PHYSICAL CHEMISTRY 5200

QUIZ 1

September 21, 2021

Please write neatly and clearly, and show all working. Three significant figures are suitable for your answers. Allocate time to each question in proportion to the available credit. Keep any explanations brief and to the point.

SOME POSSIBLY USEFUL INFORMATION (can be used without further justification):

N_A or L = 6.022×10^{23} mol^{-1} R = 8.314 J K^{-1} mol^{-1}

k or $k_B = R/N_A$

$dU = dq + dw$ $H = U + pV$

$dw = -p_{ex}\, dV$ $\gamma = C_p/C_v$

Perfect gas: $pV = nRT$ and $C_p - C_v = nR$ and pV^γ constant along an adiabat

van der Waals gas: $p = nRT/(V-b) - a(n/V)^2$

Your name SOLUTIONS

1) *20 points*

One mole of perfect gas is compressed reversibly and adiabatically from p_1,V_1 to p_2,V_2. $p_1 = 1.00 \times 10^5$ Pa and $V_1 = 0.0300\ m^3$, and $p_2 = 3.00 \times 10^5$ Pa and $V_2 = 0.0137\ m^3$. Find γ and hence C_V.

pV^γ constant so $p_1 V_1^\gamma = p_2 V_2^\gamma \therefore \left(\frac{p_1}{p_2}\right) = \left(\frac{V_2}{V_1}\right)^\gamma$

$\therefore \ln(p_1/p_2) = \gamma \ln(V_2/V_1) \therefore \gamma = \dfrac{\ln(p_1/p_2)}{\ln(V_2/V_1)}$

$= \dfrac{\ln(1/3)}{\ln(0.0137/0.0300)}$ comment: ratio means powers of 10 and units cancel

$= \dfrac{-1.099}{-0.784} = 1.40 = \dfrac{C_p}{C_V} = \dfrac{C_V+R}{C_V} = 1 + \dfrac{R}{C_V}$

$\therefore \dfrac{R}{C_V} = 0.40 \therefore C_V = R/0.40 = \underline{20.8\ J K^{-1} mol^{-1}}$

2) 15 *points*

A container has a volume of 0.0200 m^3 and at 273 K contains 3.00 mol H_2 and 1.00 mol N_2. Relative atomic masses are H = 1 and N = 14.

i) What is the total pressure p in the container?

ii) What is mol fraction of H_2?

iii) What is the partial pressure of H_2?

i) Total amount of gas $n = 4\,mol$

$$p = \frac{nRT}{V} = \frac{4\,mol \times 8.314\,JK^{-1}mol^{-1} \times 273\,K}{0.0200\,m^3}$$

$$= 4.54 \times 10^5\,Pa.$$

ii) $$x_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{N_2}} = \frac{3.00\,mol}{3.00\,mol + 1.00\,mol} = 0.75$$

iii) $$p_{H_2} = x_{H_2} \cdot p = 0.75 \times 4.54 \times 10^5\,Pa = 3.40 \times 10^5\,Pa.$$

3) *15 points*

The enthalpy of combustion of ethanol $C_2H_5OH(l)$ to make $H_2O(l)$ and $CO_2(g)$ is -1390 kJ mol^{-1}.
The enthalpy of combustion of dimethyl ether $CH_3OCH_3(l)$ to make $H_2O(l)$ and $CO_2(g)$ is -1460 kJ mol^{-1}.
The enthalpy of formation of $H_2O(l)$ is -286 kJ mol^{-1}.
The enthalpy of formation of $CO_2(g)$ is -394 kJ mol^{-1}.
All the data are for 298 K and can be assumed not to vary with T.

Use the above data to deduce
a) ΔU_{298} for the combustion of $C_2H_5OH(l)$.
b) $\Delta_f H_{298}$ for $CH_3OCH_3(l)$.
c) ΔH_{298} for the isomerization of $C_2H_5OH(l)$ to $CH_3OCH_3(l)$.

a) Combustion of ethanol

$C_2H_5OH(l) + 3O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$

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

Here $\Delta n_{gas} = -1$ so $\Delta H = \Delta U - RT$

$\therefore \Delta U = \Delta H + RT = -1390 \text{ kJ mol}^{-1} + \frac{8.314 \times 298 \text{ J}}{1000}$
$= -1388 \text{ kJ mol}^{-1}$.

b) ΔH for $CH_3OCH_3(l) + 3O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$

$= 3\Delta_f H(H_2O) + 2\Delta_f H(CO_2) - 3\Delta_f H(O_2) - \Delta_f H(CH_3OCH_3) = x$

$\therefore -1460 \text{ kJ mol}^{-1} = 3 \times -286 + 2 \times -394 - x$ kJ mol^{-1}
$= -1646 - x$ kJ mol^{-1}

$\therefore x = 1460 - 1646 \text{ kJ mol}^{-1} = -186 \text{ kJ mol}^{-1}$

c) Hess cycle

$C_2H_5OH \xrightarrow{\Delta H = x} CH_3OCH_3$

$C_2H_5OH \xrightarrow{+3O_2,\ -1390 \text{ kJ mol}^{-1}} 2CO_2 + 3H_2O$

$CH_3OCH_3 \xrightarrow{+3O_2,\ -1460 \text{ kJ mol}^{-1}} 2CO_2 + 3H_2O$

$x - 1460 \text{ kJ mol}^{-1} = -1390 \text{ kJ mol}^{-1}$

$\therefore x = 70 \text{ kJ mol}^{-1}$.