

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.

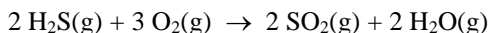
Substance	ΔH_f° (kJ/mol)	S° (J/mol·K)	ΔG_f° (kJ/mol)	$C_{p,m}$ (J/mol·K)
C ₆ H ₆ (ℓ)	49.0	173.3	124.3	136.1

In addition, the normal boiling point and enthalpy of vaporization for benzene are T_{vap}^o = 80.1 °C, ΔH_{vap}^o = 30.82 kJ/mol.

Based on the above information, find the following:

- S^o(C₆H₆(ℓ)), the absolute entropy for liquid benzene, at T = 80.1 °C.
- S^o(C₆H₆(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 ΔH_{rxn}^o and ΔS_{rxn}^o 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 ΔG_{rxn}^o 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 ΔG_{rxn}^o 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 $T = 25.0\text{ }^{\circ}\text{C}$.

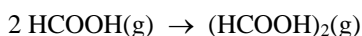
Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)	ΔG°_f (kJ/mol)	$C_{p,m}$ (J/mol·K)
$\text{CH}_3\text{OH}(\ell)$	- 238.66	126.80	- 166.27	81.6
$\text{CH}_3\text{OH}(\text{g})$	- 200.66	239.81	- 161.96	43.9

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 $^{\circ}\text{C}$.

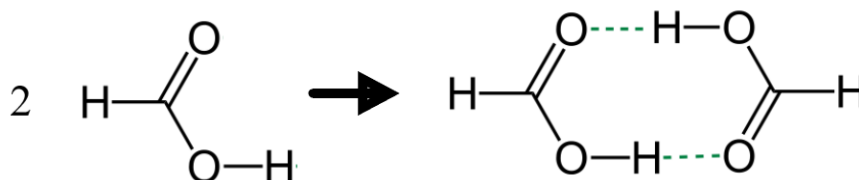
b) The experimental value for the normal boiling point for methyl alcohol is $T^{\circ}_{\text{vap}} = 64.0\text{ }^{\circ}\text{C}$. Explain why your answer in part a is different than this value.

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