

# PHYSICAL CHEMISTRY 5200

## QUIZ 2

November 4, 2021

*Please write neatly and clearly, and show all working. 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:

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

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

$$k \text{ or } k_B = R/N_A$$

$$dU = dq + dw$$

$$H = U + pV$$

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

$$\gamma = C_p/C_v$$

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

$$C_p - C_v = nR$$

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

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

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

$$A = U - TS$$

$$G = H - TS$$

$$d(\ln K) / d(1/T) = -\Delta H/R$$

$$\Delta_r G = \Delta G^\circ + RT \ln Q$$

$$\text{pH} = -\log_{10}(a_{\text{H}^+})$$

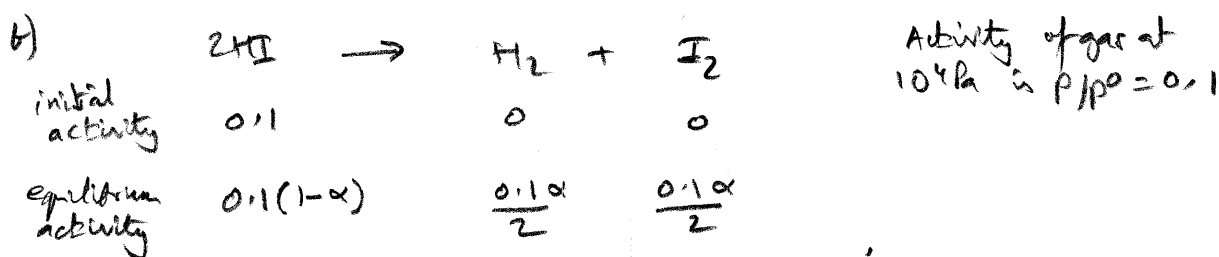
1) 20 points

Consider the dissociation of hydrogen iodide gas:  $2 \text{HI} (g) \rightarrow \text{H}_2 (g) + \text{I}_2 (g)$ . At 600 K the equilibrium constant  $K$  is 0.012, and is 0.024 at 800 K.

- What is the Gibbs energy of formation of HI (g) at 600 K?
- What is the degree of dissociation  $\alpha$  of HI, if an initial pressure of  $10^4$  Pa of pure HI in a sealed container comes to equilibrium? Do not assume  $\alpha$  is small. What is the total pressure at equilibrium?
- Using Le Chatelier's Principle, or otherwise, explain qualitatively how you expect  $K$  and  $\alpha$  to vary if (i) the container is compressed, or (ii) extra  $\text{I}_2$  is added to the system.
- Deduce  $\Delta H^\circ$  and  $\Delta S^\circ$  for the HI dissociation reaction.

$$a) \Delta G^\circ = -RT \ln K = 22063 \text{ J mol}^{-1} = \Delta_f G^\circ(\text{H}_2) + \Delta_f G^\circ(\text{I}_2) - 2 \Delta_f G^\circ(\text{HI})$$

$$\therefore \Delta_f G^\circ(\text{HI}) = -11.03 \text{ kJ mol}^{-1}$$



$$K = \frac{a_{\text{H}_2} a_{\text{I}_2}}{a_{\text{HI}}^2} = \frac{\frac{0.1\alpha}{2} \times \frac{0.1\alpha}{2}}{[0.1(1-\alpha)]^2} = \frac{\alpha^2}{4(1-\alpha)^2} = 0.012$$

$$\text{so } \frac{\alpha}{2(1-\alpha)} = \sqrt{0.012} = 0.110 \therefore \frac{\alpha}{1-\alpha} = 0.220 \therefore \alpha = 0.220 - 0.220\alpha$$

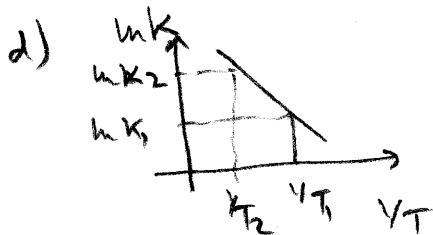
$$\therefore \alpha = \underline{\underline{0.180}}$$

$$\text{Total } p = p^\circ \left( 0.1(1-\alpha) + \frac{0.1\alpha}{2} + \frac{0.1\alpha}{2} \right) = 0.1 p^\circ = \underline{\underline{10^4 \text{ Pa}}}$$

c)  $K$  does not change with pressure or composition.

i) Shifting equilibrium does not change the total pressure (note lack of dependence on  $\alpha$  above) so  $\alpha$  does not change.

ii) Extra product shifts equilibrium towards reactants so  $\alpha$  decreases.



$$\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\therefore \ln 2 = -\frac{\Delta H}{R} \left( \frac{1}{800 \text{ K}} - \frac{1}{600 \text{ K}} \right)$$

$$\therefore \frac{\Delta H}{R} = 1664 \text{ K} \therefore \Delta H = \underline{\underline{+13.8 \text{ kJ mol}^{-1}}}$$

$$\Delta S = \frac{\Delta H - \Delta G_{600}}{600 \text{ K}} = \underline{\underline{-13.8 \text{ J K}^{-1} \text{ mol}^{-1}}}$$

2) 20 points

a) Starting with an expansion of  $dA$ , prove that  $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ . Show work and any results you rely on.

b) Use this result to deduce  $\Delta S$  for the isothermal compression of 1 mol of a van der Waals gas from volume  $V_1$  to  $V_2$ .

$$a) \quad A = U - TS = q + w - TS$$

$$\therefore dA = dq - pdV - Tds - SdT \quad \text{and} \quad dS = dq/T$$

$$\text{so } dA = \cancel{Tds} - pdV - \cancel{Tds} - SdT$$

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

Compare terms for  $dV$  and  $dT$ :

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

The second derivative  $\frac{\partial^2 A}{\partial V \partial T}$  is the same in either order so  $-\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$

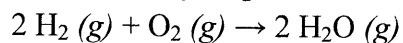
$$b) \quad \Delta S = \int_{V_1}^{V_2} dS = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{For a van der Waals gas,}$$

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \therefore \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\text{so } \Delta S = \int_{V_1}^{V_2} \frac{R}{V-b} dV = R \ln \left( \frac{V_2 - b}{V_1 - b} \right)$$

3) 10 points

The combustion of hydrogen can be written as



and, at 3000 K,  $\Delta G^\circ$  is  $-150 \text{ kJ mol}^{-1}$ .

a) Is the reaction spontaneous from left to right when the initial activity of each species is 1?

b) Is the reaction spontaneous from left to right when the initial activity of each species is 0.001?

Show work and explain your answers.

$$a) \Delta_r G = \Delta_r G^\circ + RT \ln Q \quad Q = \frac{a_{\text{H}_2\text{O}}^2}{a_{\text{H}_2}^2 a_{\text{O}_2}}$$

When all  $a=1$ ,  $Q=1$  and  $\ln Q=0$

so  $\Delta_r G = \Delta_r G^\circ < 0$  so yes, spontaneous

b) with  $a=0.001$ ,  $Q=1000$

$$\Delta_r G = -150 + \frac{8.314 \times 3000}{1000} \times \ln 1000 \text{ kJ mol}^{-1}$$
$$= +22.3 \text{ kJ mol}^{-1}$$

$> 0$  so no, not spontaneous