

CHM 3400 – Problem Set 4

Due date: Monday, February 10th. NOTE: Exam 1 is Wednesday, February 12th. Please bring a calculator, all class handouts, and one 8.5" x 11" page of notes.

Do all of the following problems. Show your work.

“...the basic law of life (is) to be ever more highly structured and to struggle against entropy.” - Vaclav Havel

1) Data for benzene (C₆H₆(ℓ)) are given below for T = 25.0 °C.

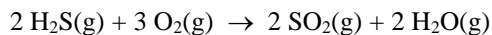
Substance	ΔH_f° (kJ/mol)	S° (J/mol·K)	ΔG_f° (kJ/mol)	$C_{p,m}$ (J/mol·K)
C ₆ H ₆ (ℓ)	49.0	173.3	124.3	136.1

In addition, the normal boiling point and enthalpy of vaporization for benzene are T_{°vap} = 80.1 °C, $\Delta H_{\text{vap}}^\circ = 30.82$ kJ/mol.

Based on the above information, find the following:

- $S^\circ(\text{C}_6\text{H}_6(\ell))$, the absolute entropy for liquid benzene, at T = 80.1 °C.
- $S^\circ(\text{C}_6\text{H}_6(\text{g}))$, the absolute entropy for benzene vapor, at T = 80.1 °C.

2) Consider the following chemical reaction:



Data for the reactants and products are given in the table below at T = 25.0 °C.

- Find the value for $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ for the above reaction at T = 25.0 °C.
- Using the data for the free energy of formation for the reactants and products, find the value for $\Delta G_{\text{rxn}}^\circ$ for the above reaction at T = 25.0 °C.
- Using the relationship

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$$

and your answer in part a, find the value for $\Delta G_{\text{rxn}}^\circ$ for the above reaction at T = 25.0 °C. Verify that you get the same answer (to within roundoff error) as found in part b of this problem.

Substance	ΔH_f° (kJ/mol)	S° (J/mol·K)	ΔG_f° (kJ/mol)	$C_{p,m}$ (J/mol·K)
H ₂ O(g)	- 241.82	188.83	- 228.57	33.58
H ₂ S(g)	- 20.63	218.79	- 33.56	34.23
O ₂ (g)	0.0	205.14	0.0	29.36
SO ₂ (g)	- 296.83	238.22	- 300.19	39.87

3) Data for methyl alcohol are given below at $T = 25.0\text{ }^{\circ}\text{C}$.

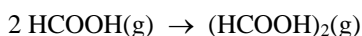
Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)	ΔG°_f (kJ/mol)	$C_{p,m}$ (J/mol·K)
$\text{CH}_3\text{OH}(\ell)$	- 238.66	126.80	- 166.27	81.6
$\text{CH}_3\text{OH}(\text{g})$	- 200.66	239.81	- 161.96	43.9

a) Based on these data, estimate the value for T°_{vap} , the normal boiling point for methyl alcohol. Give your final answer in units of $^{\circ}\text{C}$.

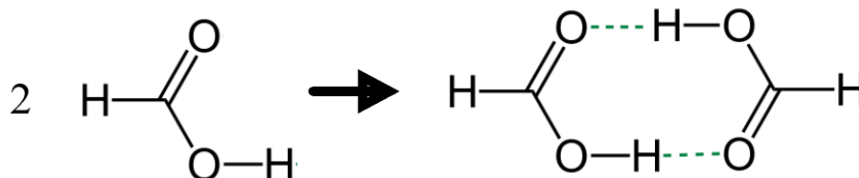
b) The experimental value for the normal boiling point for methyl alcohol is $T^{\circ}_{\text{vap}} = 64.0\text{ }^{\circ}\text{C}$. Explain why your answer in part a is different than this value.

4) Hydrogen bonding plays an important role in determining the structure of many biomolecules. Because of this, there is interest in measuring the strength of typical hydrogen bonds.

Consider the following gas phase chemical reaction involving formic acid (HCOOH)



which corresponds to the formation of a formic acid dimer in the gas phase. We can represent the reaction taking place and the structure of the dimer as shown below.



a) Based on the thermodynamic data given below (at $T = 25.0\text{ }^{\circ}\text{C}$), estimate the strength of a hydrogen bond in the formic acid dimer. Give your estimate in units of kJ/mol.

b) The strength of a typical covalent single bond is $\sim 400\text{ kJ/mol}$. How does the strength of a hydrogen bond compare to that of a typical single covalent bond?

c) Is formation of the gas phase formic acid dimer a spontaneous process for standard conditions and at $T = 25.0\text{ }^{\circ}\text{C}$? Give a thermodynamic justification for your answer.

Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)
$\text{HCOOH}(\text{g})$	- 362.63	251.0
$(\text{HCOOH})_2(\text{g})$	- 785.34	347.7

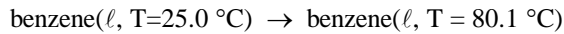
Solutions.

1) The general relationship to be used in this problem is

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{n C_{p,m}}{T} dT + \sum_{pt} \frac{n \Delta H_{pt}}{T_{pt}}$$

In this problem, we know the value for S° for one mole of liquid benzene at $T = 25.0^\circ\text{C}$, and so can use the above equation to find S° at other temperatures.

a) For the process



there is no change in phase, so we may say

$$S^\circ(\text{benzene}, \ell, T_2) = S^\circ(\text{benzene}, \ell, T_1) + \int_{T_1}^{T_2} \frac{C_{p,m}(\text{benzene}, \ell)}{T} dT$$

If we assume $C_{p,m}$ is constant over the temperature range in the problem, then

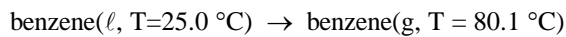
$$S^\circ(\text{benzene}, \ell, T_2) = S^\circ(\text{benzene}, \ell, T_1) + C_{p,m}(\text{benzene}, \ell) \int_{T_1}^{T_2} \frac{dT}{T}$$

$$S^\circ(\text{benzene}, \ell, T_2) = S^\circ(\text{benzene}, \ell, T_1) + C_{p,m}(\text{benzene}, \ell) \ln(T_2/T_1)$$

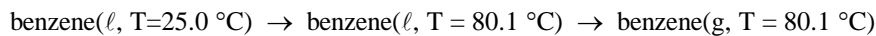
If we pick $T_1 = 25.0^\circ\text{C} = 298.15\text{ K}$, and $T_2 = 80.1^\circ\text{C} = 353.25\text{ K}$, and use the data given the problem, we get

$$\begin{aligned} S^\circ(\text{benzene}, \ell, 80.1^\circ\text{C}) &= 173.3 \text{ J/mol}\cdot\text{K} + 136.1 \text{ J/mol}\cdot\text{K} \ln(353.25 \text{ K}/298.15 \text{ K}) \\ &= 173.3 \text{ J/mol}\cdot\text{K} + 23.08 \text{ J/mol}\cdot\text{K} = 196.4 \text{ J/mol}\cdot\text{K} \end{aligned}$$

b) For the process



we can write the overall process as



and so we can say

$$S^\circ(\text{benzene}, \text{g}, T_2) = S^\circ(\text{benzene}, \ell, T_1) + \int_{T_1}^{T_2} \frac{C_{p,m}(\text{benzene}, \ell)}{T} dT + \frac{\Delta H^\circ_{\text{vap}}}{T^\circ_{\text{vap}}}$$

Where we again choose $T_1 = 25.0^\circ\text{C} = 298.15\text{ K}$ and $T_2 = 80.1^\circ\text{C} = 353.25\text{ K}$, our answer for $S^\circ(\text{benzene}, \text{g}, T_2)$ is the same as our answer in part a, except for the last term, which accounts for the additional increase in entropy for the $\ell \rightarrow \text{g}$ phase transition at the normal boiling point.

$$\text{So } S^\circ(\text{benzene}, \text{g}, 80.1^\circ\text{C}) = 196.4 \text{ J/mol}\cdot\text{K} + \frac{30820. \text{ J/mol}}{353.25 \text{ K}} = 196.4 \text{ J/mol}\cdot\text{K} + 87.25 \text{ J/mol}\cdot\text{K} = 283.6 \text{ J/mol}\cdot\text{K}$$

2) a) To find the change in enthalpy and the change in entropy for standard conditions we may use the general procedure developed in class and the data in the problem.

$$\begin{aligned}\Delta H^{\circ}_{\text{rxn}} &= [\sum \Delta H^{\circ}_{\text{f}}(\text{products})] - [\sum \Delta H^{\circ}_{\text{f}}(\text{reactants})] \\ &= [2 \Delta H^{\circ}_{\text{f}}(\text{SO}_2(\text{g})) + 2 \Delta H^{\circ}_{\text{f}}(\text{H}_2\text{O}(\text{g}))] - [2 \Delta H^{\circ}_{\text{f}}(\text{H}_2\text{S}(\text{g})) + 3 \Delta H^{\circ}_{\text{f}}(\text{O}_2(\text{g}))] \\ &= [2 (- 296.83 \text{ kJ/mol}) + 2 (- 241.82 \text{ kJ/mol})] - [2 (- 20.63 \text{ kJ/mol}) + 3 (0.0 \text{ kJ/mol})] \\ &= - 1077.30 \text{ kJ/mol} - (- 41.26 \text{ kJ/mol}) = - 1036.04 \text{ kJ/mol} \\ \Delta S^{\circ}_{\text{rxn}} &= [\sum S^{\circ}(\text{products})] - [\sum S^{\circ}(\text{reactants})] \\ &= [2 S^{\circ}(\text{SO}_2(\text{g})) + 2 S^{\circ}(\text{H}_2\text{O}(\text{g}))] - [2 S^{\circ}(\text{H}_2\text{S}(\text{g})) + 3 S^{\circ}(\text{O}_2(\text{g}))] \\ &= [2 (238.22 \text{ J/mol}\cdot\text{K}) + 2 (188.83 \text{ J/mol}\cdot\text{K})] - [2 (218.79 \text{ J/mol}\cdot\text{K}) + 3 (205.14 \text{ J/mol}\cdot\text{K})] \\ &= 854.10 \text{ J/mol}\cdot\text{K} - (1053.00 \text{ J/mol}\cdot\text{K}) = - 198.90 \text{ J/mol}\cdot\text{K}\end{aligned}$$

b) To find $\Delta G^{\circ}_{\text{rxn}}$ directly, we use

$$\begin{aligned}\Delta G^{\circ}_{\text{rxn}} &= [\sum \Delta G^{\circ}_{\text{f}}(\text{products})] - [\sum \Delta G^{\circ}_{\text{f}}(\text{reactants})] \\ &= [2 \Delta G^{\circ}_{\text{f}}(\text{SO}_2(\text{g})) + 2 \Delta G^{\circ}_{\text{f}}(\text{H}_2\text{O}(\text{g}))] - [2 \Delta G^{\circ}_{\text{f}}(\text{H}_2\text{S}(\text{g})) + 3 \Delta G^{\circ}_{\text{f}}(\text{O}_2(\text{g}))] \\ &= [2 (- 300.19 \text{ kJ/mol}) + 2 (- 228.57 \text{ kJ/mol})] - [2 (- 33.56 \text{ kJ/mol}) + 3 (0.0 \text{ kJ/mol})] \\ &= - 1057.52 \text{ kJ/mol} - (- 67.12 \text{ kJ/mol}) = - 990.40 \text{ kJ/mol}\end{aligned}$$

c) The second way to find $\Delta G^{\circ}_{\text{rxn}}$ is from the relationship

$$\begin{aligned}\Delta G^{\circ}_{\text{rxn}} &= \Delta H^{\circ}_{\text{rxn}} - T \Delta S^{\circ}_{\text{rxn}} = - 1036.04 \text{ kJ/mol} - (298.15 \text{ K}) (- 0.15290 \text{ kJ/mol}\cdot\text{K}) \\ &= - 1036.04 \text{ kJ/mol} - (- 59.30 \text{ kJ/mol}) = - 976.7 \text{ kJ/mol}\end{aligned}$$

The results for $\Delta G^{\circ}_{\text{rxn}}$ found in part b and c are different. After a lot of checking, I discovered that the table where I got my values for S° had two errors. The correct value for $S^{\circ}(\text{H}_2\text{S}(\text{g}))$ is 205.79 J/mol·K, and $S^{\circ}(\text{SO}_2(\text{g})) = 248.22$ J/mol·K. If these values are used in part a then we get $\Delta S^{\circ}_{\text{rxn}} = - 152.90$ J/mol·K, which then gives $\Delta G^{\circ}_{\text{rxn}} = - 990.45$ kJ/mol in part c, which agrees with the answer in part b to within roundoff error.

I apologize for not noticing the table I was using had incorrect values.

3) a) If we calculate the change in enthalpy and the change in entropy for the phase transition, at $T = 25.0$ °C, we get

$$\begin{aligned}\Delta H^{\circ}_{\text{vap}} &= \Delta H^{\circ}_{\text{f}}(\text{CH}_3\text{OH}(\text{g})) - \Delta H^{\circ}_{\text{f}}(\text{CH}_3\text{OH}(\ell)) \\ &= (- 200.66 \text{ kJ/mol}) - (238.66 \text{ kJ/mol}) = 38.00 \text{ kJ/mol} \\ \Delta S^{\circ}_{\text{vap}} &= S^{\circ}(\text{CH}_3\text{OH}(\text{g})) - S^{\circ}(\text{CH}_3\text{OH}(\ell)) \\ &= (239.81 \text{ J/mol}\cdot\text{K}) - (126.80 \text{ J/mol}\cdot\text{K}) = 113.01 \text{ J/mol}\cdot\text{K}\end{aligned}$$

If we assume that the values for $\Delta H^\circ_{\text{vap}}$ and $\Delta S^\circ_{\text{vap}}$ are independent of temperature, then

$$T^\circ_{\text{vap}} = \frac{\Delta H^\circ_{\text{vap}}}{\Delta S^\circ_{\text{vap}}} = \frac{38000. \text{ J/mol}}{113.01 \text{ J/mol}\cdot\text{K}} = 336.25 \text{ K} = 63.1 \text{ }^\circ\text{C}$$

b) The value found in part a is slightly different than the experimental value ($T^\circ_{\text{vap}} = 64.0 \text{ }^\circ\text{C}$) because $\Delta H^\circ_{\text{vap}}$ and $\Delta S^\circ_{\text{vap}}$ do change by a small amount with temperature.

4) a) $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_f(\text{HCOOH})_2(\text{g}) - 2 \Delta H^\circ_f(\text{HCOOH}(\text{g}))$

$$= (-785.34 \text{ kJ/mol}) - 2(362.63 \text{ kJ/mol}) = -60.08 \text{ kJ/mol}$$

If we look at the reaction taking place, $\Delta H^\circ_{\text{rxn}}$ is the enthalpy change corresponding to forming two hydrogen bonds. So the enthalpy change for breaking one hydrogen bond is

$$\Delta H_{\text{Hbond}} = - \frac{(-60.08 \text{ kJ/mol})}{2} = 30.04 \text{ kJ/mol}$$

b) This hydrogen bond is approximately one tenth the strength of a typical single covalent bond, and so it is much weaker. However, for a large molecule, like a protein molecule, where there are a large number of water molecules interacting with the protein via hydrogen bonding, this can have a significant effect on the three dimensional structure of the molecule.

c) Since we do not have data on the free energy of formation of the reactant and product, we will need to find $\Delta G^\circ_{\text{rxn}}$ as was done in part c of problem 2. We already have a value for $\Delta H^\circ_{\text{rxn}}$. For $\Delta S^\circ_{\text{rxn}}$, we get

$$\Delta S^\circ_{\text{rxn}} = S^\circ(\text{HCOOH})_2(\text{g}) - 2 S^\circ(\text{HCOOH}(\text{g}))$$
$$= (347.7 \text{ J/mol}\cdot\text{K}) - 2(251.0 \text{ J/mol}\cdot\text{K}) = -154.3 \text{ J/mol}\cdot\text{K}$$

So then $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}} = -60.08 \text{ kJ/mol} - (298.15 \text{ K})(-0.1543 \text{ kJ/mol}\cdot\text{K})$

$$= -60.08 \text{ kJ/mol} - (-46.00 \text{ kJ/mol}) = -14.08 \text{ kJ/mol}$$

Since $\Delta G^\circ_{\text{rxn}} < 0$, the reaction is spontaneous for standard conditions.