CH353 – Physical Chemistry I
Spring 2012, Unique 52135

Exam 2
Friday, 24 February 2012

Name: Key

Useful Information:

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 8.206 \times 10^{-2}\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$1\ \text{atm} = 1.01325\ \text{bar} = 1.01325 \times 10^{5}\ \text{Pa} = 760\ \text{Torr}$

$0\ ^{\circ}\text{C} = 273.15\ \text{K}$

Always assume ideal gas unless directed otherwise.

$$dU = TdS - PdV$$
$$dH = TdS + VdP$$
$$dA = -SdT - PdV$$
$$dG = -SdT + VdP$$
$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$
$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Honor Code:

"The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community."

I certify that the work on this exam is entirely my own.

Signature Date

1. (30 points) Indicate whether the following statements are true or false.

a. True False When the heat transferred in a reversible pathway is divided by the temperature at which that transfer occurs, the resulting quantity is a state function.

b. True False The temperature dependence of $\Delta H_{rxn}(T)$ is a function of the heat capacities of the reactants and products.

c. True False In any thermodynamic transformation, the change in internal energy is sufficient to determine the direction of a spontaneous process.

d. True False A system will move spontaneously to a state with fewer possible configurations.

e. True False Compression of an ideal gas always results in $\Delta S_{sys} > 0$.

f. True False $\Delta S_{sys} = C_p \ln\left(\frac{T_f}{T_i}\right) - nR\ln\left(\frac{P_f}{P_i}\right)$, assuming C_p is independent of pressure.

g. True False The entropy of any system at any temperature can be calculated exactly.

h. True False At any temperature, cyclohexane (C_6H_{12}) has greater molar entropy than benzene (C_6H_6).

i. True False Solid carbon (C(s)) comes in two forms, graphite (S_m^0 = 5.7 J K^{-1} mol^{-1}) and diamond (S_m^0 = 2.4 J K^{-1} mol^{-1}). Under standard conditions, graphite will spontaneously transform to diamond. not enough info.

2. (10 points) Arrange the following reactions according to increasing values of ΔS_{rxn}^0.

a) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$
b) $NH_3(g) + HCl(g) \rightarrow NH_4Cl\ (s)$
c) $K(s) + O_2(g) \rightarrow KO_2(s)$
d) $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

- 3 mols gas
- 2 mols gas → product is solid
- 1 mol gas
- 2 mols gas → product is gas

a < b < d < c

3. (20 points) With the following data for water, determine a) the entropy of fusion of water, b) the entropy of vaporization of water, and c) comment on any differences between your answers in a) and b).

$\Delta H^0_{fus} = 6.01$ kJ mol^{-1}
$\Delta H^0_{vap} = 40.7$ kJ mol^{-1}

a) $\Delta S^\circ_{fus} = \dfrac{\Delta H^\circ_{fus}}{T^\circ_{fus}} = \dfrac{6.01 \times 10^3 \text{ J/mol}}{273 \text{ K}}$

$\Delta S^\circ_{fus} = 22.0 \text{ J/K mol}$

b) $\Delta S^\circ_{vap} = \dfrac{\Delta H^\circ_{vap}}{T^\circ_{vap}} = \dfrac{40.7 \times 10^3 \text{ J/mol}}{373 \text{ K}}$

$\Delta S^\circ_{vap} = 109 \text{ J/K mol}$

c) The change in entropy of the system moving from liquid to gas (vaporization) is significantly larger than when the system moves from solid to liquid because of the significantly larger volume occupied by the gas compared to the liquid and the significantly higher # of ~~ne~~ configurations the system can assume in the gas phase compared to the liquid phase.

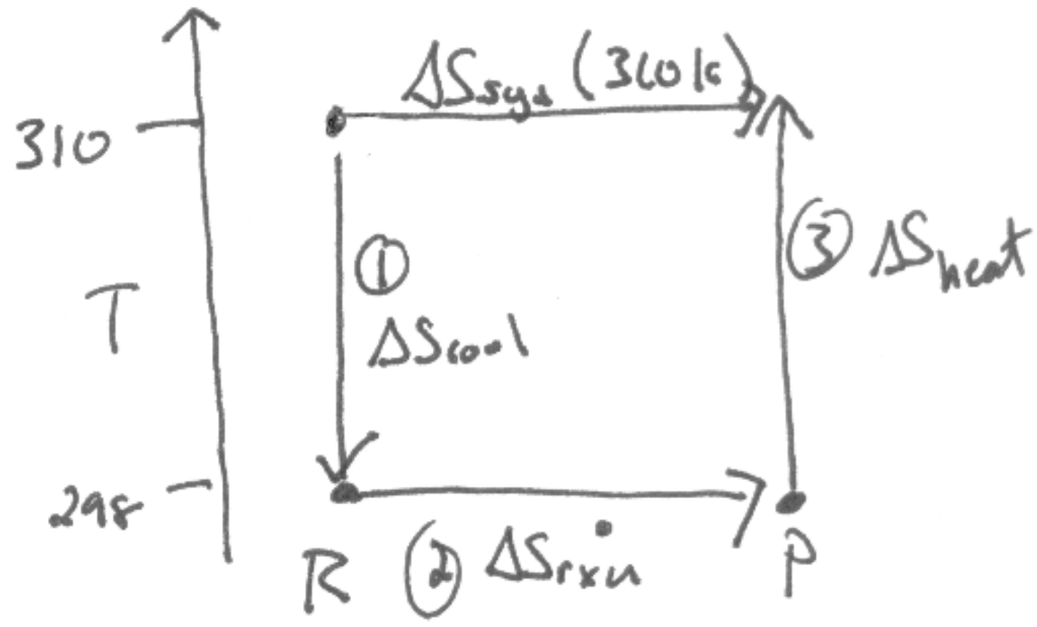
4. (20 points) The enzyme carbonic anhydrase catalyses the hydration of CO_2 gas in red blood cells:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

Determine ΔS_{sys} of this reaction at 37°C (body temperature), and justify the sign. The following data might be helpful (you may assume C_p is constant over this temperature range):

	S_m^0 (J K^{-1} mol^{-1})	C_p (J K^{-1} mol^{-1})
$CO_2(g)$	213.7	36.8
$H_2O(l)$	69.9	78.2
$H_2CO_3(aq)$	187.4	19.4

these values are at T = 298K, reaction occurs at T = 310K



$\Delta S_{sys}(310K) = \Delta S_{cool} + \Delta S_{rxn}^{\circ} + \Delta S_{heat}$

$\Delta S_{cool} = C_p(CO_2(g)) \ln\left(\frac{T_f}{T_i}\right) + C_p(H_2O(l)) \ln\left(\frac{T_f}{T_i}\right)$

$= (36.8\ J/K\,mol) \ln\left(\frac{298K}{310K}\right) + (78.2\ J/K\,mol) \ln\left(\frac{298K}{310K}\right)$

$= -1.45\ J/K\,mol + -3.10\ J/K\,mol$

$\Delta S_{cool} = -4.54\ J/K\,mol$ Sign makes sense because $T_f < T_i$

$\Delta S_{rxn}^{\circ} = \sum_{products} \upsilon S_m^{\circ} - \sum_{react} \upsilon S_m^{\circ} = [187.4 - (213.7 + 69.9)]\ J/K\,mol$

$\Delta S_{rxn}^{\circ} = -95.5\ J/K\,mol$ Sign makes sense because we are losing 1 mole of gas

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Scratch paper.

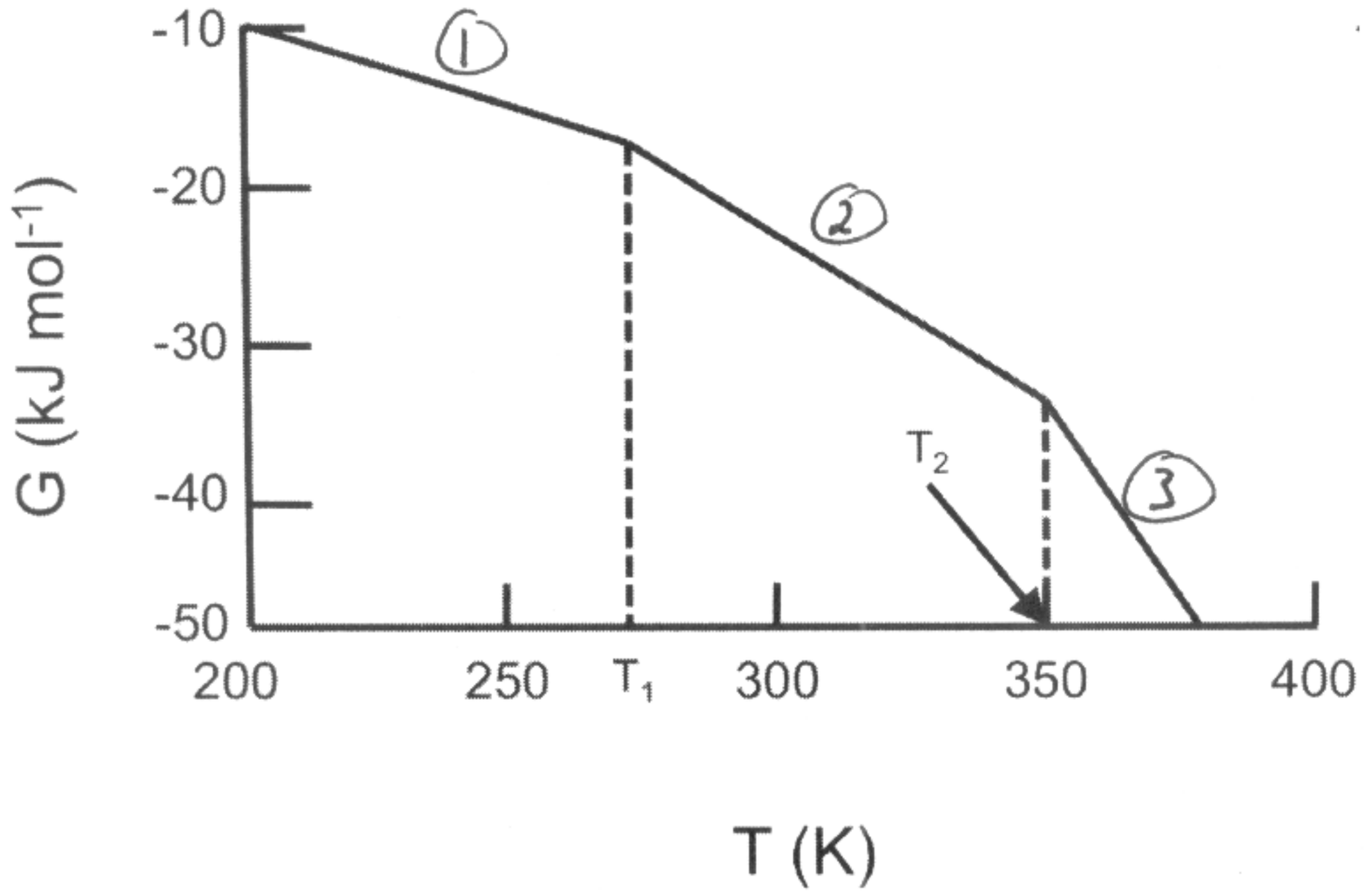
$\Delta S_{heat} = C_p(H_2CO_3)\ln\left(\frac{T_f}{T_i}\right) = (19.4\ J/kmol)\ln\left(\frac{310\ k}{298\ k}\right)$

$\Delta S_{heat} = 0.766\ J/kmol$ Sign makes sense because $T_f > T_i$

$\Delta S_{sys}(310k) = -4.54\ J/kmol + -95.5\ J/kmol + 0.766\ J/kmol$

$\Delta S_{sys} = -99.3\ J/kmol$ Sign makes sense because we are losing 1mol of gas

5. (20 points) The free energy, G, of benzene (C_6H_6) is plotted here as a function of temperature:



a) Define (in words) the physical meaning of temperatures T_1 and T_2.

T_1 = melting temp
T_2 = boiling temp

These are the temperatures of the phase transitions.

b) Describe (in words) the slopes of each segment on the figure.

Slope ① = $-S_m^\circ$ (solid)
Slope ② = $-S_m^\circ$ (liquid)
Slope ③ = $-S_m^\circ$ (gas)

In each case, the slope is the negative of the molar entropy of benzene in the phase that exists over that temperature range.