✓

f) Since there are more moles of gas on the products side, increasing pressure will shift the equilibrium toward the reactants! ✓

4. One of the effects of climate change related to global warming caused by combustion of fossil fuels is the increase of concentration of CO_2 dissolved in water (in the oceans, seas, lakes, etc.). Considering that the partial pressure of CO_2 in the air increased from 2.8×10^{-4} atm in pre-industrial times to 3.6×10^{-4} atm now, calculate the increase of molality of CO_2 in the water solution.

12.5

1 atm total pressure $P_{CO_2} = 2.8\times10^{-4}\,\text{atm}$, $x_{CO_2} = \frac{P_{CO_2}}{P_{total}} = 2.8\times10^{-4}$

Henry's Law

$$P_{CO_2,1} = b_{CO_2} K_{CO_2} \Rightarrow b_{CO_2} = \frac{P_{CO_2}}{K_{CO_2}} = \frac{2.8\times10^{-4}\,\text{atm}}{30.1\times10^{3}} = \frac{.028371\,\text{kPa}}{30.1\times10^{3}\,\text{kPa}}\frac{\text{mol}}{\text{kg}} = 9.426\times10^{-7}\,\text{mol/kg}$$ pre-industry ✓

$$b_{CO_2,2} = \frac{P_{CO_2}}{K_1} = \frac{.036477}{30.1\times10^{3}} = 1.212\times10^{-6}\,\text{mol/kg}$$ ✓

$$b_2 - b_1 = 1.212\times10^{-6} - 9.426\times10^{-7} = 2.693\times10^{-7}\,\text{mol/kg}$$ increase in dissolved CO_2 ✓

Bonus 1. One mole of an alkane C_nH_{2n+2} is burned in excess of oxygen to form $CO_2(g)$ and $H_2O(l)$ at 298.15 K and 1 bar of pressure. At constant pressure, the heat released in the process is found to be 4816.8 kJ. If the products of the combustion at 298.15 K and 1 bar of pressure are $CO_2(g)$ and $H_2O(g)$, the heat released is 4464.7 kJ. Determine the molecular formula of the alkane and its standard enthalpy of formation.

$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)\,H_2O$

$n \cdot -393.51\ \text{kJ/mol} + (n+1) \cdot -285.83\ \text{kJ/mol} - \Delta H_{alkane} = -4816.8\ \text{kJ/mol}$

$n \cdot -393.51\ \text{kJ/mol} + (n+1) \cdot -241.82\ \text{kJ/mol} - \Delta H_{f\,alkane} = -4464.7\ \text{kJ/mol}$

$n = 7$ ✓

$\Delta H_{f\,alkane} = -224.72\ \text{kJ/mol}$ ✓

alkane = C_7H_{16}

12.5

5. Consider the equilibrium $NO_2(g) \leftrightarrows NO(g) + (1/2)O_2(g)$. 1 mole of $NO_2(g)$ is placed in a vessel and allowed to come to equilibrium at a total pressure of 1 bar. An analysis of the content of the vessel gives the following results:

T	600 K	900 K
$p(NO)/p(NO_2)$	0.224	5.12

12.5

a) Calculate the equilibrium constant K at 600 and 900 K.

b) Calculate $\Delta_r G^{\varnothing}$ and $\Delta_r H^{\varnothing}$ for this reaction at 298.15 K, using only the data in the problem. Assume that $\Delta_r H^{\varnothing}$ is independent of temperature.

c) Calculate $\Delta_r G^{\varnothing}$ and $\Delta_r H^{\varnothing}$ at 298.15 K using thermochemical data tables and compare your answer with that obtained in part b).

A)

at 600°k

$P_{NO} = 0.224\, P_{NO_2} \rightarrow y_{NO} = \frac{0.224}{1.336}$

$P_{O_2} = 0.112\, P_{NO_2} \rightarrow y_{O_2} = \frac{0.112}{1.336}$

$P_T = 1\,\text{bar} = 1.336\, P_{NO_2} \rightarrow y_{NO_2} = \frac{1}{1.336}$

$\Rightarrow K_{600°k} = \frac{y_{O_2}^{1/2}\, y_{NO}}{y_{NO_2}} = 0.0648$ ✓

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at 900°k

$P_{NO} = 5.12\, P_{NO_2} \rightarrow y_{NO} = \frac{5.12}{8.68}$

$P_{O_2} = 2.56\, P_{NO_2} \rightarrow y_{O_2} = \frac{2.56}{8.68}$

$P = 8.68\, P_{NO_2} = 1\,\text{atm} \rightarrow y_{NO_2} = \frac{1}{8.68}$

$\Rightarrow K_{900°k} = \frac{y_{O_2}^{1/2}\, y_{NO}}{y_{NO_2}} = 2.78$ ✓

B)

$\ln k_2 - \ln k_1 = -\frac{\Delta_r H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow \boxed{\Delta H = +56.269\ \text{kj/mol}}$ ✓

3.76   900   600

$\ln k_1 - \ln k_0 = -\frac{\Delta H}{R}\left(\frac{1}{600} - \frac{1}{298}\right) \Rightarrow \ln k_0 = -14.16 \rightarrow \boxed{\Delta_r G^{\varnothing} = 35.082\ \text{kj/mo}}$ ✓

	NO_2	$\rightarrow$ NO	$+ \frac{1}{2} O_2$
ΔH_f	33.18	90.25	0
$\Delta G^{\varnothing}$	51.31	86.55	0

$\Rightarrow \boxed{\Delta_r H^{\varnothing} = 90.25 - 33.18 = 57.07\ \text{kj/mol}}$ ✓

$\Rightarrow \boxed{\Delta_r G^{\varnothing} - 86.55 - 51.31 = 35.24\ \text{kj/mol}}$ ✓

12.5

6. Consider the following electrochemical cell:

$$\mathrm{Pt(s)|H_2(g,}p\mathrm{)|HCl(aq,}b\mathrm{)|AgCl(s)|Ag(s)}$$

Write electrode half-reactions and the cell reaction. Determine the standard emf $E^{\varnothing}$ for this cell from standard potential data in the Data Section of your textbook. Calculate the standard Gibbs energy and the equilibrium constant for the cell reaction at 25°C. Write the Nernst equation for the cell and calculate its emf E given that the pressure of $H_2(g)$ p = 1 bar, the molality of HCl(aq) b = 0.01 mol kg^{-1}, and the mean activity coefficient of H^+ and Cl^- in the electrolyte solution follows the Debye-Hückel limiting law.

L: $2H^+ + 2e^- \rightarrow H_2(g)$ $E^{\varnothing} = 0$ ✓

R: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ $E^{\varnothing} = 0.22$ ✓

$E = 0.22 - 0 = 0.22\ V = -\dfrac{\Delta_r G^{\varnothing}}{F} \Rightarrow \Delta_r G^{\varnothing} = -2.12 \times 10^{+4}\ J\ mol$ ✓

$\ln k = \dfrac{FE}{RT} \Rightarrow \ln k = 8.56 \Rightarrow k = 5218$ ✓

$E_{cell} = E^{\ominus} - \dfrac{RT}{F} \ln Q$

$Q = \dfrac{a_{H^+}\, a_{Cl}}{p_{H_2} \rightarrow 1} = \left[b_{H^+} \gamma_{HCl} \times b_{Cl^-} \gamma_{HCl}\right]$

$A = 0.509$ $I = \frac{1}{2}\left[0.01(+1)^2 + 0.01(-1)^2\right] = 0.01 \rightarrow \log \gamma_{\pm} = -0.0509$

$\gamma = 0.89$ ✓

$\Rightarrow E_{cell} = 0.22 - \dfrac{8.314 \times 298}{9.64 \times 10^4} \ln\left[0.01 \times 0.89\right]^2 = 0.\cancel{463}\ (V)$ OK

~~0.37~~

0.46

12.5

7. Consider the following mechanism of ozone thermal decomposition:

$$O_3 \xrightarrow{k_1} O_2 + O$$
$$O_2 + O \xrightarrow{k_{-1}} O_3$$
$$O_3 + O \xrightarrow{k_2} 2O_2$$

a) Derive the rate law expression for the loss of O_3.
b) Under what conditions will the rate law expression for O_3 decomposition be first order with respect to O_3? What is the overall rate constant for O_3 decomposition in this case? What is the reaction rate-determining step then? Give a qualitative explanation of your result for the overall rate constant for O_3 decomposition in this case.

a) $$-\frac{d[O_3]}{dt} = k_1[O_3] - k_{-1}[O_2][O] + k_2[O_3][O]$$

$$\frac{d[O]}{dt} = k_1[O_3] - k_{-1}[O_2][O] - k_2[O_3][O] = 0$$

$$\Downarrow$$

$$k_1[O_3] = k_{-1}[O_2][O] + k_2[O_3][O]$$

$$\Downarrow$$

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$

$$\boxed{-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}}$$

b) For O_3 decomposition to be first order with respect to O_3, k_2 should be significantly greater than k_{-1}

The current rate law expression

$$\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}$$

becomes ....

$$-\frac{d[O_3]}{dt} = 2k_1[O_3] \quad b/c \quad k_2[O_3] >> k_{-1}[O_2]$$

which means $k_2[O_3] + k_{-1}[O_2] = k_2[O_3]$.

This means the decomposition of O_3 is first order overall

which $k_2 >> k_{-1}$

8. A certain reaction is first order, and 540 s after initiation of the reaction, 32.5% of the reactant remains.

(a) What is the rate constant for this reaction?

(b) At what time after initiation of the reaction will 10% of the reactant remain?

(a) $k = \frac{1}{t} \ln\left(\frac{[A]}{[A]_0}\right)$ $[A] = 0.325[A]_0$

$= \frac{1}{540\,s} \ln\left(\frac{1}{0.325}\right)$

$= \boxed{2.08 \times 10^{-3}\ s^{-1}}$ ✓

12.5

(b) $k = \frac{1}{t} \ln\left(\frac{[A]}{[A]_0}\right)$

$\Downarrow$

$t = \frac{1}{k} \ln\left(\frac{[A]}{[A]_0}\right)$

$= \frac{1}{2.08 \times 10^{-3}\,s^{-1}} \ln\left(\frac{1}{0.10}\right)$

$= \boxed{1.11 \times 10^{3}\ s}$

✓

Bonus 2. Show that the ratio of the half-life to the one-quarter-life, $t_{1/2}/t_{1/4}$, for a reaction that is nth order ($n > 1$) in reactant A can be written as a function of n alone (that is, there is no concentration and rate constant dependence in the ratio). To achieve this, derive the expression for $t_{1/2}/t_{1/4}$. What is $t_{1/2}/t_{1/4}$ for a second-order reaction? How your result compares with $t_{1/2}/t_{1/4}$ for a first-order reaction? (Note: the one-quarter-life is defined as the time at which the concentration falls to ¼ of the initial concentration.)

12.5

$$\frac{dC_A}{dt} = k\,C_A^{\,n} \qquad\qquad \frac{dC_A}{C_A^{\,n}} = k\,dt$$

$$\int_{C_{A_0}}^{C_A} C_A^{-n}\,dC_A = -kt \rightarrow kt = \frac{C_{A_0}^{1-n} - C_{A_1}^{1-n}}{1-n} - = kt$$

$$t_{1/2} = \frac{C_{A_0}^{1-n}\cdot\left(1 - 1/2^{\,1-n}\right)}{(1-n)k}$$

$$t_{1/4} = \frac{C_{A_0}^{1-n}\left(1 - 1/4^{\,1-n}\right)}{(1-n)k} \rightarrow \frac{t_{1/2}}{t_{1/4}} = \frac{1 - 1/2^{\,1-n}}{1 - 1/4^{\,1-n}} \Rightarrow \frac{t_{1/2}}{t_{1/4}} = f(n)$$

✓ ✓

$$n = 2 \rightarrow \frac{t_{1/2}}{t_{1/4}} = 0.33$$

$$\frac{dC_A}{dt} = -kC_A \rightarrow \ln\frac{C_A}{C_{A_0}} = -kt \rightarrow t_{1/2} = \frac{\ln 2}{k}$$

$$n = 1 \Rightarrow \quad \left.\begin{matrix} \\ t_{1/4} = \dfrac{\ln 4}{k} \end{matrix}\right\} \rightarrow \frac{t_{1/2}}{t_{1/4}} = 0.5 \;;\; n=1$$

✓