

KEY

Chem 331, Exam 1

Friday, September 21, 2007 (100 points total)

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ Torr} = 1.01325 \text{ bar} \quad (1 \text{ bar} = 10^5 \text{ Pa}); \quad 1 \text{ L} = 1 \text{ dm}^3$$

$$\mu_{J-T} = \left( \frac{\partial T}{\partial P} \right)_H, \quad \left( \frac{T_f}{T_i} \right) = \left( \frac{V_f}{V_i} \right)^{1 - \frac{C_p}{C_v}}, \quad w = -nRT \ln \frac{V_f}{V_i}$$

Problems (20 pts each) Show all work

- 1.) Two moles of an ideal monatomic gas initially at a pressure of 1.00 bar and 25°C is compressed adiabatically and irreversibly by application of a constant external pressure of 15.00 bar, until the final pressure of the gas reaches 10.00 bar. Assume the gas has molar heat capacity  $\bar{C}_v = 3R/2$  and is independent of temperature.

- (a) Calculate the heat absorbed by the gas.  
(b) Calculate the final temperature of the gas.

a)  $q = 0$  (adiabatic)

b)  $\Delta U = w \Rightarrow \int_{T_i}^{T_f} n \bar{C}_v dT = \int_{V_i}^{V_f} -P_{\text{ext}} dV$  (since ideal gas)

$$n \bar{C}_v (T_f - T_i) = -P_{\text{ext}} (V_f - V_i)$$
$$= -P_{\text{ext}} \left[ \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right]$$

rearrange:

$$T_f = T_i \frac{n \bar{C}_v + nR \frac{P_{\text{ext}}}{P_i}}{n \bar{C}_v + nR \frac{P_{\text{ext}}}{P_f}}$$
$$= 298 \frac{(2 \cdot 3R/2) + \frac{(2)(R)(15)}{1}}{(2 \cdot 3R/2) + \frac{(2)(R)(15)}{10}}$$

$$= 1639 \text{ K}$$

2.) One mole of an ideal gas expands reversibly and isothermally from 10 bar to 1.0 bar at 298.15 K.

(a) What are the values (in joules) of  $w$ ,  $q$ ,  $\Delta U$ , and  $\Delta H$ ?

(b) If the same gas is instead expanded isothermally against a constant pressure of 1.0 bar, how much work is done and what is  $\Delta U$  in this case?

$$(a) \quad w = -nRT \ln \frac{V_f}{V_i} = +nRT \ln \frac{P_f}{P_i}$$

$$= (1)(8.3145)(298.15) \ln \frac{1}{10} = -5710 \text{ J}$$

$$\Delta U = 0 \text{ (isothermal, ideal)} \quad \text{so} \quad q = -w = +5710 \text{ J}$$

$$\Delta H = 0 \quad "$$

$$(b) \quad w = - \int_{V_i}^{V_f} P_{\text{ext}} dV = -P_{\text{ext}} \Delta V$$

$$V_e = \frac{(1)(R)(298.15)}{10 \times 10^5} = 0.002479 \text{ m}^3$$

$$V_f = 10 \cdot V_i = 0.02479 \text{ m}^3$$

$$w = -(1 \times 10^5)(0.02479 - 0.002479) = -2230 \text{ J}$$

$$\Delta U = 0 \quad (\text{still isothermal, ideal})$$

3.) In the thermodynamics of elastic materials (e.g., rubber bands) the force  $f$  exerted by the material depends on both the temperature  $T$  and the stretching displacement  $L$ . Starting with the total differential of  $f$ , obtain an expression for  $\Delta f$  when both  $T$  and  $L$  change in a general stretching process. Your result should be written in terms of the experimentally

measurable quantities  $\omega = \left(\frac{1}{L}\right)\left(\frac{\partial L}{\partial T}\right)_f$  and  $\lambda = \left(\frac{1}{L}\right)\left(\frac{\partial L}{\partial f}\right)_T$ .

$$df = \left(\frac{\partial f}{\partial T}\right)_L dT + \left(\frac{\partial f}{\partial L}\right)_T dL$$

$$\left(\frac{\partial f}{\partial T}\right)_L \left(\frac{\partial T}{\partial L}\right)_f \left(\frac{\partial L}{\partial f}\right)_T = -1$$

$$\left(\frac{\partial f}{\partial T}\right)_L = \frac{-1}{\left(\frac{\partial T}{\partial L}\right)_f \left(\frac{\partial L}{\partial f}\right)_T} = -\frac{\left(\frac{\partial L}{\partial T}\right)_f}{\left(\frac{\partial L}{\partial f}\right)_T}$$

$$\left(\frac{\partial f}{\partial T}\right)_L = \frac{-L\omega}{L\lambda} = \frac{-\omega}{\lambda}$$

the other:  $\left(\frac{\partial f}{\partial L}\right)_T = \frac{1}{\left(\frac{\partial L}{\partial f}\right)_T} = \frac{1}{L\lambda}$

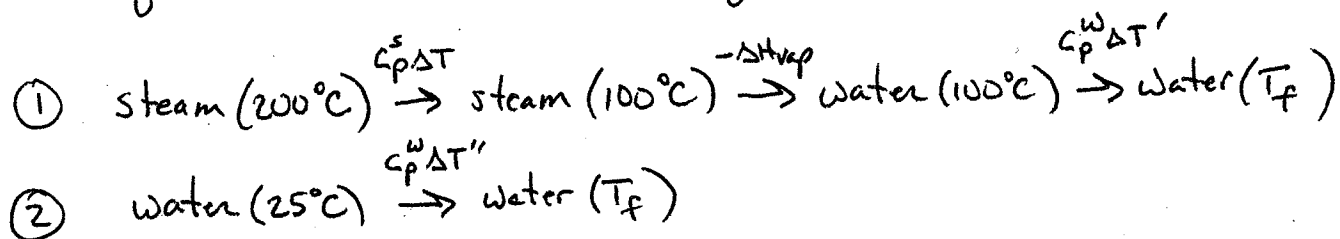
$$\Rightarrow df = -\frac{\omega}{\lambda} dT + \frac{1}{L\lambda} dL$$

$$\text{so } \Delta f = -\int_{T_i}^{T_f} \frac{\omega}{\lambda} dT + \int_{L_i}^{L_f} \frac{1}{L\lambda} dL$$

- 4.) Two moles of superheated steam at  $200^\circ\text{C}$  is injected into 50 moles of liquid water at  $25^\circ\text{C}$  at a constant pressure of 1.0 bar under adiabatic conditions. Calculate the final temperature of the water. The constant pressure heat capacities of  $\text{H}_2\text{O}(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $33.6$  and  $75.3$   $\text{J K}^{-1} \text{mol}^{-1}$ , respectively, and can be assumed to be independent of temperature. The enthalpy of vaporization at  $100^\circ\text{C}$  and 1 bar for  $\text{H}_2\text{O}$  is  $40.66 \text{ kJ mol}^{-1}$ .

$$q = 0 \quad \text{since adiabatic} \quad \textcircled{1} \quad \textcircled{2}$$

$$q_{\text{steam}} + q_{\text{w}} = 0$$



$$2 \bar{c}_p^s (100 - 200) - 2 (40.66 \times 10^3) + 2 \bar{c}_p^w (T_f - 100) + 50 \bar{c}_p^w (T_f - 25) = 0$$

$$2(33.6)(-100) - 2(40.66 \times 10^3) + 2(75.3)(T_f - 100) - 2(75.3)(100)$$

$$+ 50(75.3)T_f - 50(75.3)(25) = 0$$

$$T_f = 50^\circ\text{C}$$

5.) Multiple Choice (4 points each). Circle the one best answer.

(i) At sufficiently high temperatures, the van der Waals equation of state has the form

$$P \approx \frac{RT}{\bar{V} - b}. \text{ This implies that}$$

- (a) intermolecular attraction is most important at these temperatures.
- (b) the gas behaves like an ideal gas at these temperatures.
- (c) intermolecular repulsion is the dominant interaction at these temperatures.
- (d) the pressure is then independent of the type of gas.

(ii) A cup of water at 20°C (the system) is placed in a microwave oven and the oven is turned on for 1 minute during which it begins to boil. What are the signs (+, -, or 0) of  $q$ ,  $w$ , and  $\Delta U$ ?

- (a) +, +, +
  - (b) -, -, -
  - (c) +, -, +
  - (d) +, 0, +
- $q > 0$        $w < 0$        $\Delta U > 0$   
*heat added, vapor expands against surroundings, U increases since  $q > 0$  &  $w$  is small*

(iii) In a reversible expansion of a gas

- (a) the change in the internal energy is zero if the gas is ideal
  - (b) the heat absorbed by the system is balanced by the work performed
  - (c) the maximum amount of work is done by the system
  - (d) none of the above
- by def.*

(iv) In an adiabatic expansion of a gas, the temperature drops because

- (a) the intermolecular forces are minimized
- (b) the work done on the surroundings is obtained at the expense of the internal energy
- (c) the heat produced from the work escapes to the surroundings
- (d) the increasing disorder is balanced by a decrease in the enthalpy

(v)  $\bar{C}_p$  is a function of temperature for ethane but not for argon since

- (a) intermolecular interactions are much larger for ethane compared to argon
- (b) energy can be stored as vibrations and rotations in ethane
- (c) ethane is reactive whereas argon is not
- (d) all of the above