

# Physical Chemistry

Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.

1. (10 points) Ultrahigh vacuum studies typically use pressures on the order of  $10^{-10}$  torr. How many collisions occur with  $1 \text{ cm}^2$  of an ultrahigh-vacuum chamber at this pressure and at  $T = 298.15 \text{ K}$  in one nanosecond? [Assume the gas is air and has an average molecular weight of  $29 \text{ g mole}^{-1}$ .]

The wall-collision frequency is given by the following equation, assuming ideal-gas behavior (which should be good at this low pressure):

$$\begin{aligned} Z_{\text{wall}} &= \sqrt{\frac{P^2}{2\pi mkT}} \\ &= \sqrt{\frac{(10^{-10} \text{ torr} \times 133.322 \text{ Pa / torr})^2}{2\pi \left( \frac{0.029 \text{ kg mol}^{-1}}{6.02211415 \times 10^{23} \text{ molecule mol}^{-1}} \right) 1.3806505 \times 10^{-23} \text{ J K}^{-1} 298.15 \text{ K}}} \\ &= \sqrt{\frac{1.7774756 \times 10^{-16} \text{ Pa}^2}{1.2455107 \times 10^{-45} \text{ kg J}}} = \sqrt{1.427106 \times 10^{29} \text{ m}^{-4} \text{ s}^{-2}} \\ &= 3.78 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1} \end{aligned}$$

Having the collision frequency allows one to calculate the number of collisions with a given area in a given time:

$$\begin{aligned} N_{\text{coll}} &= Z_{\text{wall}} (\text{Area})(\text{time}) \\ &= (3.78 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}) (1 \text{ cm}^2 \times 10^{-4} \text{ m}^2 / \text{cm}^2) (1 \times 10^{-9} \text{ s}) \\ &= 37.8 \end{aligned}$$

Of course, there can only be an integral number of collisions in any specific nanosecond, so the answer is 37-38 collisions, or thereabouts.

**DO NOT WRITE  
IN THIS SPACE**

p. 1 \_\_\_\_\_/10

p. 2 \_\_\_\_\_/10

p. 3 \_\_\_\_\_/15

p. 4 \_\_\_\_\_/10

p. 5 \_\_\_\_\_/10

p. 6 \_\_\_\_\_/15

p. 7 \_\_\_\_\_/10

p. 8 \_\_\_\_\_/10

p. 9 \_\_\_\_\_/10

p. 10 \_\_\_\_\_/10

p. 11 \_\_\_\_\_/10

p. 12 \_\_\_\_\_/15

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p. 13 \_\_\_\_\_/10  
(Extra credit)

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TOTAL PTS

/135

2. (10 points) Match the best ending of the phrase from the right column with the beginning of the phrase from the left column:

<p>1) An adiabatic process occurs with no <b>(g) heat transfer</b></p> <p>2) <math>U</math> and <math>V</math> are the examples of <b>(q) state functions</b></p> <p>3) A process the direction of which can be changed by an infinitesimal change in the driving force is <b>(o) reversible</b></p> <p>4) The Joule-Thompson experiment is an example of a process that is <b>(i) isenthalpic</b></p> <p>5) An energy change in a system that does not involve the flow of heat across the boundary is <b>(s) work</b></p> <p>6) The condition at which a real gas tends to have P-V behavior like an ideal gas is characterized by the <b>(b) Boyle temperature</b></p> <p>7) The conditions for which a table of properties is given define the <b>(p) standard state</b></p> <p>8) A description of the equation of state of a gas in terms of the reduced variables suggests the hypothesis of the <b>(l) law of corresponding states</b></p> <p>9) "Two objects in thermal equilibrium with a third object are in thermal equilibrium with each other" is a statement of the <b>(t) zeroth law of thermodynamics</b></p> <p>10) In the Carnot cycle, there are two steps that are adiabatic and two steps that are <b>(k) isothermal</b></p>	<p>a) Anharmonic corrections</p> <p>b) Boyle temperature</p> <p>c) Compression factor</p> <p>d) Entropy</p> <p>e) First law of thermodynamics</p> <p>f) Heat capacity</p> <p>g) Heat transfer</p> <p>h) Irreversible</p> <p>i) Isenthalpic</p> <p>j) Isochoric</p> <p>k) Isothermal</p> <p>l) Law of corresponding states</p> <p>m) Path functions</p> <p>n) Random functions</p> <p>o) Reversible</p> <p>p) Standard state</p> <p>q) State functions</p> <p>r) Third law of thermodynamics</p> <p>s) Work</p> <p>t) Zeroth law of thermodynamics</p>
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**3. (15 points)** To determine an adiabatic flame temperature for burning of a substance in air, the effect of heating the nitrogen to high temperature must be considered. As accurately as possible, calculate the amount of heat required to raise the temperature of one mole of nitrogen from 298.15 K to 3000 K at a constant pressure of 1 bar.

This is just the change in enthalpy for heating nitrogen at constant pressure. By integration of the heat capacity, one gets a formula for this:

$$\begin{aligned}\Delta H^\theta &= \int_{T_1}^{T_2} C_{Pm}^\theta dT = \int_{T_1}^{T_2} \left( c_1 + c_2 T + c_3 T^2 + c_4 T^3 + \frac{c_5}{T^2} \right) dT \\ &= c_1 (T_2 - T_1) + \frac{c_2}{2} (T_2^2 - T_1^2) + \frac{c_3}{3} (T_2^3 - T_1^3) + \frac{c_4}{4} (T_2^4 - T_1^4) - c_5 \left( \frac{1}{T_2} - \frac{1}{T_1} \right)\end{aligned}$$

The heat capacity coefficients for nitrogen (on a molar basis) are given in Table 5.6. Substitution of these and the temperatures into the equation gives this result in joules per mole:

$$\begin{aligned}\Delta H^\theta &= (26.09200)(3000 - 298.15) + \frac{8.218801 \times 10^{-3}}{2} (3000^2 - 298.15^2) - \frac{1.976141 \times 10^{-6}}{3} (3000^3 - 298.15^3) \\ &\quad + \frac{0.159274 \times 10^{-9}}{4} (3000^4 - 298.15^4) - 0.044434 \times 10^6 \left( \frac{1}{3000} - \frac{1}{298.15} \right) \\ &= 70496.6702 + 36619.3058 - 17767.8107 + 3224.9839 + 134.22103 \\ &= 92707.4 \text{ J mol}^{-1}\end{aligned}$$

**4. (10 points)** For a gas that obeys the Redlich-Kwong equation of state, derive a formula (showing all work) for the derivative of the entropy with respect to volume at constant temperature.

One may use a Maxwell relationship given in Table 5.3 to solve this problem:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

One finds the expression for the pressure of a Redlich-Kwong gas from section 4 of the Handbook. Substitution gives:

$$\begin{aligned}\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial}{\partial T}\left(\frac{RT}{V_m - b} - \frac{a}{T^{1/2}V_m(V_m + b)}\right)\right)_V \\ &= \left(\frac{\partial}{\partial T}\left(\frac{RT}{V_m - b}\right)\right)_V - \left(\frac{\partial}{\partial T}\left(\frac{a}{T^{1/2}V_m(V_m + b)}\right)\right)_V \\ &= \frac{R}{V_m - b} + \frac{a}{2T^{3/2}V_m(V_m + b)}\end{aligned}$$

**5. (10 points)** For each reaction on the left side of the Table, give the numerical value (along with proper units) of the quantity indicated in the right-hand box, at 298.15 K. Show work below the box, but put your answer in the box.

Reaction	Quantity
(a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(liq)$	$\Delta H^\theta = -571.6 kJ$
(b) $I_2(g) \rightarrow 2I(g)$	$\Delta S^\theta = 100.9 J K^{-1}$
(c) $HCl(g) + HBr(g) \rightarrow BrCl(g) + H_2(g)$	$\Delta G^\theta = 147.7 kJ$
(d) $K(s) \rightarrow K(g)$	$P_K^\bullet = 2.52 \times 10^{-11} bar = 2.52 \times 10^{-6} Pa$
(e) $CaCO_3(s, ara) \rightarrow CaCO_3(s, cal)$	$K_a = 1.44$

(a) This is just twice the molar enthalpy of formation of liquid water, found in Table 5.8.

(b) This is the difference between the standard entropies of the materials found on Table 5.8.

$$\Delta S^\theta = 2 \times 180.8 J K^{-1} - 260.7 J K^{-1} = 100.9 J K^{-1}$$

(c) This is found by sum and difference of the free energies of formation of the various components.

$$\Delta G^\theta = -1.0 kJ + 0.0 kJ - (-95.3 kJ) - (-53.4 kJ) = 147.7 kJ$$

(d) One has to calculate the equilibrium constant for this reaction from the free-energy change. The free-energy change is just the free energy of formation of the gaseous atom, which is given in Table 5.8.

$$K = \exp\left(-\frac{\Delta G^\theta}{RT}\right) = \exp\left(-\frac{60.5 \times 10^3 J}{8.3144349 J K^{-1}(298.15 K)}\right) = \exp(-24.405) = 2.52 \times 10^{-11}$$

So, the equilibrium constant is very small. Since the activity of the solid is 1, the equilibrium constant is simply the pressure of the gas phase expressed in the units of the standard pressure (which is 1 bar = 0.1 MPa).

(e) This is identical to the calculation in (d):

$$\Delta G^\theta = -1129.1 kJ - (-1128.2 kJ) = -0.90 kJ$$

$$K = \exp\left(-\frac{\Delta G^\theta}{RT}\right) = \exp\left(-\frac{-0.90 \times 10^3 J}{8.3144349 J K^{-1}(298.15 K)}\right) = \exp(0.363) = 1.44$$

**6. (15 points)** Sulfur transforms from the rhombic form to the monoclinic form under a pressure of 1 atmosphere at 95.4°C. Its reported enthalpy of transition is 0.38 kJ mol<sup>-1</sup>. (a) What is the entropy of transition?

The entropy of transition is easily calculated from these two quantities.

$$\Delta S^\theta = \frac{\Delta H^\theta}{T_i} = \frac{380 \text{ J mol}^{-1}}{(95.43 + 273.15) \text{ K}} = 1.03 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) Assume that the heat capacity at constant pressure of rhombic sulfur is independent of temperature between 25°C and 95.4°C. What is the standard entropy of monoclinic sulfur at 95.4°C?

First calculate the standard entropy of rhombic sulfur at 95.4°C.

$$S_{rhomb,T}^\theta = S_{rhomb,298.15}^\theta + \int_{298.15}^T \frac{C_P^\theta}{T} dT = S_{rhomb,298.15}^\theta + C_P^\theta \ln\left(\frac{T}{298.15}\right)$$

The information at 298.15 K is given in Table 5.8. Substitution gives:

$$S_{rhomb,368.55}^\theta = 32.1 \text{ J K}^{-1} \text{ mol}^{-1} + 22.6 \text{ J K}^{-1} \text{ mol}^{-1} \ln\left(\frac{368.55}{298.15}\right) = 36.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

Finally, since the difference in the standard entropies of the two forms has been found in part (a), all one has to do is add that to the value just found to give the standard entropy of the monoclinic form at this temperature.

$$S_{mono,368.55}^\theta = S_{rhomb,368.55}^\theta + \Delta S^\theta = 36.9 \text{ J K}^{-1} \text{ mol}^{-1} + 1.03 \text{ J K}^{-1} \text{ mol}^{-1} = 37.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

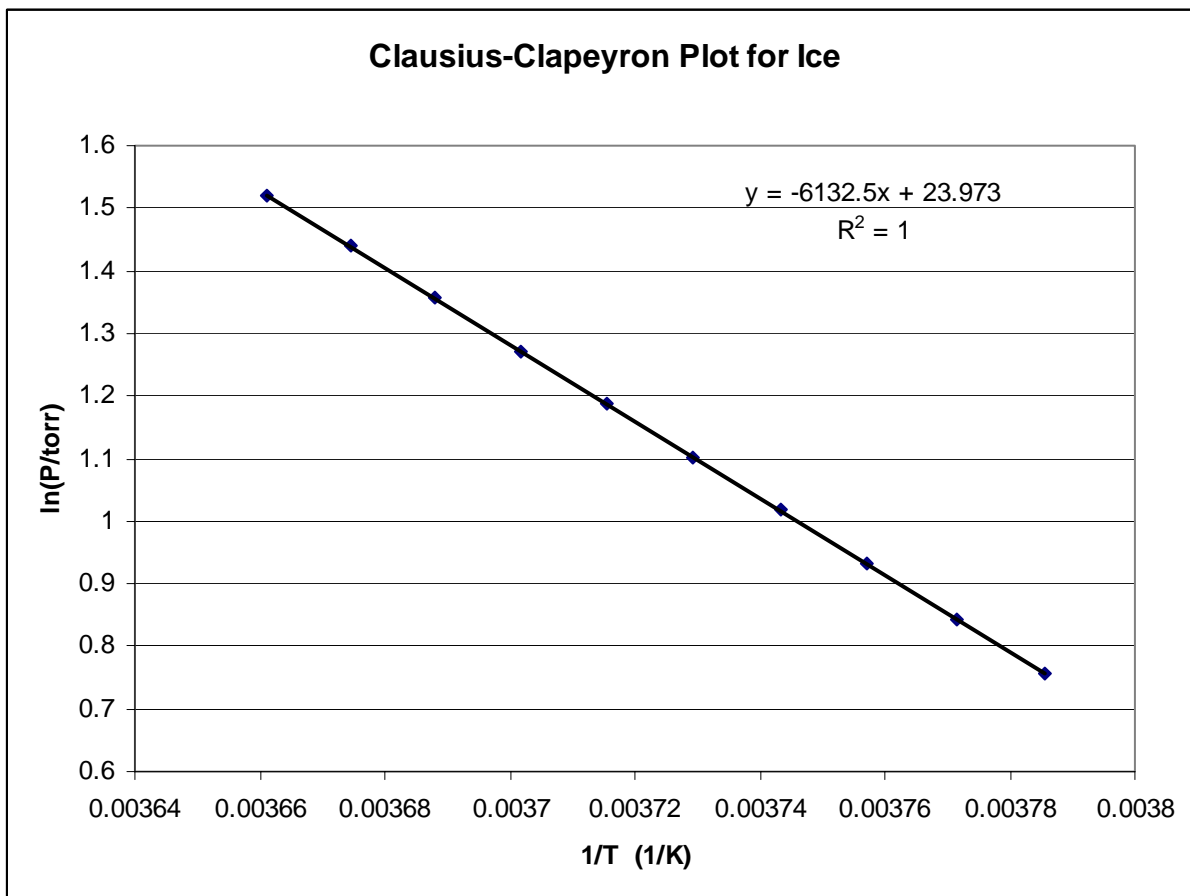
**7. (10 points)** The table gives values of the vapor pressure over ice at various temperatures, as reported in the *CRC Handbook of Chemistry and Physics*, 63<sup>rd</sup> Edition. From these data, determine the enthalpy of sublimation of water in this range. Show all work clearly, including an appropriate plot of the data. Make sure to label all axes correctly.

t (Celsius)	P (torr)	T (K)	1/T (1/K)	ln(P)
0	4.579	273.15	0.003661	1.521481
-1	4.217	272.15	0.003674	1.439124
-2	3.88	271.15	0.003688	1.355835
-3	3.568	270.15	0.003702	1.272005
-4	3.28	269.15	0.003715	1.187843
-5	3.013	268.15	0.003729	1.102936
-6	2.765	267.15	0.003743	1.017041
-7	2.537	266.15	0.003757	0.930982
-8	2.326	265.15	0.003771	0.84415
-9	2.131	264.15	0.003786	0.756591

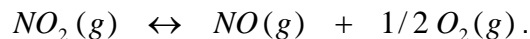
The determination of the enthalpy of sublimation requires a Clausius-Clapeyron plot of the logarithm of the pressure versus the inverse of the absolute temperature. It is shown below. According to the theory, the slope of this line is  $-\Delta H_{sub}^{\theta} / R$ .

From the slope of the trend line, one gets

$$\Delta H_{sub}^{\theta} = -R(\text{slope}) = -8.3144349 \text{ J K}^{-1} \text{ mol}^{-1}(-6132.5 \text{ K}) = 50.99 \text{ J mol}^{-1}$$



8. (10 points) Consider the equilibrium of nitrogen dioxide and nitric oxide by the following chemical reaction:



Initially exactly one mole of nitrogen dioxide is placed in a vessel. At equilibrium, the volume of the vessel is adjusted so that the total pressure is exactly 1 bar. The gas is analyzed, and  $P_{\text{NO}} / P_{\text{NO}_2} = 0.872$  at a temperature of 426.85°C. (a) Calculate  $K_p$  for this reaction at this set of conditions.

Since the gases all arise from the original material, let us create a table.

Time	NO <sub>2</sub>	NO	O <sub>2</sub>	Total pressure
0	P <sub>0</sub>	0	0	P <sub>0</sub>
Equilibrium	P <sub>0</sub> -p	p	p/2	P <sub>0</sub> +p/2
Ratio	1	x = p/(P <sub>0</sub> -p)	x/2	

One can calculate the pressure of NO<sub>2</sub> from Dalton's law:

$$P_{\text{NO}_2} + P_{\text{NO}} + P_{\text{O}_2} = 1$$

Substitution gives

$$P_{\text{NO}_2} + xP_{\text{NO}_2} + \frac{x}{2}P_{\text{NO}_2} = 1$$

$$\left(1 + x + \frac{x}{2}\right)P_{\text{NO}_2} = 1 = \left(1 + 0.872 + \frac{0.872}{2}\right)P_{\text{NO}_2}$$

which gives  $P_{\text{NO}_2} = 0.433 \text{ bar}$ . With this, one can estimate  $P_{\text{NO}} = 0.378 \text{ bar}$  and  $P_{\text{O}_2} = 0.189 \text{ bar}$

Using these values in the equilibrium equation, one may calculate

$$K_p = \frac{P_{\text{NO}} P_{\text{O}_2}^{1/2}}{P_{\text{NO}_2}} = \frac{(0.378 \text{ bar})(0.189 \text{ bar})^{1/2}}{0.433 \text{ bar}} = 0.380 \text{ bar}^{1/2}$$

(b) Calculate the standard free energy of reaction under these conditions.

Assuming that the standard pressure is 1 bar, and that the pressures are low enough that the gases may be treated as ideal, the value of  $K_p$  is also  $K_a$ . Then, one may use the standard expression to determine the free energy change.

$$\Delta G^\theta = -RT \ln K_a = -8.3144349 \text{ J K}^{-1}((273.15 + 426.85) \text{ K}) \ln(0.380) = 5631 \text{ J}$$



**9. (10 points)** A solution consisting of 390.559 grams of benzene and 299.450 grams of toluene ( $C_7H_8$ ) is an almost perfectly ideal solution. At 298.15 K, the vapor pressure of pure benzene is 94.61 torr and the vapor pressure of pure toluene is 29.06 torr.

(a) What is the mole fraction of benzene in the liquid?

Calculate the number of moles of each component.

$$n_{benzene} = \frac{390.559 g}{(6 \times 12.0107 g + 6 \times 1.00794 g)} = 5.0000$$

$$n_{toluene} = \frac{299.450 g}{(7 \times 12.0107 g + 8 \times 1.00794 g)} = 3.2500$$

The mole fraction of benzene is easily calculated from this:

$$X_{benzene} = \frac{n_{benzene}}{(n_{benzene} + n_{toluene})} = \frac{5.0000}{(5.0000 + 3.2500)} = 0.60606$$

(b) What is the total pressure above the solution at 298.15 K?

One may use Raoult's law to calculate the partial pressures and sum them to give to the total pressure.

$$\begin{aligned} P &= X_{benzene} P_{benzene}^{\bullet} + X_{toluene} P_{toluene}^{\bullet} \\ &= (0.60606 \times 94.61 \text{ torr}) + (0.39394 \times 29.06 \text{ torr}) \\ &= 57.339 \text{ torr} + 11.448 \text{ torr} = 68.787 \text{ torr} \end{aligned}$$

**10. (10 points)** The equilibrium constant for the dissolution of the sparingly soluble salt, TlCl, at 298.15 is  $K_a = 1.855 \times 10^{-4}$ . What is the solubility of TlCl in water at 298.15 K?

One must set up the equilibrium equation.

$$K_a = a_{Tl^+} a_{Cl^-} = \gamma_{\pm}^2 m^2 \quad \text{or} \quad m = \sqrt{\frac{K_a}{\gamma_{\pm}^2}}$$

One must also simultaneously satisfy the DHG equation:

$$\ln \gamma_{\pm} = -\alpha_{DH} |z_+ z_-| \left( \frac{\sqrt{I}}{1 + \sqrt{I}} \right) = -1.177 \frac{\sqrt{m}}{1 + \sqrt{m}}$$

This can be solved iteratively until self-consistency is achieved. Let's start by assuming ideality:  $\gamma_{\pm} = 1$

Substitution into the first equation gives an estimate of the concentration:

$$m^{(1)} = \sqrt{K_a} = 1.362 \times 10^{-2} \text{ mol/kg}$$

Putting this into the second equation gives the estimated activity coefficient:

$$\gamma_{\pm}^{(1)} = \exp \left[ -\frac{1.177 \sqrt{m^{(1)}}}{1 + \sqrt{m^{(1)}}} \right] = 0.884$$

This is obviously not the same as 1, so we have to iterate again:

$$m^{(2)} = \sqrt{\frac{K_a}{\gamma_{\pm}^{(1)2}}} = 1.540 \times 10^{-2} \text{ mol/kg}$$

Check the activity coefficient:

$$\gamma_{\pm}^{(2)} = \exp \left[ -\frac{1.177 \sqrt{m^{(2)}}}{1 + \sqrt{m^{(2)}}} \right] = 0.878$$

This is pretty close to the previous value, but let's iterate again:

$$m^{(3)} = \sqrt{\frac{K_a}{\gamma_{\pm}^{(2)2}}} = 1.551 \times 10^{-2} \text{ mol/kg}$$

This is even better agreement, but let's continue:

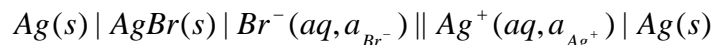
$$\gamma_{\pm}^{(3)} = \exp \left[ -\frac{1.177 \sqrt{m^{(3)}}}{1 + \sqrt{m^{(3)}}} \right] = 0.878$$

It has now converged, so the answer is  $m^{(3)} = 1.551 \times 10^{-2} \text{ mol/kg}$

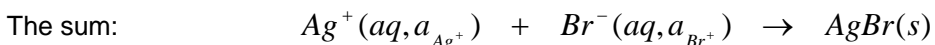
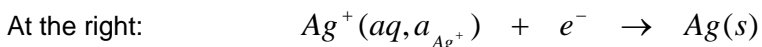
**11. (10 points)** Match the definitions in the right column with the words in left column by inserting the number of the definition in the space to the left of the word.

	<b>Word</b>	<b>Definition</b>
7	Amalgam	1. Decrease of volume in some highly charged salt solutions
13	Azeotrope	2. Dependence of $\gamma_{\pm}$ on ionic strength
9	Colligative properties	3. Equivalent conductivity at infinite dilution
5	Conductance	4. Escaping tendency of a gas
15	Electrophoretic effect	5. Inverse of resistance
4	Fugacity	6. Measure of distillation efficiency
12	Gibbs-Duhem equation	7. Metal dissolved in mercury
11	Gibbs phase rule	8. Method of undetermined multipliers
10	Henry's law	9. Properties of dilute solutions that depend only on the number of solute molecules
6	Theoretical plates	10. Proportionality of concentration of dissolved gas to the pressure
		11. Relation for determining the number of degrees of freedom
		12. Relation of activities of components of a solution
		13. Solution that boils at a constant temperature
		14. Solution that freezes at a constant temperature
		15. Viscous effect of solvent movement around an ion on the ion of opposite charge

12. (15 points) The following cell is useful for the determination of the solubility of silver bromide.



(a) What is the overall reaction for this cell, as written?



(b) What is the standard voltage of this cell at 298.15 K, assuming no junction potential?

The standard voltage of this cell is the difference between the half-cell potential of the right half-cell minus the half-cell potential of the left half-cell.

$$\begin{aligned} \mathcal{E}^\theta &= \mathcal{E}_{\text{right}}^\theta - \mathcal{E}_{\text{left}}^\theta \\ &= 0.7996V - 0.07133V \\ &= 0.72827V \end{aligned}$$

(c) What is the standard Gibbs energy change for the cell reaction, as written, at 298.15 K?

The standard Gibbs free-energy change is determined with the Nernst equation:

$$\Delta G^\theta = -nF\mathcal{E}^\theta = -(1)(96485.3383C)(0.72827V) = -70.267 kJ$$

(d) What is  $K_{sp}$  for the AgBr at 298.15 K?

$K_{sp}$  can be found from the standard free energy of the reverse of the equation in part (a). The result is

$$K_{sp} = \exp(-\Delta G^\theta / RT) = \exp\left(-\frac{70267 J}{8.3144349 J K^{-1}(298.15K)}\right) = \exp(-28.345) = 4.895 \times 10^{-13}$$

**13. (10 points, extra credit)** For an elastic system that obeys Hooke's law,  $f = k(\ell - \ell_0)$ , where  $f$  is the restoring force,  $\ell$  is the extension of the network,  $\ell_0$  is the length of the network with no force applied, and  $k$  is the force constant. Using this information and your knowledge of thermodynamics, derive an equation for the entropy of the system when it is extended to a length  $\ell$  at a temperature  $T$ .

The differential of the energy is given by three terms:

$$dU = TdS - PdV + fd\ell$$

where the last term accounts for the energy change upon stretching the network. One may define the Helmholtz energy in the usual manner.

$$A = U - TS$$

The differential change in the Helmholtz energy is given by

$$dA = -SdT - PdV + fd\ell$$

There is a Maxwell relationship based on this equation:

$$\left(\frac{\partial S}{\partial \ell}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{\ell,V}$$

One may use Hooke's law to determine the derivative on the right-hand side of this equation:

$$\left(\frac{\partial S}{\partial \ell}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{\ell,V} = \left(\frac{\partial}{\partial T} k(\ell - \ell_0)\right)_{\ell,V} = \left(\frac{\partial k}{\partial T}\right)_{\ell,V} (\ell - \ell_0)$$

Finally, integration gives the result needed:

$$\int_{\ell_0}^{\ell} \left(\frac{\partial S}{\partial \ell}\right)_{T,V} d\ell = \int_{\ell_0}^{\ell} \left(\frac{\partial k}{\partial T}\right)_{\ell,V} (\ell - \ell_0) d\ell = \left(\frac{\partial k}{\partial T}\right)_{\ell,V} \int_{\ell_0}^{\ell} (\ell - \ell_0) d\ell = \left(\frac{\partial k}{\partial T}\right)_{\ell,V} \frac{(\ell - \ell_0)^2}{2}$$

The integral on the left-hand side is the difference between the entropy at the two points. This finally yields the answer we are seeking:

$$S(\ell, T) = S(\ell_0, T) + \left(\frac{\partial k}{\partial T}\right)_{\ell,V} \frac{(\ell - \ell_0)^2}{2}$$