PHYSICAL CHEMISTRY 5200
QUIZ 2
November 5, 2020

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.

SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

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

k or $k_B = R/N_A$

$dU = dq + dw$

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

Perfect gas: $pV = nRT$ and

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

Adiabat: pV_γ is constant

$A = U - TS$

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

$pH = -\log_{10}(aH+)$

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

$H = U + pV$

$\gamma = C_p/C_v$

$C_p - C_v = nR$

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

$G = H - TS$

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

1)   20 *points*

Consider the dissociation of a general acid HA: HA*(aq)* $\rightleftharpoons$ H$^+$ *(aq)* + A$^-$ *(aq)* for which ΔG^0 at 298 K is +13.0 kJ mol^{-1} and ΔH^0 = +23.1 kJ mol^{-1}.
a) What is pK$_a$ for HA?
b) What is the degree of dissociation α of HA, and the equilibrium pH, of an initially 0.003 M solution of pure HA at 298 K? Do not assume α is small.
c) What is the equilibrium pH of an initially 0.003 M solution of HA at 298 K, to which additional A$^-$ has been added to fix [A$^-$] at 0.1 M?
d) Calculate the pH of an initially 0.003 M solution of pure HA at 273 K.

a) $K_a = e^{-\Delta G/RT} = e^{-\frac{13000}{8.314 \times 298}} = 0.00526$, $pK_a = -\log_{10} K_a = \underline{\underline{2.28}}$.

b) In terms of degree of dissociation α, the equilibrium activities are
HA $0.003(1-\alpha)$, H$^+$ and A$^-$ 0.003α so

$K_a = \dfrac{0.003^2 \alpha^2}{0.003(1-\alpha)}$ $\therefore \dfrac{\alpha^2}{1-\alpha} = \dfrac{0.00526}{0.003} = 1.75$ $\therefore \alpha^2 + 1.75\alpha - 1.75 = 0$

$\therefore \alpha = \dfrac{-1.75 \pm 3.17}{2}$ and must be positive so $\alpha = \underline{0.711}$.

$a_{H^+} = 0.003\alpha = 0.00213$ $\therefore pH = -\log_{10} 0.00213 = \underline{\underline{2.67}}$.

Or use equilibrium activities of HA $0.003 - x$, H$^+$ and A$^-$ = x
and solve $\dfrac{x^2}{0.003-x} = K_a$, obtain α from $0.003\alpha = x$.

c) Equilibrium activities are HA $0.003-x$, H$^+$ x, A$^-$ 0.1, so

$\dfrac{0.1 x}{0.003-x} = K_a$ $\therefore 0.1x = 1.58 \times 10^{-5} - 0.00526x$ $\therefore x = \dfrac{1.58 \times 10^{-5}}{0.10526} = 1.50 \times 10^{-4}$

So pH $= -\log_{10} x = \underline{\underline{3.82}}$.   Or use Henderson Hasselbach relation.

d) $\Delta S = \dfrac{\Delta H - \Delta G}{T} = +33.9$ J K^{-1} mol^{-1}, $\Delta G_{273} = 13847$ J mol^{-1} $\therefore K_a = 0.00224 = \dfrac{x^2}{0.003-x}$ for equilibrium activities of HA $0.003-x$, H$^+$ and A$^-$ x

$\therefore x = 1.70 \times 10^{-3}$ and $\underline{\underline{pH = 2.77}}$.

a_{H^+} smaller than in (b) in line with Le Chatelier's principle.

2)   *10 points*

Starting with an expansion of dH, derive an expression for $(\partial V/\partial S)_p$ in terms of S, p and T.

$$H = U + pV \quad \therefore \quad dH = dU + pdV + Vdp = TdS - p\,dV + p\,dV + Vdp$$
$$= TdS + Vdp$$

Consider $H(S,p)$ so $dH = \left(\dfrac{\partial H}{\partial S}\right)_p dS + \left(\dfrac{\partial H}{\partial p}\right)_S dp$

Compare coefficients $\left(\dfrac{\partial H}{\partial S}\right)_p = T$ and $\left(\dfrac{\partial H}{\partial p}\right)_S = V$

Second derivatives are equal $\dfrac{\partial^2 H}{\partial S \partial p} = \left(\dfrac{\partial T}{\partial p}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_p$.

3)   *20 points*

Given that at p = 1 bar the boiling point of water is 373 K, and that $\Delta_{vap}H = 40.7$ kJ mol^{-1}, predict the boiling temperature in a mountain town where p = 0.85 bar.

Integrated form of Clausius-Clapeyron equation:

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \therefore \quad \ln\left(\frac{1}{0.85}\right) = -\frac{40700 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{373\text{ K}} - \frac{1}{x}\right)$$

$\therefore \quad 3.32 \times 10^{-5}\text{ K}^{-1} = -\left(\frac{1}{373\text{ K}} - \frac{1}{x}\right)$

$\therefore \quad \frac{1}{x} = 3.32 \times 10^{-5}\text{ K}^{-1} + 2.681 \times 10^{-3}\text{ K}^{-1} = 2.71 \times 10^{-3}\text{ K}^{-1}$

$\therefore \quad x = 368 \text{ K}$.