

**PHYSICAL CHEMISTRY 3510**  
**EXAM 2**  
**October 16, 2015**

*IMPORTANT: Write neatly and lay out solutions clearly. Make sure that you give the reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation. Give units for all quantities!*

Your name: SOLUTIONS

**SOME POSSIBLY USEFUL INFORMATION:**

$$N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$dU = dq + dw$$

$$H = U + pV$$

$$dw = -p_{\text{ex}} dV$$

$$\gamma = C_p/C_v$$

$$\text{Perfect gas: } pV = nRT$$

$$C_p - C_v = nR$$

$$\text{Heat engine: } \varepsilon = (T_h - T_c)/T_h$$

$$\text{Adiabat: } pV^\gamma = \text{constant}$$

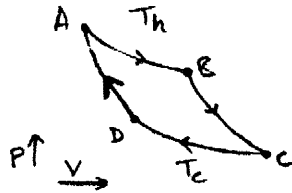
$$dS = dq_{\text{rev}}/T$$

$$G = H - TS$$

$$A = U - TS$$

1) 20 points

Consider the reversible Carnot cycle below, where the working fluid is 1 mol of perfect gas.



- When 45 J of heat is absorbed at  $T_h = 700$  K, 25 J of work are obtained. Calculate the efficiency and  $T_c$ .
- What can you say about the work obtained if the cycle was irreversible?
- What can you say about the sum of the changes in enthalpy for the four steps  $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ , and why?
- What can you say about the heat transfer in the  $B \rightarrow C$  step?

a)  $\epsilon = \frac{-w}{q_h} = \frac{25}{45} = 0.556 = \frac{700\text{K} - T_c}{700\text{K}} = 1 - \frac{T_c}{700\text{K}} \therefore T_c = 311\text{K}$ .

b) Work obtained ( $-w$ ) would be less.

c) Because  $H$  is a state function,  $\oint dH = 0$ .  $H$  must return to its initial value for any cycle.

d)  $B \rightarrow C$  is an adiabatic expansion  $\therefore q = 0$ .

2) 30 points

The volume of 1 mol of perfect gas (the system) with  $C_p = 25 \text{ J K}^{-1}$  and initially at 400 K is increased by a factor of 3. Calculate  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  for

- i) Doing this reversibly and adiabatically.
- ii) Doing this reversibly and isothermally.
- iii) Doing this irreversibly and isothermally against an external pressure  $p_{\text{ex}} = 0$ .

i) Adiabatic  $\therefore dq = 0 \therefore ds = \frac{dq_{\text{rev}}}{T} = 0 \therefore \Delta S_{\text{sys}} = \Delta S_{\text{surr}} = 0$ .

ii)  $\Delta S_{\text{sys}} = R \ln \frac{V_2}{V_1} = R \ln 3 = 9.13 \text{ J K}^{-1}$ . Reversible, so  $\Delta S_{\text{surr}} = -\Delta S_{\text{sys}}$ .

iii) Because  $S$ 's state function,  $\Delta S_{\text{sys}}$  here is the same as for (ii).

$\Delta U = q + w$ .  $w = 0$  here, and for an isothermal process  $\Delta U = 0$ , therefore  $q = 0$ . No heat to surroundings, so  $\Delta S_{\text{surr}} = 0$ .

3) 40 points

i) Starting with an expression for  $dA$  in terms of  $p$ ,  $V$ ,  $T$  and  $S$ , show that

$$(\partial p / \partial T)_V = (\partial S / \partial V)_T.$$

ii) Hence determine  $\Delta S$  for the isothermal expansion of 1 mole of a non-ideal gas which increases the volume from  $V_1$  to  $V_2$ . The equation of state for 1 mole of this gas is

$$p = (RT/V) - aT^2.$$

$$\begin{aligned} \text{i) } A = U - TS \quad \therefore dA &= dU - TdS - SdT & dU &= dq + dw \\ & & &= Tds - pdV \\ &= TdS - pdV - TdS - SdT \\ &= -pdV - SdT. \end{aligned}$$

$$\text{Consider } A(V, T): \quad dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

$$\text{By comparing terms, } \left(\frac{\partial A}{\partial V}\right)_T = -p \text{ and } \left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$\text{Because } \frac{\partial^2 A}{\partial V \partial T} = \frac{\partial^2 A}{\partial T \partial V}, \quad \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\text{ii) } \Delta S = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} - 2aT$$

$$\therefore \Delta S = \int_{V_1}^{V_2} \left(\frac{R}{V} - 2aT\right) dV = R \ln\left(\frac{V_2}{V_1}\right) - 2aT(V_2 - V_1)$$

4) 10 points

The Joule-Thompson coefficient,  $(\partial T/\partial p)_H$ , is  $0.7 \text{ K bar}^{-1}$  for a certain gas. If this gas, initially at  $298 \text{ K}$ , is expanded in a Joule-Thompson apparatus such that its pressure drops by  $30 \text{ bar}$ , what is the new temperature?

$$\left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} \text{ at constant } H \quad \text{so}$$

$$\begin{aligned} \Delta T &\approx \left(\frac{\partial T}{\partial p}\right)_H \cdot \Delta p = 0.7 \text{ K bar}^{-1} \times -30 \text{ bar} \\ &= -21 \text{ K} . \end{aligned}$$

New temperature is  $298 \text{ K} - 21 \text{ K} = 276 \text{ K}$  .