PHYSICAL CHEMISTRY 3510
EXAM 2
October 13, 2017

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 = 6.022×10^{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: $pV = nRT$

$C_p - C_v = nR$

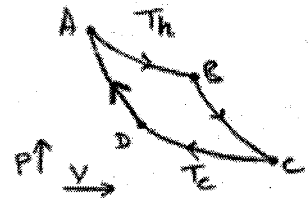
Heat engine: $\varepsilon = (T_h - T_c)/T_h$

Adiabat: pV^{γ} = constant

$dS = dq_{rev}/T$

1) *20 points*

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



a) When 45 J of heat are rejected at $T_c = 600$ K, 55 J of work are obtained. Calculate the efficiency and T_h.

b) Suppose that the engine is run backwards under different conditions and is used as a heat pump. 60 J of work are done on the engine when $T_c = 270$ K. How much heat leaves the engine at $T_h = 298$ K?

a) $q_h = -q_c - w = 45\,J + 55\,J = 100\,J.$

$\varepsilon = \frac{-w}{q_h} = \frac{55\,J}{100\,J} = 0.55$ but $\varepsilon = \frac{T_h - T_c}{T_h}$

$\therefore 1 - \frac{T_c}{T_h} = 0.55 \therefore \frac{T_c}{T_h} = 0.45 \therefore T_h = \frac{T_c}{0.45} = \frac{600K}{0.45} = 1333\,K$

b) $\varepsilon = \frac{298K - 270K}{298K} = 0.094 = \frac{-w}{q_h} = \frac{-60J}{q_h} \therefore -q_h = \frac{60\,J}{0.094}$

$= 638\,J.$

2) *30 points*

1 mol of perfect gas (the system) with constant heat capacity C_p and initially at a temperature T_1 and a pressure p_1 is expanded reversibly and adiabatically until the volume has doubled. Deduce the final temperature T_2 in terms of T_1 and γ and hence calculate q, ΔU, ΔH, ΔS and w for the system in terms of C_p, γ, T_1, T_2 and the gas constant R.

Initial conditions P_1, V_1, T_1 final $P_2, 2V_1, T_2$

pV^γ is constant so $P_1 V_1^\gamma = P_2 (2V_1)^\gamma = P_2 V_1^\gamma 2^\gamma \therefore P_2 = \frac{P_1}{2^\gamma}$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 (V_1 \times 2)}{T_2} \therefore T_2 = \frac{P_2 \cdot 2V_1 \cdot T_1}{P_1 V_1} = \frac{P_1}{2^\gamma} \cdot \frac{2}{P_1} \cdot T_1 = \frac{T_1}{2^{\gamma-1}}$$

$q = 0$ by adiabaticity

$\Delta U = C_v (T_2 - T_1) = (C_p - R)(T_2 - T_1)$.

$\Delta H = C_p (T_2 - T_1)$

$\Delta S = 0$ because $dq_{rev} = 0$

$w = \Delta U - q = \Delta U$ here $= (C_p - R)(T_2 - T_1)$.

3) *50 points*

Calorimeter experiments yield the enthalpy of combustion of acetylene gas as

$\Delta_c H_{298}$ ($C_2H_2(g)$) = -276.3 kJ mol^{-1}

and the internal energy change for combustion of liquid benzene as

$\Delta_c U_{298}$ ($C_6H_6(l)$) = -312.0 kJ mol^{-1}

Further, the molar heat capacities are given by

$C_p(C_2H_2(g)) = (45.0 + 0.01\ K^{-1}\ T - 1.0 \times 10^6\ K^2\ T^{-2})\ J\ K^{-1}\ mol^{-1}$

$C_p(C_6H_6(l)) = 136.0\ J\ K^{-1}\ mol^{-1}$ (does not change with temperature)

Use this information to calculate

a) The enthalpy of combustion of $C_6H_6(l)$.

b) ΔH_{298} for the reaction 3 $C_2H_2(g) \rightarrow C_6H_6(l)$.

c) The difference between ΔH_{600} and ΔH_{298} for the reaction in (b).

d) The entropy change for benzene, the system, when 1 mol of $C_6H_6(l)$ at 298 K is placed in a constant-temperature water bath at 350 K and irreversibly heated from 298 K to 350 K at constant pressure. What is ΔS for the surroundings (the water bath)? Is ΔS for the universe positive, zero or negative for this irreversible change?

a) $C_6H_6(l) + 7\tfrac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$H = U + pV \therefore \Delta H = \Delta U + \Delta(pV) \approx \Delta U + RT\Delta n_{gas}$

$\Delta n_{gas} = 6 - 7\tfrac{1}{2} = -1.5$

$\Delta H = \Delta U - 1.5RT = -312.0 - \frac{1.5 \times 8.314 \times 298}{1000}$ kJ mol^{-1}

$= -312.0 - 3.7$ kJ mol^{-1} $= -315.7$ kJ mol^{-1}.

b) $3C_2H_2 \xrightarrow{x} C_6H_6$

3×-276.3 kJ mol^{-1} ↘ $6CO_2 + 3H_2O$ ↙ -315.7 kJ mol^{-1}

$x - 315.7$ kJ mol^{-1} $= -828.9$ kJ mol^{-1}

$\therefore x = -513.2$ kJ mol^{-1}.

c) $\Delta C_p = (136.0 - 3 \times [45.0 + 0.01T - 1.0 \times 10^6 T^{-2}])$ J K^{-1} mol^{-1}.

$\Delta H_{600} = \Delta H_{298} + \int_{298}^{600} \Delta C_p . dT$

contd...

c) contd. so $\Delta H_{600} - \Delta H_{298} = \int_{298}^{600} 1 - 0{\cdot}03T + 3\times10^6 T^{-2} \, dT$

$$= \left[T - \frac{0{\cdot}03}{2} T^2 - 3\times10^6 T^{-1} \right]_{298}^{600}$$

$$= 600 - 298 - \frac{0{\cdot}03}{2}(600^2 - 298^2) - 3\times10^6\left(\frac{1}{600} - \frac{1}{298}\right) \quad J\,mol^{-1}$$

$$= 302 - 4068 + 5067 \ J\,mol^{-1} = 1{\cdot}30 \ kJ\,mol^{-1}.$$

d) Suppose benzene is heated reversibly:

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_{298}^{350} \frac{C_p . dT}{T} = C_p \ln\left(\frac{350}{298}\right) = 136 \times 0{\cdot}161 \ JK^{-1}\,mol^{-1}$$

$$= 21{\cdot}9 \ JK^{-1}\,mol^{-1}.$$

Because S is a state function this result is valid for irreversible heating too.

For the water bath, T is constant so the heat transfer is isothermal and reversible

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q_{sys}}{T_{surr}} = \frac{-C_p(T_2 - T_1)}{T_{surr}}$$

$$= \frac{-136 \ JK^{-1}mol^{-1} \times (350 - 298)K}{350 \ K} = -20{\cdot}2 \ JK^{-1}\,mol^{-1}$$

$$\Delta S_{uni} = 21{\cdot}9 - 20{\cdot}2 \ JK^{-1}\,mol^{-1} > 0$$

which is consistent with the 2nd Law.