Chemistry 410B **Exam 5** **Spring 2009**

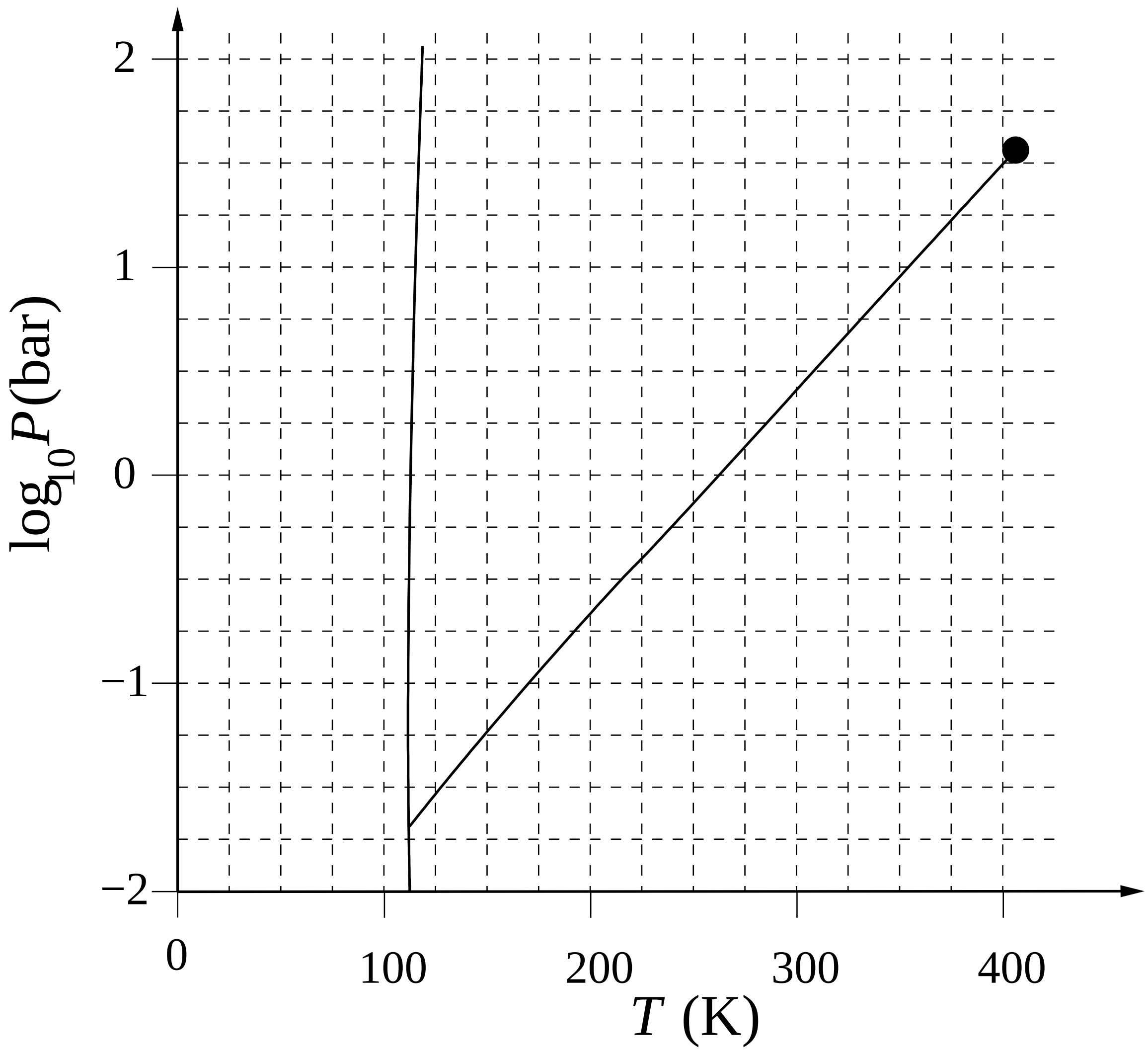
NAME:

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.



2
1
0
−1
−2
$\log_{10}P$(bar)
0
100
200
300
400
T (K)

1. **40 points.**

(a) Draw a line connecting each statement on the left with the most appropriate explanation on the right.

$\Delta_{\text{mix}}S > 0$ because	(A) C_{Pm} is bigger for the liquid than for the gas
$\Delta_{\text{vap}}H$ decreases with T because	(B) dispersion forces are generally weaker than hydrogen bonds
vapor pressure increases with T because	(C) more energy per molecule is available to break intermolecular bonds
water has a higher T_f than propane because	(D) S increases with V for each substance
water melts at a constant T as heat is added because	(E) the average energy per degree of freedom remains constant

(b) The boiling point for isobutane (2-methylpropane) is 261.3 K. Use Trouton's rule to estimate the standard **enthalpy** of vaporization.

(c) The phase diagram for isobutane is drawn on the back of the opposite page. Give T **and** P for

i. the critical point

ii. the triple point

iii. the standard state melting point.

2. Find an expression for each of the following in terms of $\Delta_{\text{vap}} H_m^{\ominus}$ and $T_b^{\ominus}$ or their derivatives:

   (a) $\Delta_{\text{vap}} E_m^{\ominus}$

   (b) $\Delta_{\text{vap}} F_m^{\ominus}$

   (c) $\Delta_{\text{vap}} \mu^{\ominus}$ at constant S

   (d) $C_{Pm}(g) - C_{Pm}(l)$ at $T_b^{\ominus}$ and 1 bar

3. It takes a $17.3\,\text{J}\,\text{mol}^{-1}$ change in entropy to heat 0.300 mol of glycerol, $C_3H_5(OH)_3$, from a solid at its melting point of 291 K to a liquid at 331 K, all at a pressure of 1 bar. The heat capacities are $150\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ for the solid and $221.9\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ for the liquid. Find $\Delta_{\text{fus}} H_m^{\ominus}$ for glycerol.

4. Osmium tetroxide (OsO_4) is a highly toxic oxidizing agent used in organic synthesis. It is a solid at room temperature, but sublimes ($\Delta_{\text{sub}} H_m^{\circ} = 56.9\,\text{kJ}\,\text{mol}^{-1}$) to a hazardous vapor which can stain corneas and cause blindness. The vapor pressure of OsO_4 at 298 K is 0.013 bar. Estimate the vapor pressure at 325 K.

equipartition $$E = \frac{1}{2}N_{\rm ep}Nk_BT = \frac{1}{2}N_{\rm ep}nRT$$

virial/van der Waals $$P = RT\left[V_m + B_2(T)V_m^2\right] \qquad RT = \left(P + \frac{a}{V_m^2}\right)(V_m \; - \; b)$$

$$B_2(T) = -\mathcal{N}_A\frac{1}{2}\mathcal{I}(\beta) \equiv -2\pi\mathcal{N}_A\int_0^{V^{1/3}}(e^{-u(R)/(k_BT)} - 1)R^2dR$$

$$a \approx \frac{16\pi\mathcal{N}_A^2\epsilon R_{\rm LJ}^3}{9} \qquad b \approx \frac{2\mathcal{N}_A\pi R_{\rm LJ}^3}{3}$$

thermo derivatives $$dE = TdS - PdV + \mu_1dn_1 + \ldots \qquad dH = TdS + VdP + \mu_1dn_1 + \ldots$$

$$dF = -SdT - PdV + \mu_1dn_1 + \ldots \qquad dG = -SdT + VdP + \mu_1dn_1 + \ldots$$

Maxwell relations $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa_x \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_x$$

$$C_P = C_V + V\alpha\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

isothermal exp: $$w_{\rm rev} = -nRT\ln\left(\frac{V_2}{V_1}\right) \qquad w_{\rm irr} = -P_{\rm ex}\Delta V$$

rev. adiabatic exp: $$w_{\rm rev} = C_V\Delta T \qquad V_2 = V_1\left(\frac{P_2}{P_1}\right)^{-C_V/(C_V+nR)}$$

Joule-Thompson: $$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\frac{2a}{RT} - b}{C_{Pm}}$$

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) \qquad \Delta S = nC_{Pm}\ln\left(\frac{T_f}{T_i}\right)$$

$$\Delta S_{\rm mix} = -R(n_A\ln X_A + n_B\ln X_B)$$

$$\Delta G_{\rm mix} = RT(n_A\ln X_A + n_B\ln X_B)$$

Gibbs-Duhem $$\sum_i n_i\mu_i = 0$$

Clausius/Claus.-Clap. $$\frac{dP}{dT} = \frac{\Delta_\phi H}{T\Delta_\phi V} \qquad \frac{d\ln P}{d\left(\frac{1}{T}\right)} = -\frac{\Delta_{\rm vap}H}{R}$$

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