Chemistry 410B **Exam 6** **Spring 2012**

NAME:

Instructions:

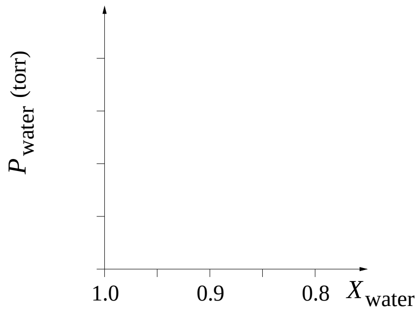
1. Keep this exam closed until instructed to begin.
2. **Please write your name on this page but not on any other page.**
3. Please silence any noisy electronic devices you have.
4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.
5. To receive 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 page portion of the exam is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase any of your work.

1. **40 points.**

(a) On the graph below, plot the vapor pressure of water over a solution of the alcohol mannitol at 298 K as a function of the mole fraction of mannitol, assuming that the solution obeys Raoult's law. The vapor pressure of pure water at 298 K is 23.8 torr. Set the values along the vertical axis so that any trend is clear.



(b) Sketch a reaction diagram (**not** a whole potential energy surface) for the minimum energy reaction path from reactants to products for the reaction

$$CH_3(g) + HCl(g) \longrightarrow CH_4(g) + Cl(g)$$

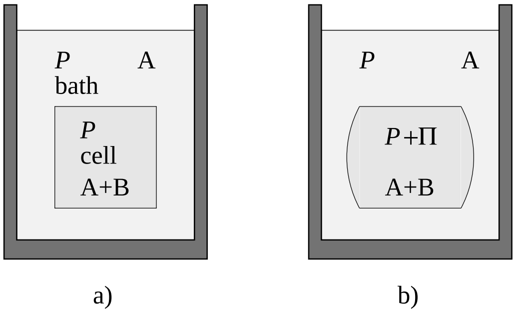
which has an activation energy of $6\,\text{kJ}\,\text{mol}^{-1}$ and a $\Delta_{\text{rxn}}E$ of $-8\,\text{kJ}\,\text{mol}^{-1}$. Label the reactants, products, and transition state (TS) on the diagram.

(c) Find the $\Delta_{\text{rxn}}G^{\ominus}$ and K_{eq} at 298 K for the reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g).$$

(d) Write the expression for K_p for the above reaction of N_2 and H_2.

2. Start with an osmotic cell as in Fig. 20.4 (reproduced below), where the volume of the cell is 10. ml and the volume of the bath (not including the cell) is 100. ml. We first add 0.100 mmol B to the cell, but then find that the osmotic pressure is too high. We compensate by adding a solute C to the bath. Neither B nor C can penetrate the semipermeable membrane. Assume that Raoult's law is satisfied by the solvent. What is the minimum number of moles C that must be added to the bath to get a pressure difference across the membrane of 0.10 bar at 298 K?



3. Write "+" or "−" or "0" to indicate whether $\Delta_{\mathrm{rxn}}S^{\circ}$ of each of the following processes is likely to be positive, negative, or zero, respectively.

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$	
formation reaction of $NaCl(s)$	
formation reaction of $Cl_2(g)$	
combustion of $CH_4(g)$	
sublimation of $CO_2(s)$	

4. Calculate the overall change in volume of the gases for the reaction

$$N_2O_4(g) \longrightarrow N_2(g) + 2O_2(g)$$

carried out adiabatically at 1.00 bar, starting from 0.100 mol N_2O_4 at 298 K.

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}= 0.6950 cm^{-1}/K
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 $S_{\text{Boltzmann}} = k_{\text{B}} \ln \Omega \qquad S_{\text{Gibbs}} = -N k_{\text{B}} \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$

partition func.s $q(T) = \sum_{\epsilon} g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)} \qquad q_{\text{rot}} \approx \frac{k_{\text{B}}T}{B} \qquad q_{\text{vib}} \approx \frac{1}{1 \; - \; e^{-\omega_e/(k_{\text{B}}T)}}$

$q_{\text{trans}}(T,V) = q'_K q'_U = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V$ (ideal gas)

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

$\gamma = \rho\sigma \langle v_{AA} \rangle \qquad \lambda = \frac{1}{\sqrt{2}\rho\sigma} \qquad \rho = \frac{N}{V} = \frac{P\mathcal{N}_A}{RT}$

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

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

isobaric heating: $\Delta S = nC_{P\text{m}} \ln\left(\frac{T_f}{T_i}\right)$

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

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

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: $\frac{dP}{dT} = \frac{\Delta_\phi H}{T \Delta_\phi V} \qquad \ln P(\text{ bar}) = \frac{\Delta_{\text{vap}} H}{R}\left[\frac{1}{T_b} - \frac{1}{T}\right]$

Gibbs phase: $d = k - p + 2$

Raoult's law: $P_{\text{A}} = P^\bullet_{\text{A}} X_{\text{A}}$

Henry's law: $P_{\text{B}} = k_X, X_{\text{B}} \qquad k_X = \lim_{X_{\text{B}} \to 0} \left(\frac{P_{\text{B}}}{X_{\text{B}}}\right)$

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

reactions: $\Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^\ominus + RT \ln \Xi$

$\ln K_{\text{eq}}(T) = -\frac{\Delta_{\text{rxn}} G^\ominus}{RT} = -\frac{\Delta_{\text{rxn}} H^\ominus}{RT} + \frac{\Delta_{\text{rxn}} S^\ominus}{R}$

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