Chemistry 410B **Final Exam Part 2** **Fall 2016**

NAME:

Instructions:

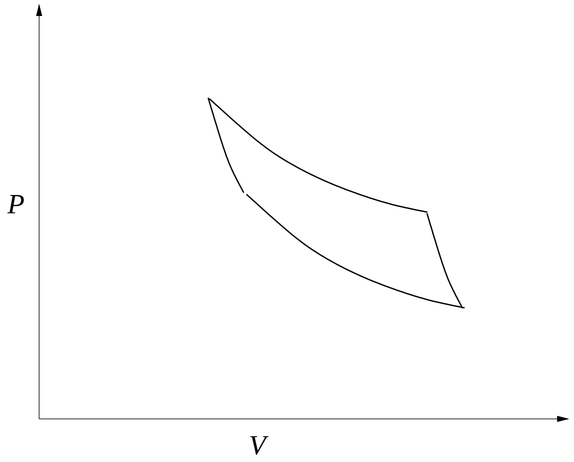
1. Please silence any noisy electronic devices you have and put any communications devices out of reach. Calculators are the only electronics permitted for the exam.
2. **Please write your name on this page but not on any other page.**
3. You may work on this part of the exam for 50 minutes.
4. You may detach the last sheet, containing tables and equations, from the exam.
5. To receive full credit for your work, please
   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (b) specify the correct units, if any, for your final answers;
   (c) use an appropriate number of significant digits for final numerical answers;
   (d) **stop writing and close your exam immediately when time is called.**

Other notes:

- The first portion of this exam (problem 1) is several short questions worth 60 points total. Partial credit for these problems is not necessarily available. Part 1 of the final exam also had a 60-point "short answer" section, so these problems will total 120 points across both halves.
- Your 5 best scores of the remaining problems, counted across *both* halves of the final exam will be worth 36 points each, for a total of 180 points. Partial credit is available for these problems, so try each problem and do not erase any of your work. The total final exam score is 300 points.
- These final exam scores and final course grades will be posted to Blackboard after all the exams have been graded.

1. 60 pts

(a) A Carnot cycle engine has the PV cycle drawn below. Explain how we could adjust one parameter to make the engine more efficient, and show on the graph how the cycle would be different.



(b) In a Monte Carlo simulation at 300 K, determine the **range of values** of the random number y (where $0 < y < 1$) such that we will keep a new trial state that has potential energy $200\,\text{cm}^{-1}$ greater than the current state.

(c) Find the vapor pressure of Br_2 at 298 K given that $\Delta_{\text{vap}}H^{\circ} = 29.96\,\text{kJ}\,\text{mol}^{-1}$ and $T_b = 331.9\,\text{K}$.

(d) The vapor pressure of ClO above a 0.100 M aqueous solution of ClO is 0.14 bar at 298 K. Find the Henry's law coefficient k_X at this temperature.

(e) A calorimeter with a bath heat capacity of $8370\,\mathrm{J\,K^{-1}}$ measures a temperature increase of 0.100 K in the bath upon the folding of a $1.63 \cdot 10^{-3}$ mol sample of cellular lysozyme. What is $\Delta_{\mathrm{rxn}} H^{\circ}$ for the folding of this protein?

(f) Write the rate law (*not* the integrated rate law) for the H_2Cl^+ intermediate in the reaction mechanism

$$\begin{aligned} \mathrm{Cl} + \mathrm{H_3^+} &\xrightarrow{k_3} \mathrm{HCl^+} + \mathrm{H_2} \\ \mathrm{HCl^+} + \mathrm{H_2} &\xrightarrow{k_4} \mathrm{H_2Cl^+} + \mathrm{H} \\ \mathrm{H_2Cl^+} + \mathrm{e^-} &\xrightarrow{k_5} \mathrm{HCl} + \mathrm{H}. \end{aligned}$$

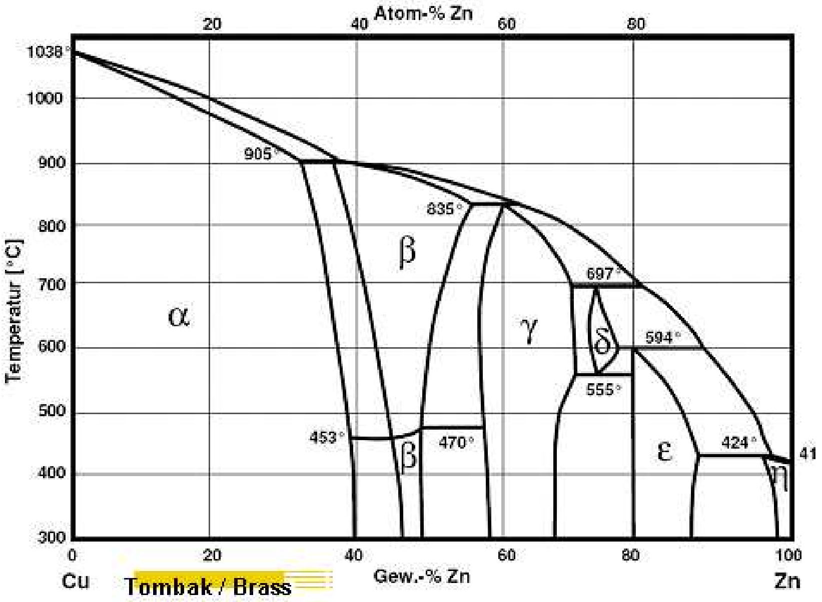
2. 3.60 g of liquid water are placed inside a chamber with a piston at 298 K. The initial volume of the liquid is negligible. The water completely evaporates, and the piston is pushed out to allow the vapor to expand reversibly and isothermally against a pressure of 0.0100 bar. Calculate w and ΔS for the process in SI units.

   (a) $w =$

   (b) $\Delta S =$

3. Recall that the pK_a of an acid HA is $-\log_{10} K_a$ where K_a is the equilibrium constant for the dissociation of HA into H^+ and A^-. The pK_a of *o*-aminobenzoic acid decreases linearly from 6.35 at 283 K to 5.50 at 323 K. What are $\Delta_{\text{rxn}}H$ and $\Delta_{\text{rxn}}S$ for the dissociation?

4. The phase diagram below describes mixtures of copper and zinc, which form brass. (Although the horizontal axis is percent weight, for copper and zinc this is roughly equal to mole fraction of Zn.)



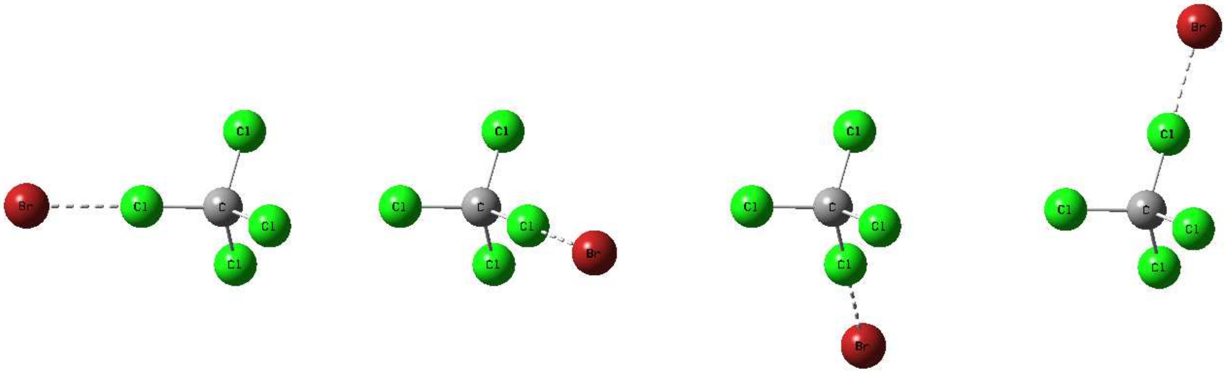
(a) The common form of brass is a "duplex" alloy that combines the α and β forms of the solid. What is the melting point for duplex brass?

(b) What is the approximate molecular formula of the low-temperature β-alloy?

(c) If have a sample of 90% Zn at equilibrium at 400°C, and we increase the temperature to 500°C, what change would we observe in the mixture?

(d) As we heat the β form of the solid from 500°C to 800°C, it becomes stable over a wider range of composition (% Zn). The opposite is true for the γ phase. How does this suggest β brass differs from γ brass?

5. In the reaction $CCl_4 + Br \longrightarrow CBrCl_3 + Cl$, the Br atom can attack the CCl_4 at any of four equivalent sites. If we calculate $\Delta_1 H^\ddagger$, $\Delta_1 S^\ddagger$, and k_1 for a reaction at one of those sites, what values should we find for $\Delta_4 H^\ddagger$, $\Delta_4 S^\ddagger$, and k_4–the parameters when we consider all four reaction sites? In other words, find $\Delta_4 H^\ddagger$, $\Delta_4 S^\ddagger$, and k_4 as functions of $\Delta_1 H^\ddagger$, $\Delta_1 S^\ddagger$, and k_1.



(a) $\Delta_4 H^\ddagger =$

(b) $\Delta_4 S^\ddagger =$

(c) $k_4 =$

6. For the reaction

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_2} \mathrm{D}$$

Eq. 14.23 gives this expression for the concentration of A in the the steady-state approximation:

$$[\mathrm{A}]' = [\mathrm{A}]_0 \left(1 - \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0}\right) \left\{\exp\left[-([\mathrm{B}]_0 - [\mathrm{A}]_0)\left(1 - \frac{k_{-1}}{k_{-1}+k_2}\right) k_1 t\right] - \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0}\right\}^{-1}.$$

(a) Simplify this equation for the case that $[\mathrm{A}]_0 = [\mathrm{B}]_0$. (You may want to use the power series approximation for e^x.)

(b) Show that your solution still gives the correct result in the limit that $t = 0$.

(c) Show that your solution still gives the correct result in the limit that $k_2 \gg k_{-1}$.

Fundamental Constants

Avogadro's number	$\mathcal{N}_A$	$6.0221367 \cdot 10^{23}$ mol^{-1}
Bohr radius	$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$5.29177249 \cdot 10^{-11}$ m
Boltzmann constant	k_B	$1.380658 \cdot 10^{-23}$ J K^{-1}
electron rest mass	m_e	$9.1093897 \cdot 10^{-31}$ kg
fundamental charge	e	$1.6021773 \cdot 10^{-19}$ C
permittivity factor	$4\pi\epsilon_0$	$1.113 \cdot 10^{-10}$ C^2 J^{-1} m^{-1}
gas constant	R	8.314510 J K^{-1} mol^{-1}
	R	0.08314510 L bar K^{-1} mol^{-1}
	R	0.08206 L atm K^{-1} mol^{-1}
hartree	$E_\mathrm{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ J
Planck's constant	h	$6.6260755 \cdot 10^{-34}$ J s
	$\hbar$	$1.05457266 \cdot 10^{-34}$ J s
proton rest mass	m_p	$1.6726231 \cdot 10^{-27}$ kg
neutron rest mass	m_n	$1.6749286 \cdot 10^{-27}$ kg
speed of light	c	$2.99792458 \cdot 10^8$ m s^{-1}

Unit Conversions

	K	cm^{-1}	kJ mol^{-1}	kcal mol^{-1}	erg	kJ
kHz =	$4.799 \cdot 10^{-8}$	$3.336 \cdot 10^{-8}$	$3.990 \cdot 10^{-10}$	$9.537 \cdot 10^{-11}$	$6.626 \cdot 10^{-24}$	$6.626 \cdot 10^{-34}$
MHz =	$4.799 \cdot 10^{-5}$	$3.336 \cdot 10^{-5}$	$3.990 \cdot 10^{-7}$	$9.537 \cdot 10^{-8}$	$6.626 \cdot 10^{-21}$	$6.626 \cdot 10^{-31}$
GHz =	$4.799 \cdot 10^{-2}$	$3.336 \cdot 10^{-2}$	$3.990 \cdot 10^{-4}$	$9.537 \cdot 10^{-5}$	$6.626 \cdot 10^{-18}$	$6.626 \cdot 10^{-28}$
K =	1	0.6950	$8.314 \cdot 10^{-3}$	$1.987 \cdot 10^{-3}$	$1.381 \cdot 10^{-16}$	$1.381 \cdot 10^{-26}$
cm^{-1} =	1.4388	1	$1.196 \cdot 10^{-2}$	$2.859 \cdot 10^{-3}$	$1.986 \cdot 10^{-16}$	$1.986 \cdot 10^{-26}$
kJ mol^{-1} =	$1.203 \cdot 10^2$	83.59	1	0.2390	$1.661 \cdot 10^{-14}$	$1.661 \cdot 10^{-24}$
kcal mol^{-1} =	$5.032 \cdot 10^2$	$3.498 \cdot 10^2$	4.184	1	$6.948 \cdot 10^{-14}$	$6.948 \cdot 10^{-24}$
eV =	$1.160 \cdot 10^4$	$8.066 \cdot 10^3$	96.49	23.06	$1.602 \cdot 10^{-12}$	$1.602 \cdot 10^{-22}$
hartree =	$3.158 \cdot 10^5$	$2.195 \cdot 10^5$	$2.625 \cdot 10^3$	$6.275 \cdot 10^2$	$4.360 \cdot 10^{-11}$	$4.360 \cdot 10^{-21}$
erg =	$7.243 \cdot 10^{15}$	$5.034 \cdot 10^{15}$	$6.022 \cdot 10^{13}$	$1.439 \cdot 10^{13}$	1	10^{-10}
J =	$7.243 \cdot 10^{22}$	$5.034 \cdot 10^{22}$	$6.022 \cdot 10^{20}$	$1.439 \cdot 10^{20}$	10^7	10^{-3}
dm^3 bar =	$7.243 \cdot 10^{24}$	$5.034 \cdot 10^{24}$	$6.022 \cdot 10^{22}$	$1.439 \cdot 10^{22}$	$1.000 \cdot 10^9$	0.1000
kJ =	$7.243 \cdot 10^{25}$	$5.034 \cdot 10^{25}$	$6.022 \cdot 10^{23}$	$1.439 \cdot 10^{23}$	10^{10}	1

distance 1 Å = 10^{-10} m

mass 1 amu = $1.66054 \cdot 10^{-27}$ kg

energy 1 J = 1 kg m^2 s^{-2} = 10^7 erg

force 1 N = 1 kg m s^{-2} = 10^5 dyn

electrostatic charge 1 C = 1 A s = $2.9979 \cdot 10^9$ esu

1 D = $3.3357 \cdot 10^{-30}$ C m = $1 \cdot 10^{-18}$ esu cm

magnetic field strength 1 T = 1 kg s^{-2} A^{-1} = 10^4 gauss

pressure 1 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2}

1 bar = 10^5 Pa = 0.98692 atm

entropy $S_{\text{Boltzmann}} = k_{\text{B}} \ln \Omega \qquad S_{\text{Gibbs}} = -Nk_{\text{B}} \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$

canonical dist. $\mathcal{P}(\epsilon) = \frac{g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)}}{q(T)}$

Maxwell-Boltzmann $\mathcal{P}_v(v) = 4\pi \left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2} v^2 e^{-mv^2/(2k_{\text{B}}T)}$

ideal gas $PV = nRT$

equipartition $E = \frac{1}{2} N_{\text{ep}} N k_{\text{B}} T = \frac{1}{2} N_{\text{ep}} nRT$

collisions $v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}} \qquad \langle v \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi m}} \qquad \langle v_{AA} \rangle = 4\sqrt{\frac{k_{\text{B}}T}{\pi m}}$

$\gamma = \rho\sigma \langle v_{AA} \rangle \qquad \lambda = \frac{1}{\sqrt{2}\rho\sigma}$

thermo derivatives $dE = TdS - PdV + \mu_1 dn_1 + \ldots \qquad dH = TdS + VdP + \mu_1 dn_1 + \ldots$

$dF = -SdT - PdV + \mu_1 dn_1 + \ldots \qquad dG = -SdT + VdP + \mu_1 dn_1 + \ldots$

$C_V = \left(\frac{T\partial S}{\partial T}\right)_{V,n} = \left(\frac{\partial E}{\partial T}\right)_{V,n} \qquad C_P = \left(\frac{T\partial S}{\partial T}\right)_{P,n} = \left(\frac{\partial H}{\partial T}\right)_{V,n}$

isothermal exp: $w_{\text{rev}} = -nRT \ln\left(\frac{V_2}{V_1}\right) \qquad w_{\text{irr}} = -P_{\min} \Delta V \qquad \Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$

adiabatic exp: $w_{\text{rev}} = C_V \Delta T \qquad \frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right)^{-C_{Vm}/R} = \left(\frac{P_2}{P_1}\right)^{-C_{Vm}/C_{Pm}}$

Sackur-Tetrode: $S_m = R\left\{\frac{5}{2} + \ln\left[\left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} \frac{RT}{\mathcal{N}_A P}\right]\right\}$

Clausius/Clapeyron $\ln P(\text{ bar}) = \frac{\Delta_{\text{vap}} H}{R}\left[\frac{1}{T_b} - \frac{1}{T}\right]$

Gibbs phase $d = k - p + 2$

colligative props. $\Delta T_f = -\frac{RT^{\bullet 2}_f X_{\text{B}}}{\Delta_{\text{fus}} H} \qquad \Pi = RT[\text{B}]$

reactions $T_{\text{ad}} = T_1 - \frac{\Delta H_{,\text{rxn}}(T_1)}{C_P(\text{products})}$

$\ln K_{\text{eq}} = -\frac{\Delta_{\text{rxn}} G}{RT}$

rate constants $k_{\text{SCT}} = p\sigma_{AB} \left(\frac{8k_{\text{B}}T}{\pi\mu}\right)^{1/2} e^{-E_a/(RT)} \mathcal{N}_A \qquad k_{\text{TST}} = \frac{k_{\text{B}}T}{Ch} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/(RT)}$