

## CHE 1214 – Basic Concepts in Chemistry II

### (C) General Physical Chemistry (Tutorial on Thermodynamics II)

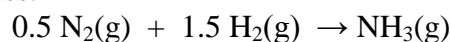
1. An *adiabatic* system consisting of a thermally insulated reaction vessel, with a 10  $\Omega$  resistance heater inside, is connected to a 20 V power supply, which is switched on for 50 s.
  - (i) Analyse the change in internal energy,  $\Delta U$ , of the system.
  - (ii) Repeat the analysis for an *isothermal diathermic* system (i.e. the system is in contact with a thermal reservoir such as a water bath).
2. The internal energy  $U$  of a monatomic ideal gas is  $U = \frac{1}{2}Nm\langle v^2 \rangle$ , where  $N$  is the number of atoms,  $m$  is the mass of one atom, and the kinetic theory of gases gives the mean-square speed  $\langle v^2 \rangle$  of the atoms as  $= 3pV/Nm$ .
  - (i) How does  $U$  depend on temperature?
  - (ii) Does  $U$  depend on pressure or volume, at constant temperature?
3. A volume of an ideal gas is contained within a cylinder with a frictionless piston at one end. When the internal volume of the cylinder is  $V_1 = 1 \text{ dm}^3$ , the outward pressure on the piston is  $p_1 = 10 \text{ atm}$ . The piston is held stationary by an opposing pressure consisting of 1 atm due to air outside and 9 atm due to nine weights sitting on the piston (each weight exerts 1 atm pressure). Calculate the work done if:
  - (i) all of the weights are removed quickly together;
  - (ii) five of the weights are removed quickly together, the system allowed to equilibrate, and then the remaining four weights are removed quickly;
  - (iii) the weights are removed one at a time, the system being allowed to come to equilibrium at each step.Discuss how the *maximum* amount of work could be extracted from the system. Calculate this value.
4. One mole of an ideal gas is carried through the following cycle:

		A		B		C	
	1	→	2	→	3	→	1
V/ dm <sup>3</sup>	22.4		22.4		44.8		22.4
T/ K	273		546		546		273

Assuming that each process is carried out reversibly:

- (i) Calculate the pressure at each state, 1, 2, and 3.
  - (ii) Name each process, A, b, and C.
  - (iii) Obtain expressions for the heat flow  $q$ , the work  $w$ , and the internal energy change  $\Delta U$  for each process.
  - (iv) Calculate numerical values for  $q$ ,  $w$  and  $\Delta U$  for the complete cycle.
5. Derive expressions for  $U_m$ ,  $H_m$ ,  $C_V$  and  $C_p$  for an ideal gas, evaluate them at 298 K, using the result from the kinetic theory of gases that  $U_m = (3/2)pV$ .
6.
  - (i) 100 g of  $\text{KNO}_3$  ( $\Delta_{\text{sol}}H^\theta(298 \text{ K}) = +34.9 \text{ kJ mol}^{-1}$ ) is added to 1 dm<sup>3</sup> of water ( $C_p(\text{H}_2\text{O}) = 75.29 \text{ J K}^{-1} \text{ mol}^{-1}$ ) at 298 K in an adiabatic container. What is the temperature of the water when the salt has all dissolved?
  - (ii) Repeat the calculation for  $\text{AlCl}_3$  ( $\Delta_{\text{sol}}H^\theta(298 \text{ K}) = -329 \text{ kJ mol}^{-1}$ ).

7. Calculate the reaction enthalpy for the process:



At 700 K (the appropriate temperature for ammonia synthesis), given that for  $\text{NH}_3(\text{g})$ ,  $\Delta_f H^\circ(298.15 \text{ K}) = -46.11 \text{ kJ mol}^{-1}$ , and the variation of  $C_p$  with temperature can be represented approximately by the equation:  $C_p = a + bT + cT^{-2}$ . Values for the constants  $a$ ,  $b$  and  $c$  are:

	$a/(\text{J K}^{-1} \text{ mol}^{-1})$	$b/(\text{J K}^{-2} \text{ mol}^{-1})$	$c/(\text{J K mol}^{-1})$
$\text{N}_2$	28.58	$3.77 \times 10^{-3}$	$-0.50 \times 10^5$
$\text{H}_2$	27.28	$3.26 \times 10^{-3}$	$+0.50 \times 10^5$
$\text{NH}_3$	29.75	$25.1 \times 10^{-3}$	$-1.55 \times 10^5$

8. Show that the following functions have exact differentials:

(i)  $x^2y + 3y^2$       (ii)  $x \cos(xy)$       (iii)  $t(t + e^s) + 25 s$

9. Prove that, when the internal energy is expressed as a function of temperature and pressure only, then for a process at constant pressure,

$$dq = C_p dT + \left[ \left( \frac{\partial U}{\partial p} \right)_T + p \left( \frac{\partial V}{\partial p} \right)_T \right] dp.$$

10. Sketch the following diagrams for the reversible Carnot cycle of an ideal gas with constant  $C_p$  and  $C_v$ :

- (a) pressure versus volume;      (b) temperature versus pressure;  
 (c) internal energy versus pressure;      (d) enthalpy versus pressure;  
 (e) volume versus temperature;      (f) volume versus internal energy.

11. For any substance, the following relationship can be obtained:

$$p + \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V.$$

- (i) Using the above equation, show that for a perfect gas the internal energy is independent of volume and pressure.

- (ii) Show that, for a one mole of a van der Waals gas,  $\left( \frac{\partial U}{\partial V} \right)_T = \frac{a}{V^2}$ .

12. Show that the change in enthalpy of a van der Waals gas in a reversible isobaric process is given by

$$\Delta H = bRT \left( \frac{1}{V_2 - b} - \frac{1}{V_1 - b} \right) - \frac{2a}{V_2} + \frac{2a}{V_1}.$$