PHYSICAL CHEMISTRY 3510
EXAM 2
October 19, 2018

IMPORTANT: Write neatly and lay out solutions clearly. Make sure that you give the reasoning or work 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 or $L = 6.022 \times 10^{23}$ mol^{-1}

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

$dU = dq + dw$

$H = U + pV$

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

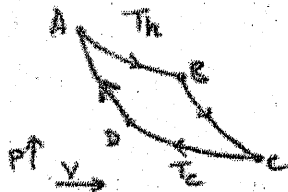$\gamma = C_p/C_v$

Perfect gas: $pV = nRT$

$C_p - C_v = nR$

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

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

$dS = dq_{rev}/T$

1)   *25 points*
    a) Consider the reversible Carnot cycle below, where the working fluid is 1 mol of perfect gas.

       When 20 J of heat are absorbed at $T_h = 700$ K, 12 J of work are obtained. Calculate the efficiency and T_c. How much heat is rejected at T_c?

    b) A sample of vibranium has $C_p = (18.0 + 0.02 \text{ K}^{-1} T - 1.0 \times 10^6 \text{ K}^2 T^{-2}) \text{ J K}^{-1}$. What are ΔH and ΔS for cooling this sample reversibly from a temperature $T = 298$ K to 250 K at constant pressure?

a)
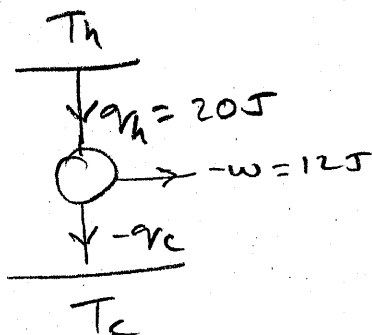
$$\varepsilon = -w/q_h = 12J/20J = 0.6$$

$$q_h = -w - q_c \quad \therefore \quad 20J = 12J - q_c$$

$$\therefore \quad q_c = -8J.$$

b) $C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \therefore \quad dH = C_p \cdot dT$ at const P $\therefore \quad \Delta H = \int_{T_1}^{T_2} C_p \cdot dT$

$$= \int_{298}^{250} \left(18 + 0.02T - 10^6 T^{-2}\right) dT = \left[18T + 0.01T^2 + 10^6 T^{-1}\right]_{298}^{250}$$

$$\approx \left[4500 + 625 + 4000 - 5364 - 888 - 3356\right] = -483 \text{ J}.$$

For a reversible change, $dS = \frac{dH}{T} \quad \therefore \quad \Delta S = \int_{298}^{250} \left(18T^{-1} + 0.02 - 10^6 T^{-3}\right) dT$

$$= \left[18 \ln T + 0.02T + 5 \times 10^5 T^{-2}\right]_{298}^{250} \approx \left[99.4 + 5.0 + 8.0 - 102.5 - 6.0 - 5.6\right]$$

$$= -1.7 \text{ J K}^{-1}.$$

see homework 2B.2
                                   3A.3

2)   *35 points*

1 mol of perfect gas (the system) with constant volume capacity $C_V = 21$ J K^{-1} mol^{-1} and initially at a temperature $T_1 = 300$ K and a pressure $p_1 = 5 \times 10^5$ Pa is expanded reversibly and adiabatically until it reaches a final pressure $p_2 = 3 \times 10^5$ Pa. Deduce the final volume V_2 and temperature T_2 and hence calculate q, ΔU, ΔH, ΔS and w for the system.

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \quad \therefore \quad V_2^{\gamma} = \left(\frac{P_1}{P_2}\right) V_1^{\gamma}$$

$$C_p = C_V + R = 29.314 \ JK^{-1} \ mol^{-1} \quad \therefore \quad \gamma = C_p/C_V = \frac{29.314}{21} = 1.396$$

$$\therefore V_2^{\gamma} = \left(\frac{5}{3}\right) V_1^{\gamma} \qquad P_1 V_1 = nRT_1 \quad \therefore \quad V_1 = \frac{8.314 \times 300}{5 \times 10^5} m^3 = 0.00499 \ m^3 .$$

$$= \left(\frac{5}{3}\right) \times 0.00499^{1.396} = 0.00102 .$$

$$V_2 = exp\left(\frac{\ln 0.00102}{1.396}\right) = \underline{0.00719 \ m^3} .$$

$$P_2 V_2 = nRT_2 \quad so \quad T_2 = \frac{3 \times 10^5 \times 0.00719}{8.314} K = \underline{\underline{260 \ K}} .$$

$\Delta T = -40 K .$

$q = 0$ because adiabatic.

$\Delta U = C_V \cdot \Delta T = -840 \ J \ mol^{-1} .$

$\Delta H = C_p \cdot \Delta T = -1173 \ J \ mol^{-1} .$

$\Delta S = \int \frac{dq}{T} = 0$ because $dq = 0 .$

$\Delta U = q + w$ (First Law) so $w = \Delta U - q = \Delta U$ here $= -840 \ J \ mol^{-1} .$

see homework questions 2E, 3-5

3) **40** *points*

   a) Consider U as a function of T and V to derive a general expression for the differential of U in terms of dT and dV. Hence deduce the general result, with $\pi_T = (\partial U/\partial V)_T$, that

$(\partial U/\partial T)_p = \pi_T(\partial V/\partial T)_p + C_V$

   C_V is the heat capacity at constant volume.

   b) Explain briefly, and qualitatively, why you would expect $\pi_T = 0$ for a perfect gas. Use the above result to evaluate ΔU for heating 1 mol of N_2 gas from 298 K to 500 K reversibly at constant pressure. Treat N_2 as a perfect gas and use the information that $C_V = (32 - 1000 \text{ K}/T)$ in J K^{-1}.

a) see notes

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{so} \quad dU = C_V \cdot dT + \pi_T dV.$$

b) No intermolecular forces so no change in U as molecules move apart (increase in v).

with $\pi_T = 0$, $\left(\frac{\partial U}{\partial T}\right)_p = C_V$

$$\Delta U = \int_{T_1}^{T_2} dU = \int \left(\frac{\partial U}{\partial T}\right)_p dT = \int_{T_1}^{T_2} C_V dT = \left[32T - 1000 \ln T\right]_{T_1}^{T_2}$$

$$= \left[32(500-298) - 1000 \ln\left(\frac{500}{298}\right)\right]$$

$$= 6464 - 518 \text{ J} = 5946 \text{ J}.$$