CHEM 154 Midterm Exam Solutions

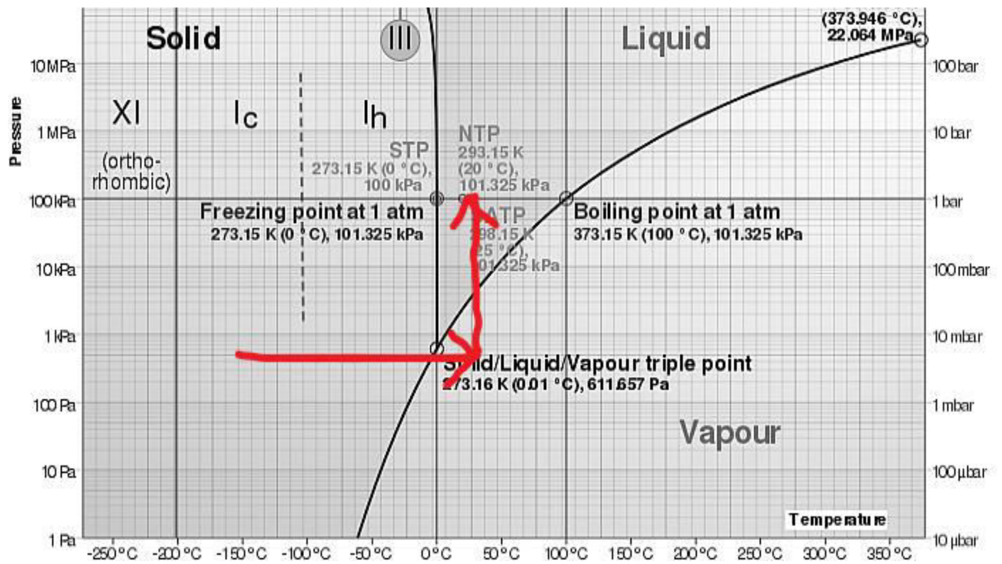
November 12, 2020

1. **[9 marks total]** You are an engineer on Mars charged with extracting water from the northern ice cap and building a pipeline to transport it back to a colony. Your pipeline will be well-insulated and be able to carry liquids or gases. The colony environment is at 1 atm pressure and 25˚C but conditions at the northern ice cap are -150 ˚C and 600 Pa. You have access to industrial heaters and pumps.

Data

ΔH_{fus} = 6.01 kJ/mol
ΔH_{sub} = 51.1 kJ/mol
ΔH_{vap} = 44.0 kJ/mol
$C_{P,m}[H_2O(l)]$ = 75.38 J/(mol K)
$C_{P,m}[H_2O(g)]$ = 36.57 J/(mol K)
$C_{P,m}[H_2O(s)]$ = 32.0 J/(mol K)
(averaged for temp. range)

Phase Diagram of Water



a) Describe in words the process you will use to harvest and transport the water. Draw this process on the phase diagram to the right. Your description should include the phase of the water in each part of your process, the temperature and pressure of any phase changes, and the kind of phase change(s) that occur.

There are different possible processes one could choose. This solution describes one possibility in which the solid ice at -150 ˚C and 600 Pa (below the Ic/Ih phase boundary) is heated to the solid/gas coexistence curve just below the triple point at 611 Pa. The water sublimes at a temperature just below 0 ˚C, and the resulting vapour is heated to prevent redeposition in the pipeline (say to 25 ˚C). When the gas arrives at the colony, the pressure is increased until it equilibrates with the pressure there (1 atm). In doing so, the system crosses the vapour/liquid coexistence curve at a pressure of about 4 kPa and condenses to liquid.

b) Will the fluid in the pipeline be liquid or gas?

Gas, for this process. However, it could be liquid if alternate processes are used.

c) How much heat is required per mole to get the water into the pipeline?

The process involves heating in 3 stages

Stage 1: warm ice from -150 ˚C to 0 ˚C

$$q_1 = nC_{P,m}[\mathrm{H_2O(s)}]\Delta T = 1\ \mathrm{mol} \times 32.0\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 150\ \mathrm{K}$$
$$= 4800\ \mathrm{J} = 4.80\ \mathrm{kJ}$$

Stage 2: sublime ice

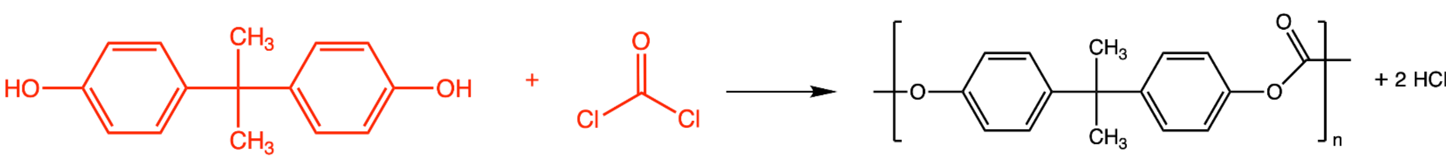
$$q_2 = n\Delta H_{sub} = 1\ \mathrm{mol} \times 51.1\ \mathrm{kJ\ mol^{-1}} = 51.1\ \mathrm{kJ}$$

Stage 3: warm gas from 0 ˚C to 25 ˚C

$$q_3 = nC_{P,m}[\mathrm{H_2O(g)}]\Delta T = 1\ \mathrm{mol} \times 36.57\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 25\ \mathrm{K}$$
$$= 914\ \mathrm{J} = 0.914\ \mathrm{kJ}$$

The total heat for the process is then 4.80 kJ + 51.1 kJ + 9.14 kJ = 56.8 kJ .

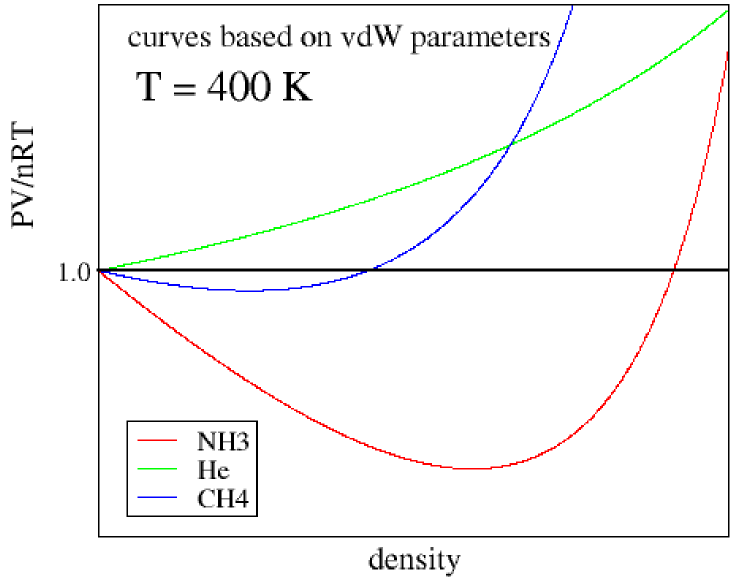
2. **[6 marks total]** Consider the polymer shown in the reaction below.
   a) Draw the monomers that must react to produce the products shown.



b) Is this polymer expected to be more or less stiff than high density polyethylene? Explain why.

Both HDPE and this polymer are linear chains but HDPE, with its carbon-carbon backbone, has only London dispersion interactions between the chains. This polymer has those interactions plus dipole-dipole interactions arising from the ester groups so the inter-chain interactions are expected to be stronger, making the polymer harder to deform and hence stiffer.

3. **[6 marks total]** On the graph, sketch and label predictions for curves of PV/nRT versus density (at fixed T) for the gases He, CH_4 and NH_3. Briefly explain what causes the curves to have the shapes you've drawn.



At low density all gases behave ideally so curves start at 1.0. At higher density, curves dip below 1.0 because attractive intermolecular forces cause the pressure to be less than ideal (for He there is no dip due to its very weak intermolecular forces). Because ammonia has greater forces than methane which in turn are greater than He, the curve for ammonia should have the largest deviation from 1.0 at low densities, followed by methane then helium. At still higher densities, repulsive forces from the sizes of the particles (crowding) make the pressure increase beyond the ideal value so the curves climb greater than 1.0. The biggest particles are expected to increase the fastest in this region.

4. **[6 marks total]** Consider the following reactions of ethyne:

$$C_2H_2(g) + Cl_2(g) \rightarrow C_2H_2Cl_2(l) \qquad \Delta H^0 = -257.4 \text{ kJ}$$
$$C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(g) \qquad \Delta H^0 = -1256.2 \text{ kJ}$$

Given $\Delta H^0{}_f[CO_2(g)] = -393.5$ kJ/mol and $\Delta H^0{}_f[H_2O(g)] = -241.8$ kJ/mol, find the enthalpy of formation for $C_2H_2Cl_2(l)$, in kJ/mol.

There are several ways to answer this question. Subtracting the second reaction from the first gives an enthalpy of $\Delta H^0 = -257.4$ kJ + 1256.2 kJ = 998.8 kJ for the reaction

$$2\ CO_2(g) + H_2O(g) + Cl_2(g) \rightarrow 5/2\ O_2(g) + C_2H_2Cl_2(l)$$

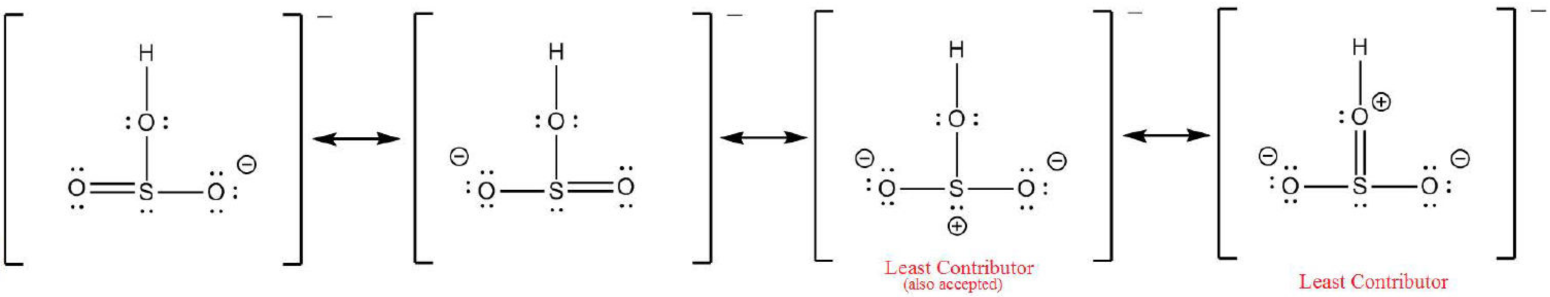
Using heats of formation for this reaction (remembering those for oxygen and chlorine are zero because these elements are in their standard state) gives

$\Delta H^0 = 998.8$ kJ = 1 mol x $\Delta H_f^0[C_2H_2Cl_2(l)]$ – 2 mol x (-393.5 kJ/mol) – 1mol x (-241.8 kJ/mol)

Isolating the desired value gives $\Delta H_f^0[C_2H_2Cl_2(l)] = -30$ kJ/mol. One could also have used the second reaction to solve for $\Delta H_f^0[C_2H_2(g)]$ and then used this in the first reaction.

5. **[6 marks total]** Sodium hydrogen sulfite, $NaHSO_3$, is added to wines to prevent oxidation and preserve flavor.

   a) Draw all valid Lewis structures that contribute to the resonance hybrid of the hydrogen sulfite anion, HSO_3^-, (H is bonded to O). Show all bonds as lines and lone pairs as dots; indicate formal charges and overall charges where applicable.

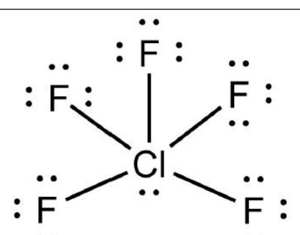
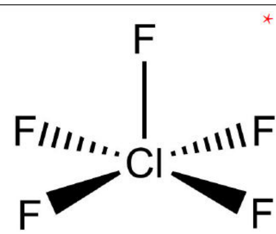
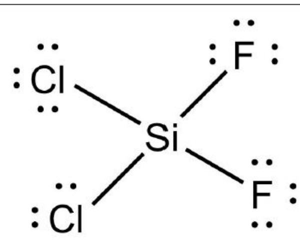
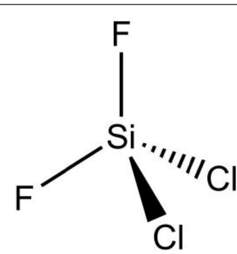


Structures with negative formal charges on central hypervalent atoms are not valid.

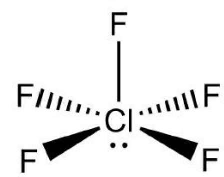
   b) Write the words "Least Contributor" directly beneath the structure that contributes the least to the resonance hybrid. Below, explain why that structure is the least contributor.

The Least Contributor has the greatest separation of formal charge compared with all the others resonance structures so is least favoured.

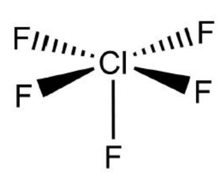
6. **[6 marks totals]** Complete the table by drawing for each molecule the best Lewis structure and a perspective diagram, as well as indicating whether it is polar. For the Lewis structure, show all bonds as lines and lone pairs as dots.

Molecule	Best Lewis Structure	Perspective Diagram	Polar ? (Yes/No)
ClF_5		 *	Yes
$SiCl_2F_2$			Yes

* acceptable:



or



7. **[6 marks total]** Use bond enthalpies to estimate ΔH^0, in kJ, for the reaction:

$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$$

Bond Enthalpies in kJ/mol			
C–C	350	C–H	410
C=C	611	C–O	350
C≡C	835	C–F	450
H–H	436	C–Cl	330
H–Cl	432	C–Br	270
H–Br	366	C–N	300

The enthalpy change comes from examining the bonds that have been broken and formed in the reaction, being careful to consider the correct Lewis structures for each species.

$$\begin{aligned}\Delta H^0 &= 1\text{ mol} \times E(C\equiv C) + 2\text{ mol} \times E(C\text{–}H) + 1\text{ mol} \times E(H\text{–}H)\\ &\quad - 1\text{ mol} \times E(C=C) - 4\text{ mol} \times E(C\text{–}H)\\ &= 835\text{ kJ} + 2 \times 410\text{ kJ} + 436\text{ kJ} - 611\text{ kJ} - 4 \times 410\text{ kJ}\\ &= -160\text{ kJ}\end{aligned}$$

Complete the table to the right by indicating the signs of q and w when the reaction written above is performed at constant standard pressure. Briefly state the reasons for your choices.

Quantity	+ or - ?
q	-
w	+

At constant pressure, $q = q_P = \Delta H$ and since $\Delta H < 0$ (from above) then $q < 0$. The exothermic reaction releases heat to the surroundings.

The number of moles of gas decreases for the forward reaction so the volume of the system is decreasing ($\Delta V < 0$) meaning work is positive (since $w = -P_{ext}\,\Delta V$ when pressure is constant). The surroundings are doing work on the system so the system is gaining energy.