PHYSICAL CHEMISTRY 5200

QUIZ 1

September 26, 2019

Please write neatly and clearly, and <u>show all working</u>. Allocate time to each question in proportion to the available credit. Keep any explanations brief and to the point.

Your name: _____ SOLUTIONS _____

SOME POSSIBLY USEFUL INFORMATION:

N_A or $L = 6.022 \times 10^{23}$ mol^{-1} $\qquad\qquad$ $R = 8.314$ J K^{-1} mol^{-1}

k or $k_B = R/N_A$

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

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

Perfect gas: $pV = nRT$ $\qquad$ and $\qquad$ $C_p - C_v = nR$

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

1)   20 *points*
a) The system is one mole of van der Waals gas. What is the work done on the system if it is isothermally expanded from initial pressure and volume p_1 and V_1 to final values p_2 and V_2, at a temperature T?

b) At the critical point, where $T = T_c$, $p = p_c$ and $V = V_c$, there is a horizontal inflection on a plot of p versus V. Obtain equations for the first and second derivatives of p as a function of V for a van der Waals gas, and show that they are both zero at the critical point when
$V_c = 3b$, $p_c = a/(27b^2)$, $T_c = 8a/(27Rb)$.

a) $dw = -P_{ex}\,dV = -p\,dV$ for reversible process

$$= -\left(\frac{RT}{V-b} + \frac{a}{V^2}\right)dV \text{ here}$$

so $w = -\int_{V_1}^{V_2} p\,dV = -\left[RT \ln(V-b) + a/V\right]_{V_1}^{V_2}$

$$= -\left[RT\left(\ln(V_2-b) - \ln(V_1-b)\right) + a\left(\tfrac{1}{V_2} - \tfrac{1}{V_1}\right)\right]$$

$$= RT \ln\left(\frac{V_1-b}{V_2-b}\right) + a\left(\tfrac{1}{V_1} - \tfrac{1}{V_2}\right).$$

b) $\dfrac{dp}{dV} = RT \cdot -(V-b)^{-2} + 2aV^{-3}$, at critical point $= -RT_c(V_c-b)^{-2} + \dfrac{2a}{V_c^3}$

$$= -R \cdot \frac{8a}{27Rb}(2b)^{-2} + \frac{2a}{27b^3} = -R \cdot \frac{8a}{27Rb} \cdot \frac{1}{4b^2} + \frac{2a}{27b^3} = 0,$$

$\dfrac{d^2p}{dV^2} = RT \cdot 2(V-b)^{-3} - 6aV^{-4}$, at critical point $= \dfrac{2RT_c}{(V_c-b)^3} - \dfrac{6a}{V_c^4}$

$$= 2R \cdot \frac{8a}{27Rb} \cdot \frac{1}{8b^3} - \frac{6a}{81b^4} = \frac{1}{b^4}\left(\frac{2}{27} - \frac{6}{81}\right) = 0.$$

2)   15 *points*

One mole of a perfect gas with $C_V = 32$ J K^{-1} mol^{-1} is expanded reversibly and adiabatically from an initial pressure of 8×10^4 Pa and an initial temperature of 298 K to a final volume of 0.07 m^3. You may assume the result that pV^γ is constant. Calculate q, ΔU, ΔH and w.

$$C_p = C_V + R = 40.314 \text{ J K}^{-1}\text{mol}^{-1} \quad \therefore \gamma = \frac{C_p}{C_V} = \frac{40.314}{32} = 1.26$$

Initially, $P_1 V_1 = RT_1$ $\therefore V_1 = \frac{RT_1}{P_1} = \frac{R \times 298}{8 \times 10^4} \text{ m}^3 = 0.031 \text{ m}^3$

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad \therefore P_2 = P_1 \cdot \left(\frac{V_1}{V_2}\right)^\gamma = 8 \times 10^4 \text{ Pa} \times \left(\frac{0.031}{0.07}\right)^{1.26}$$

$$= 2.87 \times 10^4 \text{ Pa}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \therefore T_2 = T_1 \times \frac{P_2 V_2}{P_1 V_1} = 298K \times \frac{2.87 \times 10^4 \times 0.07}{8 \times 10^4 \times 0.031}$$

$$= 241 K \quad \therefore \Delta T = -57 K.$$

$q = 0$ because adiabatic.

$\Delta U = C_V \cdot \Delta T = 32 \times -57 \text{ J} = -1824 \text{ J}.$

$\Delta H = C_p \cdot \Delta T = 40.3 \times -57 \text{ J} = -2297 \text{ J},$

$\Delta U = q + w \quad \therefore w = \Delta U$ here $= -1824 \text{ J}.$

3)   *15 points*
The enthalpy of combustion of $C_2H_5OH(l)$ to make $H_2O(l)$ and $CO_2(g)$ is -1368 kJ mol^{-1}.
The enthalpy of combustion of $CH_3OCH_3(g)$ to make $H_2O(l)$ and $CO_2(g)$ is -1462 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}.
The heat capacities C_p for $O_2(g)$, $C_2H_5OH(l)$, $CH_3OCH_3(g)$, $H_2O(l)$ and $CO_2(g)$ are 29, 112, 66, 75 and 37 J K^{-1} mol^{-1}, respectively. All the data are for 298 K and can be assumed not to vary with T.

Deduce
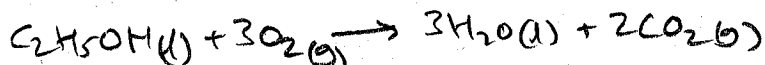a) ΔU_{298} for the combustion $C_2H_5OH(l)$.
b) ΔH_{900} for the combustion $C_2H_5OH(l)$ at 900 K.
c) ΔH_{298} for the isomerization of $CH_3OCH_3(g)$ to $C_2H_5OH(l)$ [dimethyl ether to ethanol].

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

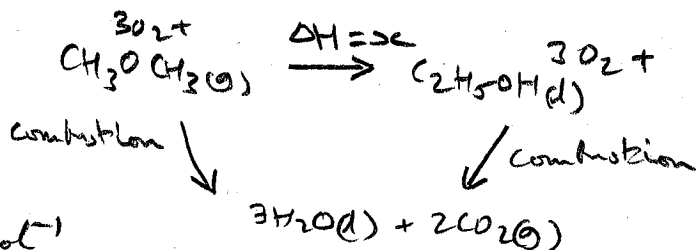$$C_2H_5OH(l) + 3O_{2(g)} \longrightarrow 3H_2O(l) + 2CO_2(g)$$

so $\Delta n_{gas} = 2 - 3 = -1$

$\Delta U_{298} = \Delta H_{298} + RT = -1368 \text{ kJmol}^{-1} + \dfrac{8.314 \times 298}{1000} \text{ kJmol}^{-1}$

$\approx -1366 \text{ kJmol}^{-1}$.

b) $\left(\dfrac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p = (3 \times 75 + 2 \times 37 - 3 \times 29 - 112)$ J K^{-1} mol^{-1}

$= 100$ J K^{-1} mol^{-1}.

$\Delta H_{900} = \Delta H_{298} + \displaystyle\int_{298}^{900} \Delta C_p \, dT = -1368 + (900 - 298) . \underbrace{\dfrac{100}{1000}}_{\text{convert J} \to \text{kJ}}$ kJ mol^{-1} ← ΔC_p

$= -1368 + 60.2$ kJ mol^{-1}

≈ -1308 kJ mol^{-1}.

c) Make a Hess cycle such as

$CH_3OCH_{3(g)} \xrightarrow{\Delta H = x} C_2H_5OH(l)$ $3O_2 +$ $3O_2 +$

combustion $\downarrow$ $\downarrow$ combustion

$3H_2O(l) + 2CO_2(g)$

$x - 1368 \text{ kJmol}^{-1} = -1462 \text{ kJmol}^{-1}$

$\therefore x = -94 \text{ kJmol}^{-1}$.

4