Practice Final Exam for Chem 431

1. Calculate the entropy change of the system and the surroundings for a diatomic van der Waal's gas (Assume a = 0.242 atm L^2/mol^2 and b = 0.00265 L/mol).

a. reversible isothermal expansion of 0.02 moles of gas from 0.5 L to 7.0 L at 300 K.
b. reversible isothermal expansion of 0.02 moles of gas from 0.5 L to 7.0 L at 500 K.
c. constant pressure expansion of 0.02 moles of gas against 0.07 atm of pressure at 300 K.
d. heating 0.02 moles of gas reversibly from 300 K to 500 K at constant volume.

Solution:

a. Isothermal expansion dU = 0, δq = -δw = -PdV for an ideal gas.

In fact, this is somewhat subtle for the van der Waals gas since we have already shown in Quiz 3 that:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{nR}{V-nb}\right) - \frac{nRT}{V-nb} + \frac{n^2a}{V^2}$$

$$= \frac{n^2a}{V^2}$$

Thus, for a van der Waal's gas:

$$dU = \frac{n^2a}{V^2}dV = \delta q - PdV$$

$$\delta q = \left(P - \frac{n^2a}{V^2}\right)dV$$

From the van der Waals' equation: $P = nRT/(V-nb) - n^2a/V^2$

$$\Delta S = \int \frac{\delta q_{rev}}{T} = \int_{V_1}^{V_2} \frac{\left(P - \frac{n^2a}{V^2}\right)dV}{T}$$

$$= \int_{V_1}^{V_2} \frac{n}{(V-nb)}dV$$

$$= nR\ln\left(\frac{V_2-nb}{V_1-nb}\right)$$

For an ideal gas you would have.
ΔS_{sys} = nR ln(V_2/V_1) = (0.02 moles)(8.314 J/mole-K) ln(7.0/0.5) = 0.435 J/K for the system

ΔS_{surr} = -nR ln(V_2/V_1) = -(0.02 moles)(8.314 J/mole-K) ln(7.0/0.5) = -0.435 J/K for the surroundings

For the van der Waal's gas you have:

$$\Delta S_{sys} = (0.02\ mol)(8.31\ J/mol\text{–}K)\ \ln\left(\frac{7.0 - 0.02(0.0265)}{0.5 - 0.02(0.0265)}\right)$$

$$= 0.493\ J/K$$

As above for an ideal gas ΔS_{system} = -$\Delta S_{surroundings}$
b. is the same as a. except that T = 500 K. Note that for an ideal gas the entropy is the same as in part a. There is no temperature dependence to the entropy change.

c. for the constant pressure expansion we calculate the entropy change for the system along a reversible path (as always). The entropy change is identical to the above value in part a. (assuming T = 300 K). However, the entropy change for the surroundings should be calculated along an irreversible path.

$$\Delta S_{surr} = \frac{q}{T} = \frac{-P\Delta V}{T} = \frac{(0.07\ atm)(7.0\ L\ - 0.5\ L)}{300\ K} = -0.00151\ L\text{–}atm/K = -\ 0.154\ J/K$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = +\ 0.285\ J/K$$

d. The heating is reversible so we know that ΔS_{surr} = -ΔS_{sys}.
ΔS_{sys} = = nC_v ln(T_2/T_1) = (5/2)nR ln(T_2/T_1) = (0.02 moles)(2.5 x 8.314 J/mole-K) ln(500/300) = 0.212 J/K for the system.

2. A.Given the following data at 50 ^{o}C determine the activity and activity coefficient for iodoethane (I) and ethylacetate (E) at a mole fraction of x_E = 0.6282.

x_I	P_I (torr)	P_E (torr)
0.0000	0.0	280.4
0.0579	20.0	266.1
0.1095	52.7	252.3
0.1918	87.7	231.4
0.2353	105.4	220.8
0.3718	155.4	187.9
0.5478	213.3	144.2

0.6349	239.1	122.9
0.8253	296.9	66.6
0.9093	322.5	38.2
1.0000	353.4	0.000

The Henry's law constants are $K_{H,I}$ and $K_{H,E}$ should be calculated from the relationship:
$P_{total} = x_1 P_1^* \exp\{x_2^2/4\} + x_2 P_2^* \exp\{x_1^2/4\}$

Solution: The Henry's law constants are (from the above formulae):
$k_{H,1} = P_1^* \exp\{1/4\}$ and $k_{H,2} = P_2^* \exp\{1/4\}$
We get the pure vapor pressures from the table.
$k_{H,I}$ = (353.4 torr) exp{1/4} = 453.8 torr for iodoethane
$k_{H,E}$ = (280.4 torr)exp{1/4} = 360.0 torr for ethyl acetate

When the mole fraction of $x_E = 0.6282$, then $x_E = 0.3718$.
Look up the vapor pressures in the table to find
P_I = 155.4 torr and P_E = 187.9 torr

In the Raoult's law standard state we have:
$a_I = P_I/P_I^* = 155.4/353.4 = 0.4397$
$a_E = P_E/P_E^* = 187.9/280.4 = 0.6701$

The activity coefficients are obtained from
$\gamma_I = a_I/x_I = 0.4397/0.3718 = 1.183$
$\gamma_E = a_E/x_E = 0.6701/0.6282 = 1.067$

The Henry's law activities are calculated using the Henry's law constant instead of the vapor pressure of the pure substance.
$a_I = P_I/\ k_{H,I} = 155.4/453.8 = 0.3424$
$a_E = P_E/\ k_{H,E} = 187.9/360.0 = 0.5219$

The activity coefficients are obtained from
$\gamma_I = a_I/x_I = 0.3424/0.3718 = 0.9209$
$\gamma_E = a_E/x_E = 0.5219/0.6282 = 0.8308$

Using the data above for 50 ^{o}C and a mole fraction $x_E = 0.6282$, calculate the free energy and entropy of mixing for a one mole of a regular solution of iodoethane and ethyl acetate using the Raoult's law standard state activity.

Compare the ideal free energy of mixing with non-ideal free energy of mixing (You may use molar quantities for free energy and entropy).

Solution:

Ideal

$\Delta_{mix}G^{id} = RT(x_E \ln x_E + x_E \ln x_E)$

$= (8.31 \text{ J/mol-K})(323 \text{ K})(0.3718\ln(0.3718) + 0.6282\ln(0.6282))$

$= -1771 \text{ J/mol} = -1.771 \text{ kJ/mol}$

$\Delta_{mix}S^{id} = -R(x_E \ln x_E + x_E \ln x_E) = 5.48 \text{ J/mol-K}$

Non-ideal

$\Delta_{mix}G = RT(x_E \ln a_E + x_E \ln a_E)$

$= (8.31 \text{ J/mol-K})(323 \text{ K})(0.3718\ln(0.4397) + 0.6282\ln(0.6701))$

$= -1495 \text{ J/mol} = -1.495 \text{ kJ/mol}$

$\Delta_{mix}S = -R(x_E \ln x_E + x_E \ln x_E) = 5.48 \text{ J/mol-K}$

Comments:

The non-ideality does not change the entropy of mixing. It changes the free energy. The difference (i.e. excess free energy) arises from an enthalpy of mixing that is present in the non-ideal solution.

You may think of the solution to this problem in terms of excess quantities. The excess free energy is the difference between the "real" and ideal free energy:

$G^E = \Delta_{mix}G - \Delta_{mix}G^{id}$

It is easy to show that

$\Delta_{mix}G = RT(x_E \ln x_E + x_E \ln x_E + x_E \ln\gamma_E + x_E \ln\gamma_E)$

and therefore

$G^E = RT(x_E \ln\gamma_E + x_E \ln\gamma_E)$

The difference between an ideal and a non-ideal solution is in the enthalpy. The entropies are the same.

$\Delta_{mix}G = \Delta_{mix}G^{id}$

and therefore

$S^E = 0$

This means that the excess free energy is equal to the enthalpy of mixing. $G^E = \Delta_{mix}H$. This is not discussed well in Chapter 24, but can be found in problems 24-37 and 24-56.

3. Calculate the thermodynamic efficiency of an engine that runs at 430 K if the exhaust temperature is 310 K.

Solution:

$$\eta = \frac{T_{hot} - T_{cold}}{T_{hot}} = \frac{430\ K\ - 310\ K}{430\ K} = 0.279$$

4. A. Given the expression

dU = TdS - PdV

Solution:

H = U + PV

dH = dU + PdV + VdP

dH = TdS - PdV + PdV + VdP

dH = TdS + VdP

G = H - TS

dG = dH - TdS - SdT

dG = TdS + VdP - TdS - SdT

dG = -SdT + VdP

A = U - TS

dA = dU - TdS - SdT

dA = TdS - PdV - TdS - SdT

dA = -SdT - PdV

B. Derive an expression for the Maxwell relation for the total derivative of dA.

Solution: Since dA is an exact differential the second cross derivatives are

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT - \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$\Rightarrow \frac{\partial^2 A}{\partial T \partial V} = \frac{\partial^2 A}{\partial V \partial T}$$

equal. Formally we express this as follows.

Using the expression for dA above we see that:

$$dA = -SdT - PdV$$
$$\Rightarrow \frac{\partial S}{\partial V} = \frac{\partial P}{\partial T}$$

C. Use the Maxwell relation for dA to derive the Clausius-Clapeyron equation for the coexistence for curve of a liquid and vapor.

Solution: Starting with the Maxwell relation we assume a change in molar entropy and molar volume for the phase transition are $\Delta_{phase}S$ and $\Delta_{phase}V$, respectively.

$$\frac{\Delta_{phase}S}{\Delta_{phase}V} = \frac{dP}{dT}$$

Since, $\Delta_{phase}G = 0$ for the phase transition we have that $\Delta_{phase}S = \Delta_{phase}H/T$. Since we are considering vaporization as the specific phase transition we can

$$\frac{\Delta_{phase}H}{T\Delta_{phase}V} = \frac{dP}{dT}$$

assume that volume change is equal to the molar volume of the vapor. This is true because the molar volume of the liquid is >1000 times less than that of the vapor.

$$\frac{\Delta_{vap}H}{TV_{vapor}} = \frac{dP}{dT}$$
$$\frac{\Delta_{vap}H}{T\left(RT/P\right)} = \frac{dP}{dT}$$
$$\frac{\Delta_{vap}H}{R}\frac{dT}{T^2} = \frac{dP}{P}$$
$$\frac{\Delta_{vap}H}{R}\int_{T_1}^{T_2}\frac{dT}{T^2} = \int_{P_1}^{P_2}\frac{dP}{P}$$
$$\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \ln\left(\frac{P_2}{P_1}\right)$$

5. At 90 ^{o}C, the vapor pressure of toluene is 400 torr and that of o-xylene is 150 torr. What is the composition of the liquid when the liquid mixture boils at 90 ^{o}C when the pressure is 180 torr? What is the composition of the vapor produced?

Solution:

$P_{tol}^* = P_1^* = 400$ torr , $P_{xyl}^* = P_2^* = 150$ torr
If the vapor pressure at boiling is 180 torr then the mole fraction in the liquid is:

$$x_1 = \frac{P_{total} - P_2^*}{P_1^* - P_2^*} = \frac{180 - 150}{400 - 150} = 0.12$$

Obviously, $x_2 = 1 - x_1 = 0.88$. Thus, the composition of the liquid is determined. The composition of the vapor is given by Dalton's law.

$$y_1 = \frac{P_1}{P_{total}} = \frac{x_1 P_1^*}{P_{total}} = \frac{(0.12)400\ torr}{180\ torr} = 0.267 \quad , y_2 = 0.733$$

Note that the more volatile component (toluene) has a larger mole fraction in the vapor than it does in the liquid as out intuition suggests.

6. The enthalpy of fusion of anthracene is 28.8 kJ/mol and its melting point is 217 ^{o}C. Calculate its ideal solubility in benzene.

Solution: We use the following logic. At the normal melting $\Delta_{fus}G = 0$. At any other temperature we use the concept of chemical potential. The chemical potential in the solid and solution must be equal at all temperatures.

$$\mu_2^*(s) = \mu_2^*(l) + RT \ln x_2$$

Solving for $\ln x_2$

$$\ln x_2 = \frac{\mu_2^*(s) - \mu_2^*(l)}{RT} = -\frac{\Delta_{fus}G}{RT}$$

$$\ln x_2 = -\frac{\Delta_{fus}G}{RT} + \frac{\Delta_{fus}G}{RT^*}$$

$$\ln x_2 = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T^*} - \frac{1}{T}\right)$$

$$x_2 = \exp\left\{\frac{\Delta_{fus}H}{R}\left(\frac{1}{T^*} - \frac{1}{T}\right)\right\}$$

Substituting in the values for anthracene given above.

$$x_2 = \exp\left\{\frac{28{,}800\ J/mol}{8.31\ J/mol\text{–}K}\left(\frac{1}{490\ K} - \frac{1}{300\ K}\right)\right\} = 0.0113$$

Note that this is the mole fraction (which is an acceptable answer to this problem). To convert this into a concentration we would use the known molar masses and to calculate the mass percentage of each of the species, which can be used to calculate molality. Then using the density of benzene we could calculate the volume of benzene to obtain a molarity, if desired.

7. Prior to the discovery that Freon-12 ($CF2_2Cl_2$) was harmful to the Earth's ozone layer, it was frequently used as the dispersing agent in spray cans for hair spray. Its enthalpy of vaporization at its normal boiling point of T_{boil} = -29.2 ^{o}C is 20.25 kJ/mol. Estimate the pressure that a can of hair spray using Freon-12 had to withstand at 40 ^{o}C, the temperature of a can that has been standing in sunlight. Assume that $\Delta_{vap}H$ is a constant over the temperature range involved and equal to its value at -29.2 ^{o}C.

Solution: The Clausius-Clapeyron equation gives the pressure of a vapor in equilibrium with its liquid at elevated temperature. Starting with the equation derived in Problem 4 above we solve for the pressure.

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

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

And substitute in the values given above.

$$P_2 = (1\ atm)\exp\left\{\frac{20250\ J/mol}{8.31\,J/mol\text{–}K}\left(\frac{1}{244\ K}-\frac{1}{313\ K}\right)\right\}$$

$$= 9\ atm$$

8. The equilibrium constant for the reaction I_2 (s) + Br_2 (g) = 2 IBr (g) is 0.164 at 25 ^{o}C. (a) Calculate Δ_rG for this reaction (b) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at 0.164 atm and 25 ^{o}C. Find the partial pressure of IBr (g) at equilibrium. (c) In fact, solid iodine has a vapor pressure of 0.005 atm at 25 ^{o}C. Find the partial pressure of IBr (g) accounting for the vapor pressure of iodine.

Solution:

a. First we can calculate Δ_rG^o using

Δ_rG^o = -RT ln K_{eq} = (8.31 J/mol-K)(298 K)ln(0.164) = +4477 J/mol

= +4.48 kJ/mol

The reaction quotient can be expressed as:

$$Q = \frac{P_{IBr}^2}{P_{Br_2}}$$

Using standard conditions $P_{IBr} = P_{Br2} = 1$ atm, so Q = 1 and lnQ = 0.
Since
$\Delta_r G = \Delta_r G^o + RT \ln Q$
we have
$\Delta_r G = \Delta_r G^o = +4.48$ kJ/mol

b. Make a table

Condition	Br_2	IBr	Total
Initial	0.164	0	0.164
Equilibrium	0.164-x	2x	0.164+x
Partial pressure	(0.164-x) /(0.164+x)*0.164	2x /(0.164+x)*0.164	0.164

$$K_{eq} = \frac{P_{IBr}^2}{P_{Br_2}} = \frac{\left(\frac{2x}{0.164 + x}\right)^2 P^2}{\frac{0.164 - x}{0.164 + x} P} = \frac{4x^2 P}{0.0268 - x^2}$$

$$0.0268 K_{eq} - x^2 \left(K_{eq} + 4P\right) = 0$$

$$x = \sqrt{\frac{0.0268 K_{eq}}{\left(K_{eq} + 4P\right)}} = \sqrt{\frac{0.0268(0.164)}{5\left(0.164\right)}} = 0.0732$$

$$P_{IBr} = \frac{2x}{0.164 + x} P = \frac{2(0.0732)}{0.237} 0.164 = 0.101\ atm$$

c. The true vapor pressure is that of the equilibrium shown minus the contribution from I_2. In other words we correct the given total pressure of 0.164 atm by adding the pressure of I_2 ($P_{I2} = 0.005$ atm). The corrected vapor pressure is 0.169 atm.

Condition	Br_2	I_2	IBr	Total
Initial	0.159	0.005	0	0.164
Equilibrium	0.159-x	0.005	2x	0.156+x
Partial pressure	(0.159-x) /(0.164+x)P	0.005	2x/(0.164+x)P	0.164

$$K_{eq} = \frac{P_{IBr}^2}{P_{Br_2}} = \frac{\left(\frac{2x}{0.164 + x}\right)^2 P^2}{\frac{0.159 - x}{0.164 + x} P} = \frac{4x^2 P}{0.026 - 0.005x - x^2}$$

$$0.026K_{eq} - 0.005K_{eq}x - \left(K_{eq} + 4P\right)x^2 = 0$$

$$x = \frac{-0.005K_{eq} \pm \sqrt{\left(0.005\right)^2 K_{eq}^2 + 4(0.026)K_{eq}\left(K_{eq} + 4P\right)}}{2\left(K_{eq} + 4P\right)}$$

$$= 0.0704$$

$$P_{IBr} = \frac{2x}{0.164 + x} P = \frac{2(0.0704)}{0.234} 0.164 = 0.986 \ atm$$

The equilibrium is shifted to the left as predicted by Le Chatelier's principle.

9. Calculate the entropy change when 180 grams of boiling water are poured into a stainless steel bowl weighing 110 grams at 25 °C. Assume that the molar mass of the metal in the bowl is 55 grams/mole. The heat capacity of water is 75 J/mole-K and that of bowl is 25 J/mole-K.

Solution: First we must calculate the equilibrium temperature.

$$T_{eq} = \frac{n_1 C_{p1} T_1 + n_2 C_{p2} T_2}{n_1 C_{p1} + n_2 C_{p2}}$$

$$= \frac{(10\ mol)(75\ J/mol\text{–}K)373\ K + (2\ mol)(25\ J/mol\text{–}K)298\ K}{(10\ mol)(75\ J/mol\text{–}K) + (2\ mol)(25\ J/mol\text{–}K)}$$

$$= 368.3\ K$$

Now we calculate the entropy change of the water and bowl separately.

$$\Delta S_{water} = n_1 C_{p1}\left(\frac{T_{eq}}{T_1}\right) = (10\ mol)(75\ J/mol\text{–}K)\ln\left(\frac{368.3}{373}\right)$$

$$= -9.51\ J/K$$

$$\Delta S_{bowl} = n_2 C_{p2}\left(\frac{T_{eq}}{T_2}\right) = (2\ mol)(25\ J/mol\text{–}K)\ln\left(\frac{368.3}{298}\right)$$

$$= +10.59\ J/K$$

$$\Delta S_{total} = \Delta S_{water} + \Delta S_{bowl} = +1.08\ J/K$$

The process is spontaneous. If you get a negative entropy for a heat transfer problem, you know that you have made a mistake somewhere. Heat transfer from a hotter to a colder body is always spontaneous.

10. Calculate the equilibrium constant for the reaction :

I_2 (g) + Cl_2 (g) $\leftarrow\rightarrow$ 2 ICl (g)

Use the molecular partition functions and the available data given below.

M(Cl) = 35.45 a.u., M(I) = 126.9 a.u.
$k_B = 0.697\ cm^{-1}/K = 1.38 \times 10^{-23}$ J/K

Note that rotational partition functions for homonuclear diatomics should include a symmetry number of 2.

Species	ν (cm^{-1})	R_e (pm)	D_e (kJ/mol)
I_2	204	266	151
Cl_2	534	199	243
ICl	380	234	104

Solution:
The equilibrium constant is given by

$$K_{eq} = \frac{\left(\frac{q_{ICl}}{V}\right)^2}{\left(\frac{q_{I_2}}{V}\right)\left(\frac{q_{Cl_2}}{V}\right)}$$

The partition function of each species can be decomposed into rotational, vibrational and translational contributions. This is done for an analogous reaction in McQuarrie and Simon on page 1070.

$$q = q_{trans} q_{rot} q_{vib}$$

Note that the form of the partition functions is very similar since all of the species in the reaction are diatomics. There is a symmetry number of Cl_2 and I_2 since they have identical structure under rotation by 180^o whereas ICl does not. In ICl the position of the I and Cl atoms are switched by a 180^o rotation.

$$\frac{q_{Cl_2}}{V} = \left(\frac{2\pi m_{Cl_2} kT}{h^2}\right)^{3/2} \left(\frac{T}{2\Theta_{rot,Cl2}}\right) \frac{1}{\left(1 - e^{-\Theta_{vib,Cl2}/T}\right)} e^{D_o(Cl_2)/RT}$$

$$\frac{q_{I_2}}{V} = \left(\frac{2\pi m_{I_2} kT}{h^2}\right)^{3/2} \left(\frac{T}{2\Theta_{rot,I2}}\right) \frac{1}{\left(1 - e^{-\Theta_{vib,I2}/T}\right)} e^{D_o(I_2)/RT}$$

$$\frac{q_{ICl}}{V} = \left(\frac{2\pi m_{ICl} kT}{h^2}\right)^{3/2} \left(\frac{T}{\Theta_{rot,ICl}}\right) \frac{1}{\left(1 - e^{-\Theta_{vib,ICl}/T}\right)} e^{D_o(ICl)/RT}$$

The D_o are $D_e - h\nu/2$, which means that they are the dissociation energies D_e corrected for the zero point energy $h\nu/2$. We can calculate these first: In kJ/mol these are obtained by:

$N_A hc\nu/2000$ where n is in wavenumbers (cm-1). Note that c (the speed of light) is used to convert to s-1 (Hz). Then you use Planck's constant to obtain energy in Joules. Finally, multiply by Avagadro's number and divide by 1000 to obtain the value in kJ/mol.

For Cl_2: ν = 523 cm^{-1} and $N_A hc\nu/2000$ = 0.318 kJ/mol

For I_2: ν = 204 cm^{-1} and $N_A hc\nu/2000$ = 0.122 kJ/mol

For ICl: ν = 380 cm^{-1} and $N_A hc\nu/2000$ = 0.227 kJ/mol

Thus, we see that the zero point motion is quite a small correction to the dissociation energies

For Cl_2: D_o = (243 - 0.318) kJ/mol = 242.68 kJ/mol

For I_2: D_o = (151 - 0.122) kJ/mol = 150.90 kJ/mol

For ICl: D_o = (104 - 0.227) kJ/mol = 103.77 kJ/mol

Next we can calculate the rotational temperatures. First we need the moments of inertia ($I = \mu R^2$).

$$For\ Cl_2:\ I = \frac{35.45\ amu}{2}\left(1.672 \times 10^{-27} kg/amu\right)\left(199 \times 10^{-12} m\right)^2$$
$$= 1.047 \times 10^{-45} kgm^2$$

$$For\ I_2:\ I = \frac{126.9\ amu}{2}\left(1.672 \times 10^{-27} kg/amu\right)\left(266 \times 10^{-12} m\right)^2$$
$$= 7.506 \times 10^{-45} kgm^2$$

$$For\ ICl:\ I = \frac{(35.45)126.9\ amu}{35.45 + 126.9}\left(1.672 \times 10^{-27} kg/amu\right)\left(234 \times 10^{-12} m\right)^2$$
$$= 2.537 \times 10^{-45} kgm^2$$

$$\Theta_{rot,Cl2} = \left(\frac{h^2}{8\pi I^2 k}\right) = 0.384\ K$$
$$\Theta_{rot,I2} = \left(\frac{h^2}{8\pi I^2 k}\right) = 0.0536\ K$$
$$\Theta_{rot,ICl} = \left(\frac{h^2}{8\pi I^2 k}\right) = 0.158\ K$$

These values are appropriate. The greater the mass the greater the moment of inertia and therefore the smaller the spacing of the rotational levels. Next we need to vibrational temperature.

$$\Theta_{vib,Cl2} = \left(\frac{h\nu}{k}\right) = \frac{534\ cm^{-1}}{0.697\ cm^{-1}/K} = 750.3\ K$$
$$\Theta_{vib,I2} = \left(\frac{h\nu}{k}\right) = \frac{204\ cm^{-1}}{0.697\ cm^{-1}/K} = 292.7\ K$$
$$\Theta_{vib,ICl} = \left(\frac{h\nu}{k}\right) = \frac{380\ cm^{-1}}{0.697\ cm^{-1}/K} = 545.2\ K$$

There several ways to work this problem from this point. One way is to break the equilibrium constant up into contributions from translation, rotation, vibration and electronic energy levels. This method has the advantage that many constants will cancel. We have the following.

$$K_{trans} = \frac{m_{ICl}^3}{m_{I_2}^{3/2} m_{Cl_2}^{3/2}} = \frac{162.35^3}{70.90^{3/2} 253.8^{3/2}} = 1.77$$
$$K_{rot} = \frac{4\Theta_{rot,Cl2}\Theta_{rot,I2}}{\Theta_{rot,ICl}^2} = \frac{4(0.384)(0.0536)}{0.158^2} = 3.30$$
$$K_{vib} = \frac{\left(1-e^{-\Theta_{v,Cl2}/T}\right)\left(1-e^{-\Theta_{v,I2}/T}\right)}{\left(1-e^{-\Theta_{v,ICl}/T}\right)^2} = \frac{\left(1-e^{-750.3/298}\right)\left(1-e^{-292.7/298}\right)}{\left(1-e^{-545.2/298}\right)^2}$$
$$= 0.82$$
$$K_{elec} = \frac{e^{2D_o(ICl)RT}}{e^{D_o(I2)/RT}} = e^{\{2D_o(ICl) - D_o(Cl2) - D_o(I2)\}/RT}$$
$$= e^{-45/2.476} = 7.19 \times 10^{-9}$$

Notice that the electronic component dominates. The answer we are after is the product of these four contributions so
K = 3.44 x 10^{-7}