Chemistry 271, Section 22xx and 23xx
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University of Maryland, College Park

General Chemistry and Energetics
Exam II (100 points total)

Your Name: Key BEIWE

Your SID #:

Your Section #:

November 7, 2011

You have 53 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$K_a = [H^+][A^-]/[HA]$ $\quad$ $pH = -\log([H^+])$ $\quad$ $K_b = [HA][HO^-]/[A^-]$

$K_w = [H^+][HO^-]$ $\quad$ $pH = pK_a + \log [A^-]/[HA]$ $\quad$ $\Delta G° = -RT\ln K_{eq}$

$R = 0.08206$ L·atm/mole K $\quad$ 0 °C = 273.15 K $\quad$ $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$\Delta S - q/T \geq 0$ $\quad$ R = 8.314 J/mole K = 1.987 cal/mole K

$S = k_B \ln W$ $\quad$ $\Delta G = \Delta H - T\Delta S$ $\quad$ $E = \Sigma\, n_i\, \varepsilon_i$

$W = N!/(\prod n_i!)$ $\quad$ $n_i/n_0 = \exp[-(\varepsilon_i - \varepsilon_0)/kT]$ $\quad$ $N = \Sigma\, n_i$

$R = N_A k_B$ $\quad$ $k_B = 1.38 \times 10^{-23}$ J/K $\quad$ $t' = t - vx/c^2$

Chemical standard state: 1 M solutes, pure liquids, 1 atm gases

$K_p = K_c(RT)^{\Delta n}$ $\quad$ $P^2/a^3 = 4\pi^2/MG$ $\quad$ $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Biochemical standard state: pH 7, all species in the ionic form found at pH 7

nano: 10^{-9} $\quad$ pico: 10^{-12} $\quad$ zepto: 10^{-21}

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

+1 point extra credit for filling in this box

1. (15 pts) Short Answer

(2 pts each)
Fill in the blanks: (or particles among energy levels) +2 each = 12

The Boltzmann distribution describes the distribution of energy among particles that is observed in each of the microstates that comprise the predominant configuration of the ensemble system +1, which is all of the microstates available at a given total energy.

(1 pt each)
What is the sign of ΔG for any process that occurs spontaneously at constant P, T? $\ominus$

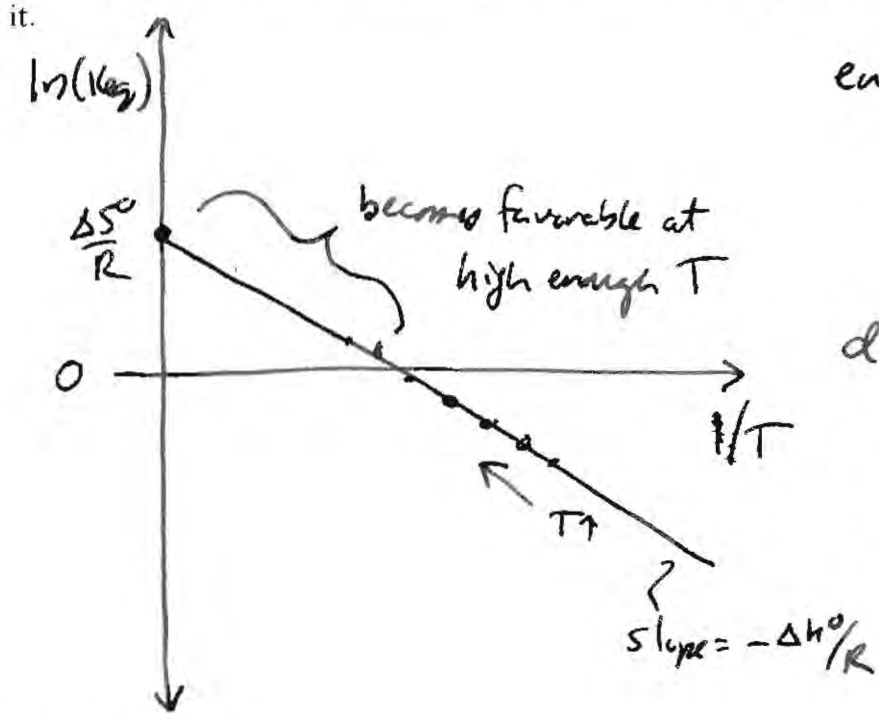
This a special case of the (circle one) First Law, [✓ Second Law], or Third Law of thermodynamics.

The free energy has reached a minimum when a system has reached equilibrium

+1 each

2. (15 pts) van't Hoff

(a; 8 pts) Draw a van't Hoff plot for an endothermic disordering reaction. Label the axes, and show how you would determine ΔH° and ΔS° from the plot. If there is a region where the reaction is spontaneous, label it.



endothermic −
$\Delta H^\circ > 0$
slope $= -\frac{\Delta H^\circ}{R} < 0$

disordering
$\Delta S^\circ > 0$
$\Delta S^\circ/R$ y-intercept > 0

(+1) for idea
(+2) for correct slope + intercept, (+2) for indicating slope $= -\frac{\Delta H^\circ}{R}$ and int $= \Delta S^\circ/R$
(+2) for labels
(+1) for region of spontaneity

Score for the page__________

(b; 7 pts) Starting From the van't Hoff equation, show that if you know the equilibrium constant at one temperature T_1, the equilibrium constant at temperature T_2 is given by the following equation:

$$K_2 = K_1 \times \exp\left[\left(\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$\ln(K_2) = \left(-\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T_2}\right) + \frac{\Delta S^\circ}{R}$$

(+1) for van't Hoff

$$- \quad \ln(K_1) = \left(-\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T_1}\right) + \frac{\Delta S^\circ}{R}$$

$$\ln(K_2) - \ln(K_1) = \left(-\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(+2) for idea of substraction

$$\ln(K_2) = \ln(K_1) + \left(\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(+2) for solving for $\ln(K_2)$

exponentiate both side

$$K_2 = K_1 \cdot e^{\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \quad ✓$$

(+2) for final answer if it came from somewhere

3. (20 pts) Boltzmann Distribution

(a; 6 pts) We often speak of "*k*T" as the energy available from thermal motion. What is the population relative to the ground state (n_i/n_0) of a state with an energy of *k*T above the ground state? What about a state with an energy of 10 *k*T? ↖ i

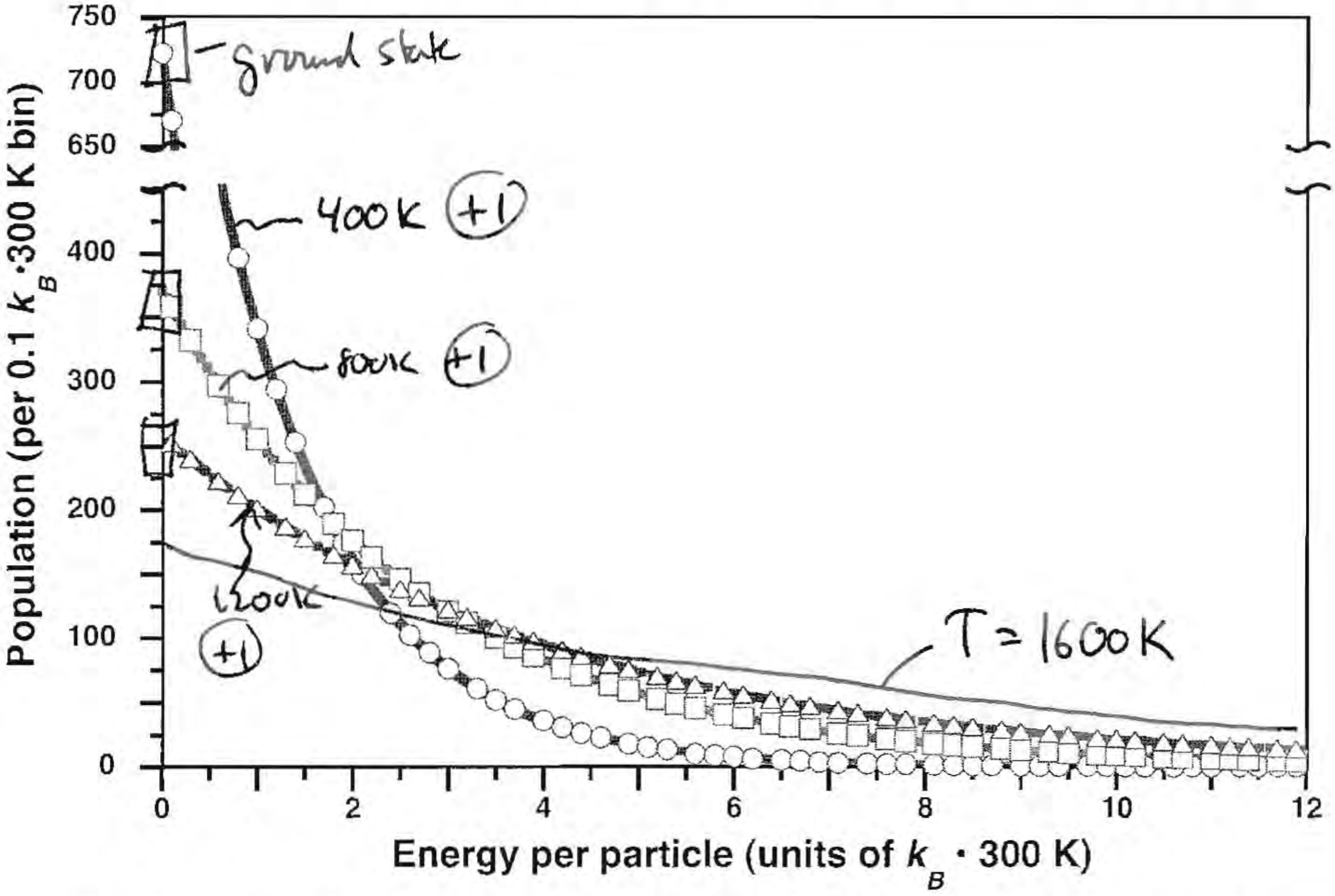
$$\underbrace{\frac{n_i}{n_0} = e^{-(\varepsilon_i - \varepsilon_0)/kT}}_{(+1)} = e^{\overset{\uparrow}{-(kT-0)/kT}} = e^{-1} = 0.37 \text{ or } 37\%$$

(+2) for plugging in (+1)

$$\frac{n_i}{n_0} = e^{-10kT/kT} = e^{-10} = 4.53 \times 10^{-5}$$ or ~~4.5~~ 0.00453%

(+2)

Boltzmann Distributions at Three Temperatures, $N = 10000$



(b; 6 pts) The temperatures of the three curves are 400, 800, and 1200 K. Indicate which temperature is which on the graph above, and how do you know?

(+3) The higher the temperature, the greater the population of molecules with higher energies

(+2)

(c; 2 pts) Identify the ground state populations for each distribution on the graph. ground state

(d; 3 pts) Sketch in the distribution for T = 1600 K. (+1) for any curve

(+1) for normalized

(+1) for y-intercept below the one for 800K

(e; 3 pts) Why are the areas under all four curves the same?

The curves are normalized

because the total population is

(+3) the area under the curve - constant.

(total probability = 1 is fine too)

Score for the page____________

4. (30 pts) Practical Thermodynamics

(a; 25 pts) The water-gas shift reaction [$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$] is exothermic, which makes hydrogen production complicated because the syngas reaction that provides the feedstock is done at very high temperature. From the data in the table for 25 °C, calculate ΔH°_{rxn} and ΔS°_{rxn}. Assuming that ΔH°_{rxn} and ΔS°_{rxn} are constant with T, calculate the free energy change ΔG°_{rxn} at 200 °C, the equilibrium constant at 200 °C, and the temperature at which the equilibrium constant is equal to 1.

	ΔH°_f in **kJ/mol**	S° in **J/(mol K)**
R →	ΔH°_f (CO) = −110.5	S° (CO) = 197.7
P →	ΔH°_f (CO_2) = −393.5	S° (CO_2) = 213.6
P →	ΔH°_f (H_2) = 0	S° (H_2) = 130.6
R →	ΔH°_f (H_2O, g) = −241.8	S° (H_2O, g) = 188.8
	ΔH°_f (CH_4) = −74.8	S° (CH_4) = 186.2
	ΔH°_f (C, graphite) = 0	S° (C, graphite) = 5.7
	ΔH°_f (O_2) = 0	S° (O_2) = 205

$$\Delta H^\circ_{rxn} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$ (+2)

$$= (-393.5 - 0)\ \text{kJ/mol} - (-110.5 - 241.8)\ \text{kJ/mol}$$

5

$$\Delta H^\circ_{rxn} = (-393.5 + 352.3)\ \text{kJ/mol} = \boxed{-41.2\ \text{kJ/mol}}$$ (+3) (5)

CO_2 is very stable!

The k is important!

$$\Delta S^\circ_{rxn} = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}) = (213.6 + 130.6) - (197.7 + 188.8)\ \text{J/mol K}$$ (+2)

$$\Delta S^\circ_{rxn} = (344.2 - 386.5)\ \text{J/mol K} = \boxed{-42.3\ \text{J/mol K}}$$ (+3) (5)

Relatively small ΔS° since $\Delta n = 0$ — H_2 is a symmetric diatomic

$$\Delta G^\circ_{rxn}(200^\circ C) = \Delta H^\circ - T\Delta S^\circ$$ (+2) (+1)

$$= -41200\ \text{J/mol} - (473.15\ \text{K})(-42.3\ \text{J/mol K})$$

exothermic ordering rxn → K ↓ as T ↑

$$= \boxed{-21200\ \text{J/mol}}$$ (+2) (5)

$$K_{eq}(200^\circ C = 473.15\ \text{K}) = e^{-\Delta G^\circ/RT} = e^{+21200/(8.314 \times 473.15)} = e^{+5.38}$$ (+2)

R in J/mol K

$$= \boxed{218}$$ (+2) (+2) (4)

$$\text{For } K_{eq} = 1,\ \ln(K_{eq}) = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-41200\ \text{J/mol}}{-42.3\ \text{J/mol K}} = \boxed{974\ \text{K}} = 701\ ^\circ C$$ (+2) (+2) (6)

for either

Score for the page__________

BRIGE

(b; 5 pts) Why is choosing the temperature at which to carry out an exothermic reaction often a balancing act? Name another reaction that poses the same challenge.

(+3) – One would like to raise the temperature to make the reaction go faster, +1 but then the equilibrium becomes less +2 favorable. [Or state that desired T is low to ↑ K_{eq}]

(+2) – The Haber rxn, Protein folding, combustion

DNA hybridization

fetal development

(+1) breakdown of NH_4NO_3

5. (20 pts) Hemoglobin and Linkage

Consider the competitive binding of chloride (Cl^-) and oxygen (O_2) to hemoglobin. We know that the R state of Hb binds O_2 better than the T state. We are told that Cl^- binds better to the T state than to the R state.

(6 pts) Draw the linkage cycle that shows that O_2 binding favors the R state over the T state.

(+2) for any linkage

(+2) for the right one

(+2) for statement about K's

Hb Hb

$$\begin{tikzcd} R + O_2 \arrow[r, shift left, "K_1"] \arrow[d, shift left] & R \cdot O_2 \arrow[l, shift left] \arrow[d, shift left] \\ T + O_2 \arrow[u, shift left, "K_4"] \arrow[r, shift left] & T \cdot O_2 \arrow[l, shift left, "K_3"] \arrow[u, shift left, "K_2"'] \end{tikzcd}$$

Hb·H⁺ Hb·H⁺

$K_1 K_2 = K_3 K_4$

$K_1 > K_3$

so $K_4 > K_2$ so O_2-bound state favors R more.

(6 pts) Draw the linkage cycle that shows that Cl^- binding favors the T state.

(+2) (+2) (+2)

$$\begin{tikzcd} R + Cl^- \arrow[r, shift left, "K_5"] \arrow[d, shift left] & R \cdot Cl^- \arrow[l, shift left] \arrow[d, shift left] \\ T + Cl^- \arrow[u, shift left, "K_8"] \arrow[r, shift left] & T \cdot Cl^- \arrow[l, shift left, "K_7"] \arrow[u, shift left, "K_6"'] \end{tikzcd}$$

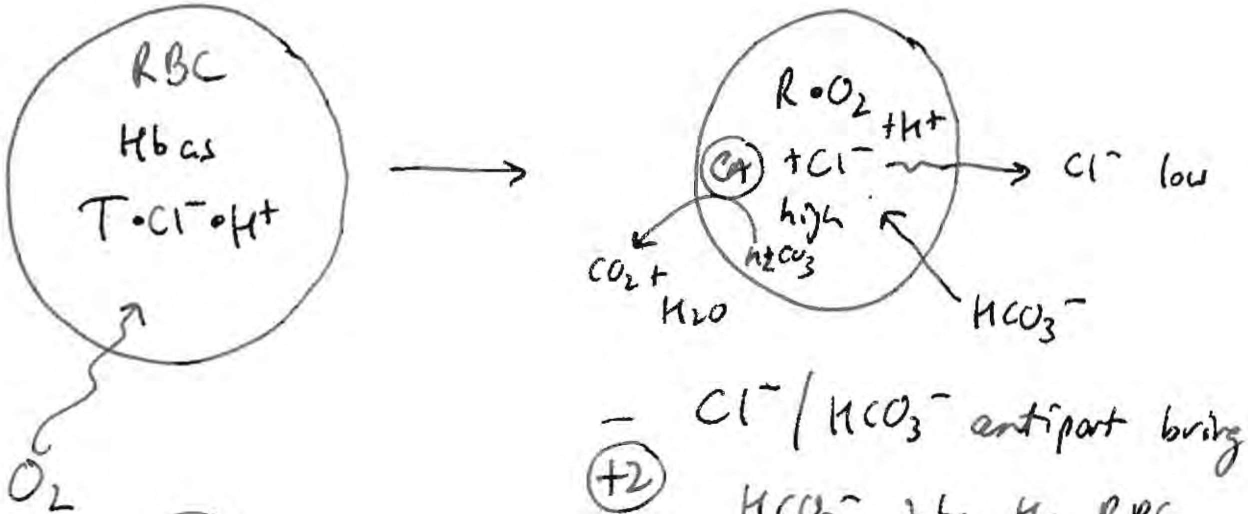
$K_5 K_6 = K_8 K_7$

$K_7 > K_5$

so $K_6 > K_8$, i.e. Cl^- binding favors T state more.

BRIGE

(8 pts) Saturation with O_2 in the lungs tend to drive Cl^- off Hb. Recalling that carbonic anhydrase is located in the red blood cell (RBC), how does chloride release help to accelerate the conversion of H^+ and bicarbonate back to CO_2 and water so that the CO_2 can be exhaled?



- Cl^- / HCO_3^- antiport brings HCO_3^- into the RBC (+2)

(+2)

- Deprotonation of Hb occurs upon binding O_2

- $H^+ + HCO_3^- \rightarrow H_2CO_3$ rapidly

- carbonic anhydrase converts carbonic acid to $CO_2 + H_2O$ (+2)

- Cl^- diffusing out has the effect of concentrating HCO_3^- at the site of the enzyme that gets rid of it. (+2)

Page	Score
1	/1
2	/23
3	/13
4	/14
5	/25
6	/17
7	/8
Total	**/101**

Score for the page____________

1. (15 pts) Short Answer

(2 pts each)
Fill in the blanks: (or particles among energy levels) (+2) each

The Boltzmann distribution describes the distribution of energy among particles that is observed in each of the microstates that comprise the predominant configuration of the ensemble, which is all of the microstates available at a given total energy.

(1 pt each)
What is the sign of ΔG for any process that occurs spontaneously at constant P, T? (−)

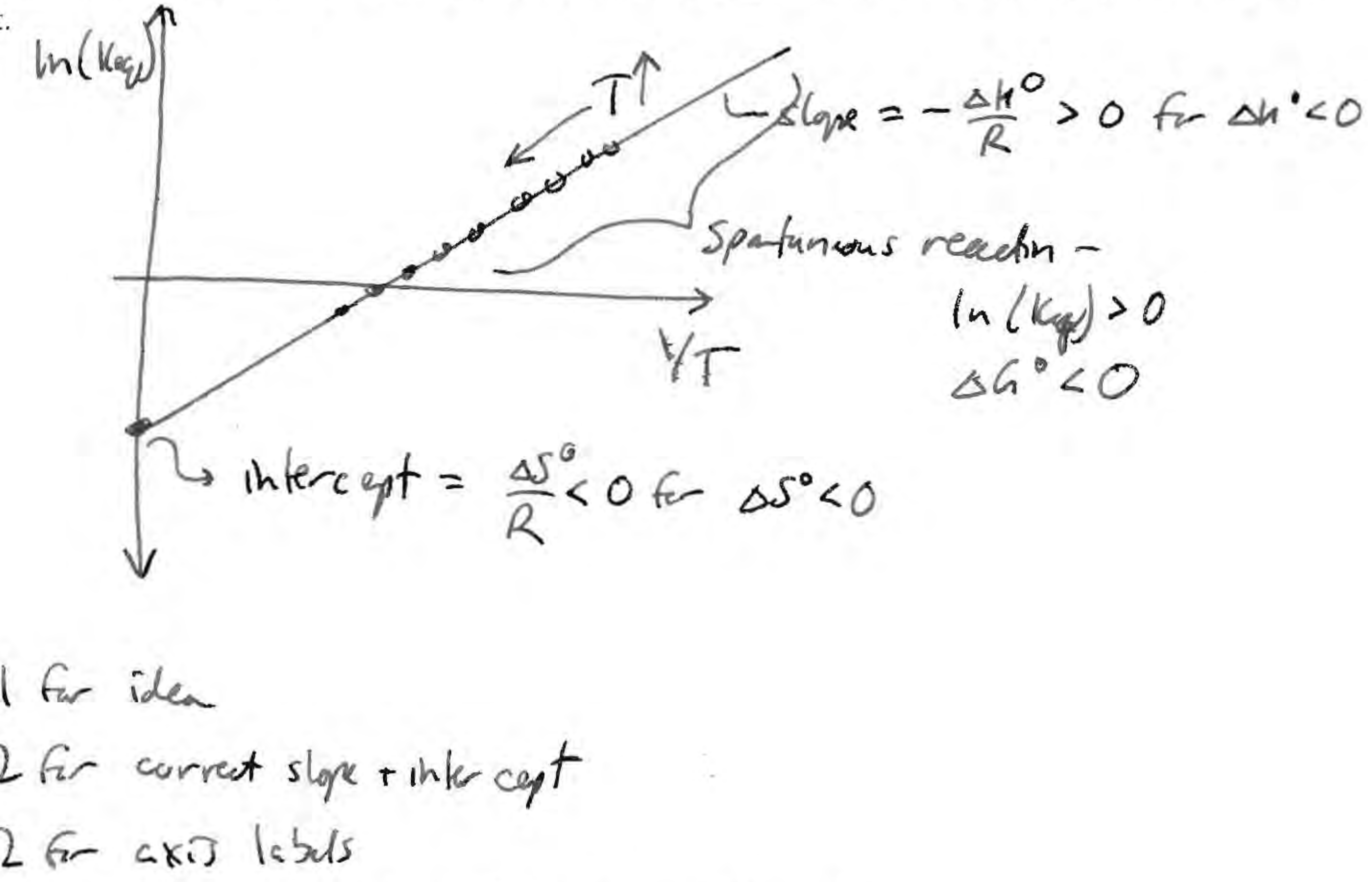
This a special case of the (circle one) First Law, [✓ Second Law], or Third Law of thermodynamics.

The free energy has reached a minimum when a system has reached equilibrium.

(+1) each

2. (15 pts) van't Hoff

(a; 8 pts) Draw a van't Hoff plot for an exothermic ordering reaction. Label the axes, and show how you would determine $\Delta H°$ and $\Delta S°$ from the plot. If there is a region where the reaction is spontaneous, label it.



+1 for idea
+2 for correct slope + intercept
+2 for axis labels
+2 for indicating values for slope + intercept
+1 for region of spontaneity

Score for the page__________

(b; 7 pts) Starting ↓ From the van't Hoff equation, show that if you know the equilibrium constant at one temperature T_1, the equilibrium constant at temperature T_2 is given by the following equation:

$$K_2 = K_1 \times \exp\left[\left(\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right]$$

$$\ln(K_2) = \left(\frac{-\Delta H^\circ}{R}\right)\left(\frac{1}{T_2}\right) + \frac{\Delta S^\circ}{R}$$ ⊕1 for van't Hoff

$$-\quad \ln(K_1) = \left(\frac{-\Delta H^\circ}{R}\right)\left(\frac{1}{T_1}\right) + \frac{\Delta S^\circ}{R}$$

$$\ln(K_2) - \ln(K_1) = \left(\frac{-\Delta H^\circ}{R}\right)\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$ ⊕2 for idea of subtraction

exponentiate → $$K_2 / K_1 = e^{\left[-\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]} = e^{+\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$\text{So}\quad K_2 = K_1\, e^{\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$ ⊕2 for trying to solve for ln K_2 or K_2

⊕2 for final answer if it was obtained fairly

3. (20 pts) Boltzmann Distribution

(a; 6 pts) We often speak of "kT" as the energy available from thermal motion. What is the population relative to the ground state (n_i/n_0) of a state with an energy of kT above the ground state? What about a state with an energy of 5 kT?

↑ i

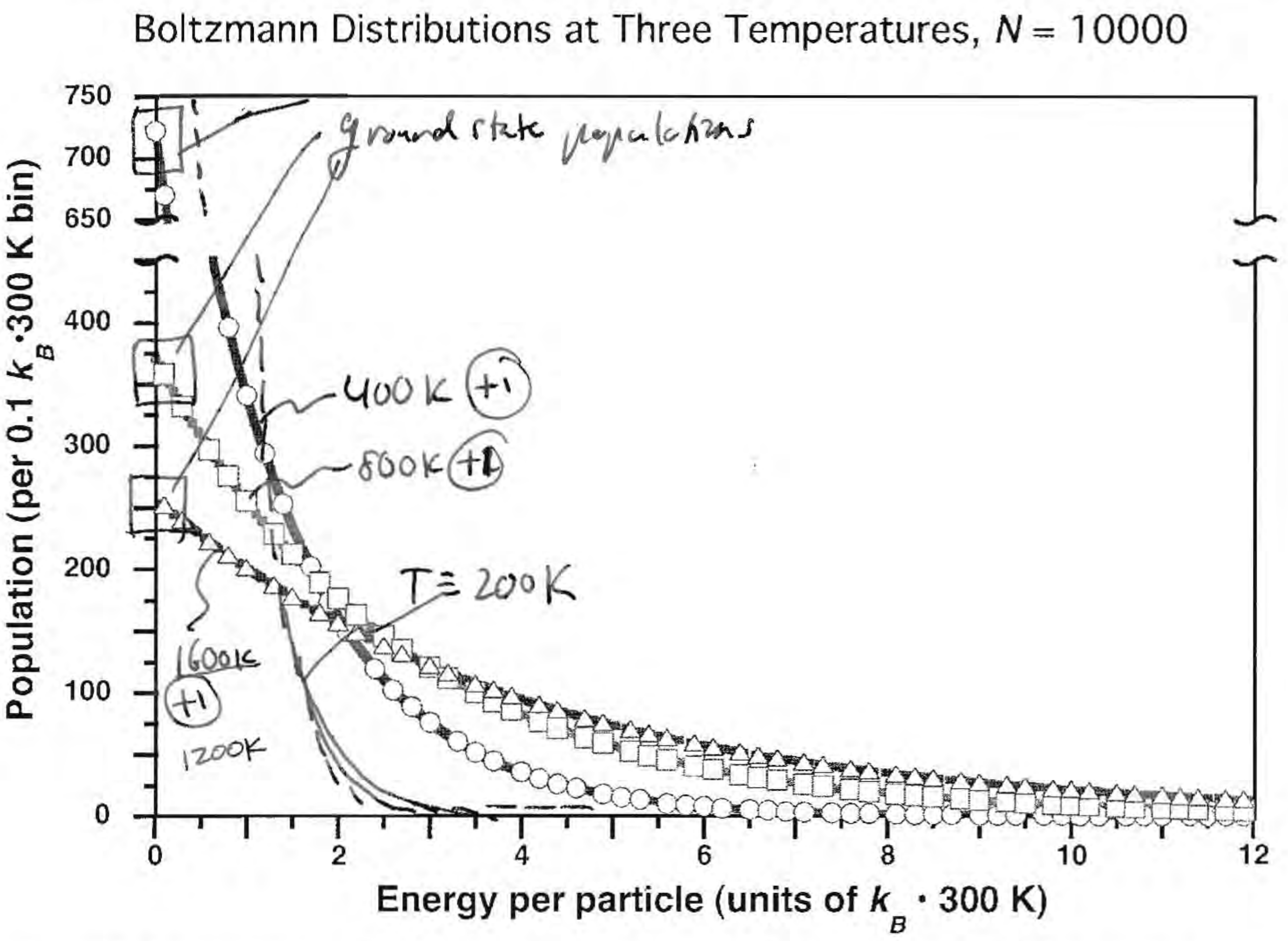
$$\frac{n_i}{n_0} = e^{-(\varepsilon_i-\varepsilon_0)/kT} = e^{-(kT-0)/kT} = e^{-1} = 0.37 \text{ or } 37\%$$

⊕1 ⊕2 for plugging in ⊕1

For $\varepsilon_i = 5kT$, $$\frac{n_i}{n_0} = e^{-5kT/kT} = e^{-5} = 6.73\times10^{-3} \text{ or } 0.67\%$$

⊕2

Score for the page____________



(b; 6 pts) The temperatures of the three curves are 400, 800, and 1200 K. Indicate which temperature is which on the graph above, and how do you know?

(+3) The higher the temperature, the higher the population of molecules in excited states.

(c; 2 pts) Identify the ground state populations for each distribution on the graph. Boxes on graph (+2)

(d; 3 pts) Sketch in the distribution for T = 200 K.

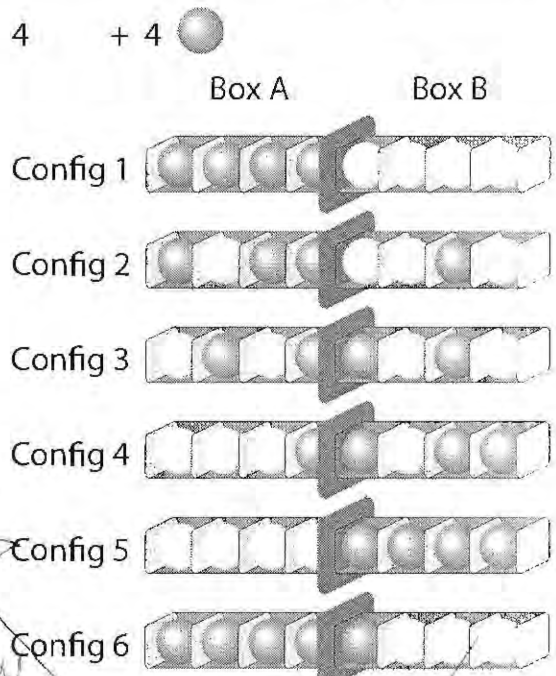
(+1) for any curve
(+1) for normalized
(+1) for y-intercept above the one for 400K, sharp dropoff

(e; 3 pts) Why are the areas under all four curves the same?

- The curves are normalized (+3) because the total population is the area – it's a constant (or – total probability = 1 is okay).

4. (20 pts) Entropy of Mixing (from Dill and Bromberg)

Consider four grey and four white balls that are distributed randomly into four slots on each side of a barrier as shown. We can count the number of balls of each color on each side, but we can't tell which boxes they are in.



(a; 12 pts) Calculate the number of microstates *W* for each of configurations 1-6, i.e. calculate how many of the microstates that are included in the entire ensemble comprise each configuration. (Hint: you only need to do three independent calculations.)

$W_1 = W_A \cdot W_B = 1 \times 1 = 1$ 6 ~~8~~ pts

$W_2 = 4 \cdot 4 = 16$ for all this w/ 8! -W

$W_3 = \frac{4!}{2!2!} \cdot \frac{4!}{2!2!} = \left(\frac{24}{4}\right)^2 = 36$

$W_4 = 16$

$W_5 = 1$

$W_6 = \underline{\underline{0}}$ - it's impossible

(+2) each 8 ~~10~~ pts + this

+9 total if W's aren't multiplied

(b; 3 pts) If we start with 30 of each color, calculate *W* for 15:15 mixtures of white and grey on each side

ratio +1 pt

$W_{15:15} = \overset{(+2)}{\left(\frac{30!}{15!\,15!}\right)^2} = (1.55\times10^8)^2 = 2.41\times10^{16}$ (+1) +1 for something that looks right, for right answer (+2 w/out the square)

(30 ways to place first white ball, ×29×28×27…, 15! of ustates are indistinguishable)

(c, 5 pts) Calculate the entropy change for mixing two pure sets of 30 balls to make the uniform mixture.

$\Delta S = \overset{(+2)}{k \ln W_{15:15}} - k \ln W_{pure} = k \ln \frac{2.4\times10^{16}}{2}$ ~~+2~~ (+1)

2 → B/W on either side (W₁+W₅ above – full credit for W=1)

$= k_B \cdot 37.03 = 37 \times \overset{(+1)}{1.38\times10^{-23}}$ J/mol K

$\Delta S = 5.11\times10^{-22}$ J/mol K (+1)

(still small because 30 isn't very many particles)

5. (30 pts) Practical Thermodynamics

(a; 25 pts) The water-gas shift reaction [CO (*g*) + H_2O (*g*) ⇌ CO_2 (*g*) + H_2 (*g*)] is exothermic, which makes hydrogen production complicated because the syngas reaction that provides the feedstock is done at very high temperature. From the data in the table for 25 °C, calculate $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$. Assuming that $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$ are constant with T, calculate the free energy change $\Delta G°_{rxn}$ at 300 °C, the equilibrium constant at 300 °C, and the temperature at which the equilibrium constant is equal to 1.

$\Delta H°_f$ in **kJ/mole**	S° in **J/(mol K)**
$\Delta H°_f$ (CO) = –110.5	S° (CO) = 197.7
$\Delta H°_f$ (CO_2) = –393.5	S° (CO_2) = 213.6
$\Delta H°_f$ (H_2) = 0	S° (H_2) = 130.6
$\Delta H°_f$ (H_2O, *g*) = –241.8	S° (H_2O, *g*) = 188.8
$\Delta H°_f$ (CH_4) = –74.8	S° (CH_4) = 186.2
$\Delta H°_f$ (C, graphite) = 0	S° (C, graphite) = 5.7
$\Delta H°_f$ (O_2) = 0	S° (O_2) = 205

$\Delta H°_{rxn} = \sum \Delta H_f°(\text{products}) - \sum \Delta H_f°(\text{reactants})$ (+2)

$= (-393.5 - 0) - (-110.5 - 241.8)$ kJ/mol

$\Delta H°_{rxn} = (-393.5 + 352.3)$ kJ/mol

$= \boxed{-41.2 \text{ kJ/mol}}$ (+3)

CO_2 is very stable! (5 pts to here)

The K is important!

$\Delta S°_{rxn} = \sum S°(\text{products}) - \sum S°(\text{reactants}) = (213.6+130.6) - (197.7+188.8)$ J/mol K (+2)

$= (344.2 - 386.5)$ J/mol K $= \boxed{-42.3 \text{ J/mol K}}$ (+3)

Relatively small ΔS° b/c Δn = 0, H_2 is a symmetric diatomic (5 pts)

$\Delta G°_{rxn}(300°C) = \Delta H° - T\Delta S°$ (+2)

(+1)

$= -41200 \text{ J/mol} - (573.15 \text{ K})(-42.3 \text{ J/mol K})$

$= -16955 = \boxed{-17000 \text{ J/mol}}$ (+2) (5 pt)

$K_{eq}(300°C) = e^{-\Delta G°/RT} = e^{+17000/(8.314 \times 573.15)} = e^{+3.56}$ (+2)

R in J/mol K

$K_{eq} = \boxed{35.1}$ (+2) (4 pts)

For $K_{eq} = 1$, must have $\ln(K_{eq}) = 0 = \Delta G° = \Delta H° - T\Delta S°$ (+2)

So $T = \dfrac{\Delta H°}{\Delta S°} = \dfrac{-41200 \text{ J/mol}}{-42.3 \text{ J/mol K}} = \boxed{974 \text{ K}} = 701 °C$ (6 pts)

(+2) (+2)

Score for the page____________

GRAY

(b; 5 pts) Why is choosing the temperature at which to carry out an exothermic reaction often a balancing act? Name another reaction that poses the same challenge.

- One would like to run the reaction at as low a

(+3) temperature as possible to maximize K_{eq}, but then it will go too slowly to be useful

[or state that one would like to run it hot to ↑ rate]

(+2) The Haber rxn ($N_2 + 3H_2 \rightleftharpoons 2NH_3$)

.... or DNA hybridization ok

combustion

Page	Score
1	/1
2	/23
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4	/14
5	/20
6	/25
7	/5
Total	**/101**

Score for the page____________