Exam 1
CHM 3400, Dr. Chatfield

Read through the questions thoroughly, set up the answers carefully, show your work, and be neat. There are 5 questions; each is worth 20 points. There is also an extra credit problem at the end. Partial credit will be given when the instructor can follow your train of thought. Credit will not be given for answers without work or reasoning. If you have difficulty with a question, go on and return to it later. Check your work.

GOOD LUCK!

1. Provide descriptions or definitions of the following. Employ graphs and equations where helpful.

a) 1st Law of Thermodynamics

The energy of an isolated system is constant.

b) Reversible process

A process is called reversible if the direction of change can be altered by an __infinitesimal__ change in the conditions.

c) Why is enthalpy often a more natural state function than internal energy for describing chemical processes in the laboratory?

Changes in enthalpy or enthalpy are most easily measured on the basis of heat flow ΔH is equal to the heat flow at constant pressure, whereas the ΔU is equal to the heat flow at constant volume. Constant pressure is the more usual laboratory situation, so ΔH is usually more useful than ΔU.

d) Explain the physical meaning of the constants a and b in the van der Waals equation.

a represents the attractive intermolecular forces
b represents the molecular volume

2.

a) Calculate the work (w) for the isothermal expansion of 2.00 mol Ar from 2.00 L to 4.00 L at 0 °C against a constant external pressure of 11.1 bar. Give your answer in kJ.

$$w = -P_{ex}\,\Delta V = -11.1\,bar\,(4L - 2L) = -22.2\,L\text{-}bar$$

$$\boxed{w = -2.22\,kJ}$$

b) Calculate the work for the isothermal, reversible expansion of 2.00 mol Ar from 2.00 L to 4.00 L at 0 °C. Use a 2nd order virial equation for Ar. The value of the 2nd virial coefficient, B, is -21.7 $cm^3\,mol^{-1}$. Give your answer in kJ.

$$w = -\int P_{ex}\,dv \overset{rev}{=} -\int p\,dv \qquad \text{from } z = \frac{p\bar{V}}{RT} = 1 + \frac{B}{V}$$

$$\frac{RT}{V}\left(1 + \frac{B}{V}\right) = \frac{nRT}{V} + \frac{n^2 RTB}{V^2}$$

$$w = -nRT\int \frac{1}{V}\,dv - n^2 RTB\int \frac{1}{V^2}\,dv \qquad -21.7\,cm^3/mol = 0.0217\,L/mol$$

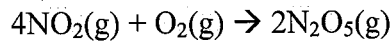$$= -nRT\ln\frac{V_f}{V_i} + n^2 RTB\left(\frac{1}{V_f} - \frac{1}{V_i}\right)$$

0.08314
L-bar $K^{-1}mol^{-1}$ 2 mol   273 K

$$= -31.5 + 0.5 = -31.0\,L\text{-}bar = \boxed{-3.10\,kJ = w}$$

3. One mole of nitrogen dioxide (NO_2) is combusted at a pressure of P = 1 bar according to the chemical equation:

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$$

Some thermodynamic data available are:

substance	$\Delta_f H^O$ (kJ/mol; 298 K)	$\bar{C}_p$ (J K^{-1} mol^{-1}; 298 K)
$NO_2(g)$	33.2	37.2
$O_2(g)$		29.4
$N_2O_5(g)$	11.3	84.5

a) Calculate $\Delta_r H°$ at 298 K. Give your answer in kJ.

$$\Delta_r H°(298K) = 2(11.3) - [4(33.2) + 0] = -110.2 \text{ kJ/mol}$$

/

b) Calculate $\Delta_r H°$ at 398 K. Give your answer in kJ.

$$\Delta C_p = 2(84.5) - [4(37.2) + 29.4] = -9.2 \text{ J K}^{-1}\text{mol}^{-1}$$

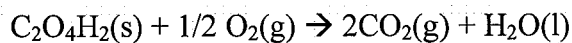$$\Delta_r H°(398K) = \Delta_r H°(298K) + \Delta C_p \Delta T$$

$$\uparrow$$

$$398K - 298K = 100K$$

$$\boxed{\Delta_r H°(398K) = -110.2 - 0.9}$$
$$\boxed{= -111.1 \text{ kJ}}$$

4. In a bomb calorimeter, 0.900 g of oxalic acid [$C_2O_4H_2(s)$, M = 90.0 g/mol] is combused (the chemical equation is below). The temperature of the calorimeter rises from 25.00 °C to 27.58 °C. The heat capacity of the calorimeter is measured to be C_V = 1000.0 J K^{-1}.

$$C_2O_4H_2(s) + 1/2\ O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$

a) Determine ΔU for the combustion process.

$$2.58\ K$$

$$\Delta U = -\Delta U_{surr} = -C_V \Delta T = -2580\ J = -2.580\ kJ$$

$$\uparrow$$
$$1000.0\ JK^{-1}$$

b) Determine the standard enthalpy of combustion (per mole) for oxalic acid, Δ_cH^O, at 298 K.

$$n = \frac{0.900 g}{90 g/mol} = 0.01\ mol$$

$$\Delta \bar{u} = \frac{\Delta u}{n} = -258\ kJ/mol$$

$$\Delta H° = \Delta \bar{u} + (P_f V_f - P_i V_i)$$
$$\underbrace{}$$
$$\approx \boxed{\Delta n_g RT}$$ $\Delta n_g = 2 - \frac{1}{2} = 1.5$

$$\overset{n(CO_2)}{\underset{\downarrow}{}} \quad \overset{n(O_2)}{\underset{\swarrow}{}}$$

$$\uparrow$$
$$298 K$$

$$= 3716\ J/mol = 3.716\ kJ/mol$$

$$\Delta H°_c = -258.0 + 3.716 = \boxed{-254.3\ kJ/mol = \Delta_cH°}$$

5. Liquids can sometimes be supercooled; that is, they can be cooled below the freezing point as long as they are not seeded with a small crystal. Calculate ΔH for the freezing of 1 mol of liquid water supercooled to -10 $^\circ$C, using the data provided. You may assume that the heat capacity is independent of temperature.

Data for water:
$\Delta_{fus}H^\circ(0\ ^\circ C) = 6.01$ kJ mol^{-1}, $\bar{C}_p(l) = 75.3$ J K^{-1} mol^{-1}, $\bar{C}_p(s) = 39.1$ J K^{-1} mol^{-1}
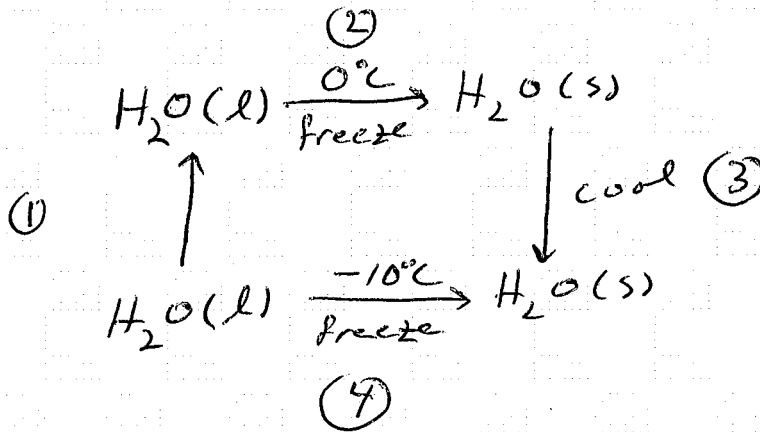
$$\Delta_{Freeze}H^\circ(-10^\circ C) = \underbrace{\bar{C}_p(l)(273K - 263K)}_{\text{①}} + \underbrace{\Delta_{Freeze}H^\circ(0^\circ C)}_{\text{②}} + \underbrace{\bar{C}_p(s)(263K - 273K)}_{\text{③}}$$

$$= -\Delta_{fus}H^\circ(0^\circ C)$$

$$= \underbrace{75.3\ J/mol}_{0.753\ kJ/mol} - 6.01\ kJ/mol \underbrace{- 391\ J/mol}_{0.391\ kJ/mol}$$

$$\Delta_{Freeze}H^\circ(-10^\circ C) = -5.65\ kJ/mol$$

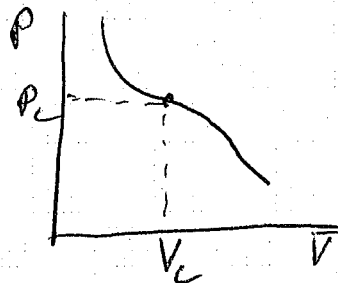$$\boxed{\Delta H = \Delta_{Freeze}H^\circ(-10^\circ C) \cdot 1\ mol = -5.65\ kJ}$$

FOR EXTRA CREDIT (8 points)

6. For a 2nd order virial equation, derive an expression for the 2nd virial coefficient, B, in terms of the critical molar volume V_c. Recall that the critical point is an inflection point in a graph of P vs $\bar{V}$.

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{B}{\bar{V}}$$

$$P = \frac{RT}{\bar{V}} + \frac{RTB}{\bar{V}^2}$$

At critical point, $\left(\frac{dP}{d\bar{V}}\right)_T = 0$ and $\left(\frac{d^2P}{d\bar{V}^2}\right)_T = 0$

Using $\left(\frac{dP}{d\bar{V}}\right)_T = -\frac{RT}{\bar{V}^2} - \frac{2RTB}{\bar{V}^3} = 0$

$$0 = \bar{V} + 2B$$

$$B = -\frac{1}{2}\bar{V} \quad \text{at critical point } (\bar{V} = V_c)$$

$$\boxed{B = -\frac{1}{2}V_c}$$

Using $\left(\frac{d^2P}{d\bar{V}^2}\right)_T = 0 \implies \boxed{B = -\frac{1}{3}V_c}$

- Overdetermined
- Either answer OK
- There is enough information to determine $\underline{\underline{2}}$ constants (B, C or a, b)