Chemistry 410B **Exam 5** **Fall 2016**

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 portion of the exam (problem 1) 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) Fill in the appropriate symbol: =, >, or <:

i. ΔS_T $\square$ 0

ii. ΔG $\square$ 0 for a spontaneous process at constant T and P

iii. S_T $\square$ 0

iv. μ_A $\square$ μ_B when A and B are in equilibrium

v. $S(T = 0\,\text{K})$ $\square$ 0

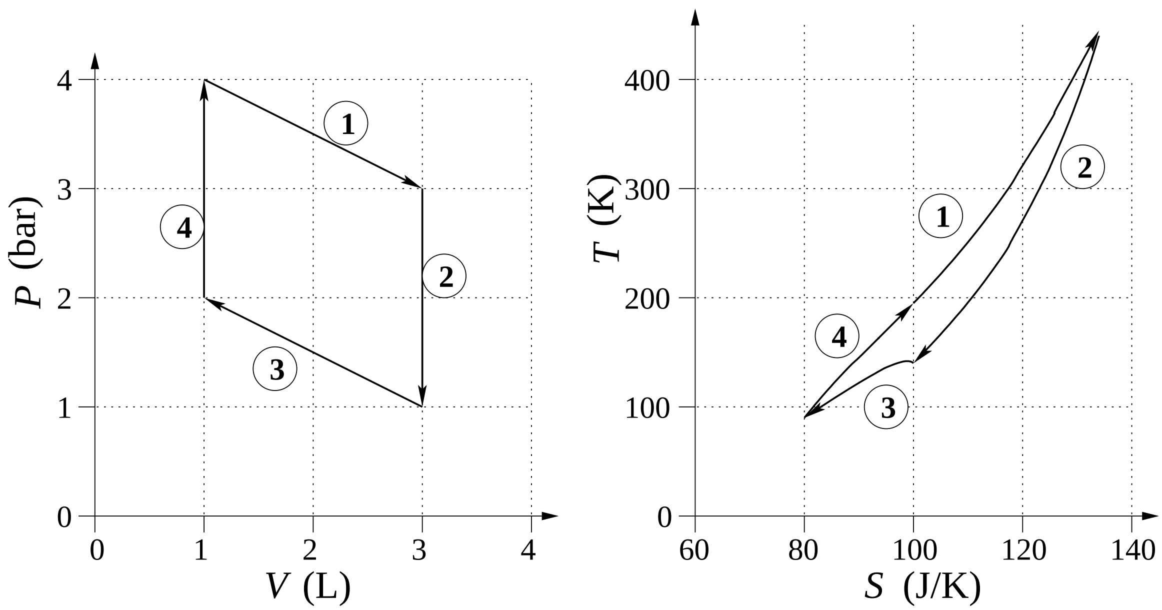
(b) Draw in all the additional spins needed for periodic boundary conditions in the grid below, and calculate the total interaction energy (in terms of D) for the spin with the box around it.

+	+	+	[+]
+	−	+	+
−	+	+	−
+	−	−	−

(c) Find the heat needed to raise the temperature of 2.50 mol graphite from 298 K to 323 K at constant pressure, if $C_{Pm} = 8.23\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$.

(d) The $\Delta_\text{vap}H^\circ$ of water at 373 K is $40.65\,\text{kJ}\,\text{mol}^{-1}$. Find $\Delta_\text{vap}S^\circ$.

2. An imaginary engine operates on a cycle with the PV and TS graphs shown below. (This is **not** a Carnot cycle.) use the graphs to calculate the efficiency of the engine.



3. Calculate the absolute molar entropy of CO at **498 K** and 1.00 bar, assuming that only translations and rotations contribute. The rotational constant is $1.93\,\mathrm{cm}^{-1}$.

4. The vapor pressure of acetone is 0.0526 bar at 263.8 K and 0.526 bar at 312.7 K. Find the latent enthalpy of vaporization in $\mathrm{kJ\,mol}^{-1}$.

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	$E_h = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ 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

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

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

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

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

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

$$S_{m,\mathrm{rot}} = R\left(\ln\frac{k_{\mathrm{B}}T}{B} + 1\right)$$

$$\Delta S_{\mathrm{mix}} = -R(n_{\mathrm{A}}\ln X_{\mathrm{A}} + n_{\mathrm{B}}\ln X_{\mathrm{B}})$$

$$\Delta G_{\mathrm{mix}} = RT(n_{\mathrm{A}}\ln X_{\mathrm{A}} + n_{\mathrm{B}}\ln X_{\mathrm{B}})$$

Clausius/Clapeyron $$\frac{dP}{dT} = \frac{\Delta_\phi H}{T\Delta_\phi V}$$

$$\ln P(\,\mathrm{bar}) = \frac{\Delta_{\mathrm{vap}}H}{R}\left[\frac{1}{T_b} - \frac{1}{T}\right]$$

Substance	T_f (K)	$\Delta_{\mathrm{fus}}H_m^\circ$ (kJ mol^{-1})	T_b (K)	$\Delta_{\mathrm{vap}}H_m^\circ$ (kJ mol^{-1})
N_2	63.15	0.719	77.36	5.57
CO	68	0.83	81.6	6.04
Ar	83.8	1.12	87.30	6.43
O_2	54.5	0.44	90.20	6.820
CH_4	90.75	0.94	111.67	8.19
Kr	115.8	1.37	119.93	9.08
Xe	161.5	1.81	165.11	12.62
C_2H_6	90.3	2.86	184.55	14.69
C_3H_8	85.5	3.53	231.0	19.04
Cl_2	171.6	6.40	239.11	20.41
NH_3	195.41	5.66	239.82	23.33
CH_3Cl	176.1	6.431	249.06	21.40
CH_2Cl_2	178.01	6	313	28.06
Br_2	265.9	10.57	331.9	29.96
$CHCl_3$	209.6	8.8	334.32	29.24
CCl_4	250.0	3.28	349.9	29.82
H_2O	273.15	6.008	373.15	40.65