

Constants: $F=96485 \text{ C/mol}$
 $1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$

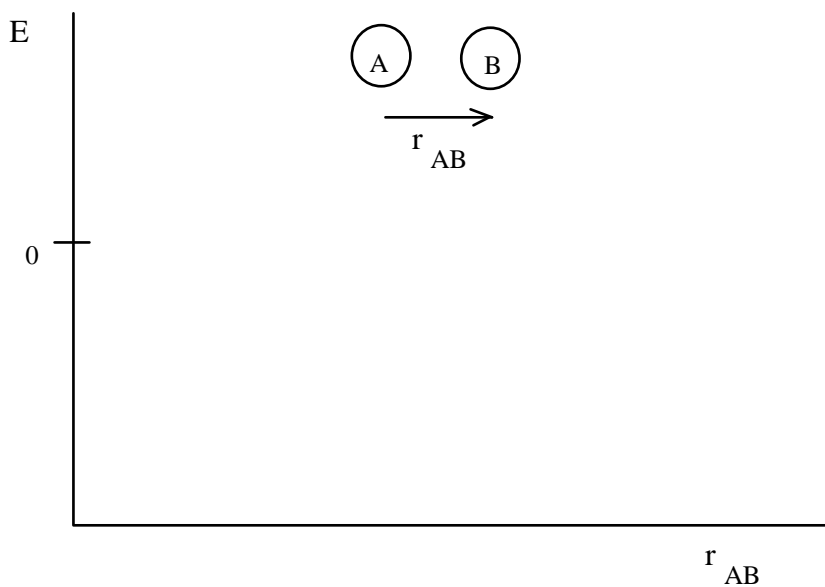
$R=8.314$ (you know units)
 $1 \text{ bar} = 750.1 \text{ torr}$

$2.303RT/F=0.05916 \text{ V}$
 $RT/F=0.02569 \text{ V}$

Part I.

Answer **9** of the following **11** questions. If you answer more than **9**, cross out the ones you wish not to be graded. Only the first **9** questions will be graded. (11 points each.)

1. A solution of solvent A and solute B has relative forces $A-A$, $B-B < A-B$. Are the activity coefficients for the solvent less than one or greater than one?
2. The half life of the reaction $2A \rightarrow B$ was unaffected by the initial concentration of A. What is the order of the reaction with respect to A?
3. On the plot below sketch the Lennard-Jones (Van der Waals) energy curve for two atoms separated by a distance r_{AB} . Label the distance that is the sum of the Van der Waal's radii of the two atoms on the plot.



4. Write the K_{sp} expression for Ag_2SO_4 in pure water. The result should be expressed in terms of K_{sp} , γ_{\pm} and m_s , the solubility.

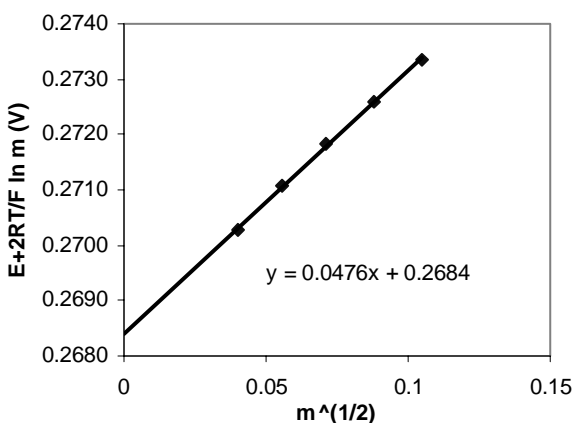
5. Calculate the ionic strength of m-molar $\text{Cr}_2(\text{SO}_4)_3$. The result should be expressed in terms of m.

6. The rate constant for the disappearance of chlorine in the reaction of NO with Cl_2 to form NOCl is $4.5 \text{ M}^{-2} \text{ s}^{-1}$ at 0.0°C and $8.0 \text{ M}^{-2} \text{ s}^{-1}$ at 22.0°C . What is the activation energy for this reaction?

7. The emf of the cell $\text{Pt}|\text{H}_2(\text{g}, P^\ominus)|\text{HCl}(\text{aq}, m)|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Hg}(\text{l})$ gives the voltages (at 298.15 K):

$m/(\text{mol kg}^{-1})$	1.6077×10^{-3}	3.0769×10^{-3}	5.0403×10^{-3}
E	0.60080	0.56825	0.54366 V
$E + 2RT/F \ln(m)$	0.27026	0.27106	0.27183 V

A plot of $E + 2RT/F \ln(m)$ versus $m^{1/2}$ is shown below based on the voltages, above. Determine the standard emf of the cell and the mean ionic activity coefficient of HCl at $1.6077 \times 10^{-3} \text{ m}$.



For problems 8 and 9:

For the reaction $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ at equilibrium at two temperatures:

T/K	P(NO ₂)/mmHg	P(N ₂ O ₄)/mmHg
298.	46.0	23.0
305.	68.0	30.0

(You can use a 1 atm standard state if you like, rather than a 1 bar standard state, but in any event remember to take the standard state into account.)

8. Calculate $\Delta_r G^\circ$ for the reaction at 298. K.

9. Calculate $\Delta_r H^\circ$ for the reaction (over the temperature range of the experiment).

10. At 30°C the vapor pressures of pure toluene and pure benzene are 36.7 and 118.2 torr, respectively, and the two liquids form an ideal solution. For a solution containing 0.500 mole fraction toluene, calculate the total vapor pressure and the mole fraction of toluene in the vapor phase.

11. Calculate the cell voltage of the cell $\text{Zn} | \text{Zn}^{2+}(0.500\text{m}) | \text{Cu}^{2+}(0.100\text{m}) | \text{Cu}$. Note the concentrations of the Zn^{2+} and Cu^{2+} . Use the standard cell potentials at the front of the room. The activity coefficients from standard tables are for $\text{Zn}^{2+}(0.500\text{m})$: $\gamma_{\pm} = 0.0630$ and for $\text{Cu}^{2+}(0.100\text{m})$: $\gamma_{\pm} = 0.160$ when sulfate salts are used to make the cell. $T = 298.15 \text{ K}$

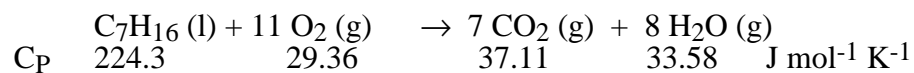
Part III

Answer **3** of the following **4** questions. If you answer more than **3**, cross out the one you wish not to be graded. Only the first **3** questions will be graded. (12 points each.)

1. Calculate the standard internal energy of formation of liquid methyl acetate, $\text{C}_3\text{H}_6\text{O}_2$, from its standard enthalpy of formation, which is $-442.0 \text{ kJ mol}^{-1}$ at 298.15 K .

2. For a closed system, $dS_{\text{univ}} = \left(\frac{1}{T} - \frac{1}{T_{\text{surr}}}\right)dq + \left(\frac{P}{T} - \frac{P_{\text{ext}}}{T}\right)dV$. Argue that for an adiabatic process the work term always gives $dS_{\text{univ}} > 0$ for a spontaneous process.

3.) $\Delta_r H^\circ$ for the following reaction is $-4854 \text{ kJ mol}^{-1}$ at 298. K. This would be a reasonable guess for the heat of combustion of gasoline in an automobile engine, except that the temperature in an engine is more like 500. K. Calculate $\Delta_r H^\circ$ at 500. K. The heat capacities are listed below the corresponding reactants and products.



4. Instead of assuming that the volume of a condensed phase is constant when pressure is applied, assume only that the compressibility, κ_T , is constant. Starting at an initial volume of V_o and an initial pressure of P_o show that, when the pressure is changed isothermally by Δp , G changes to

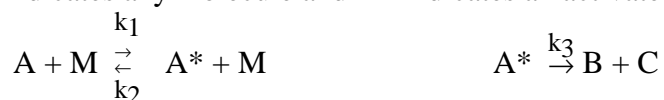
$$\Delta G = V_o \Delta p (1 - \frac{1}{2} \kappa_T \Delta p) \quad \text{or equivalently} \quad \Delta G = V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2$$

where $\Delta p = P - P_o$. (You can end up with either formula; they are the equivalent.)

Part III

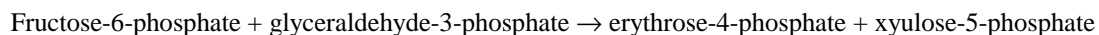
5. 15pts) One mole of an ideal monoatomic gas is expanded adiabatically and reversibly from an initial pressure of 5.00 atm and temperature of 298 K to a final temperature of 115 K. Calculate q , w , and ΔU .

6. 15pts) The following mechanism has been suggested to explain how first order reactions occur. The M indicates any molecule and A* indicates an activated reactant molecule:



The corresponding rate law is: $\frac{d[B]}{dt} = \frac{k_1 k_3 [A][M]}{k_2 [M] + k_3}$. (a) Use the steady state approximation on [A*] to show that the mechanism agrees with the given rate law. Since you have the answer, make sure to show all your steps.

7. 15pts) Under standard conditions, one of the steps in the photosynthetic production of glucose does not occur spontaneously:



where $\Delta_r G^\circ = +6.28 \text{ kJ mol}^{-1}$ at 298.2K. Schematically write this reaction as $F + G \rightarrow E + X$.

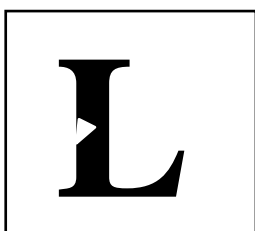
Can this reaction take place spontaneously in a chloroplast where the concentrations are as follows? $F=53.0 \times 10^{-5} \text{M}$, $G=3.20 \times 10^{-5} \text{M}$, $E=2.00 \times 10^{-5} \text{M}$, $X=2.10 \times 10^{-5} \text{M}$

(Make sure to show all of your work for full credit.)

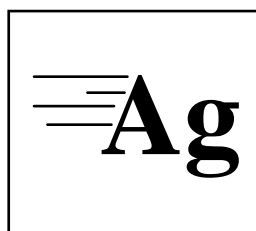
8. 20pts) Show that $\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P$

Make sure to **include the reasons** for each step. For example, you might use statements such as "since H is a state function", "from the definition of heat capacity(or whatever)", or "dividing by dP gives the desired result", etc.

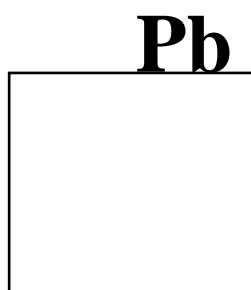
Extra credit (2 pts each, 4 points max): Decipher the pictograms below. The first one is an example.



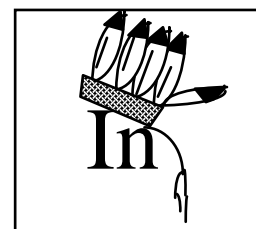
Nicked-L = Nickel



Element name



Saying



Element name