

## LISTA PROBLEMAS 2



a) CONSTANTE DE EQUILIBRIO  $K_p$

$$K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 \cdot P_{\text{Cl}_2}}$$

b)  $\Delta \bar{H}_r^\circ = 2 \cdot \Delta \bar{H}_f^\circ \text{NOCl} - (2 \cdot \Delta \bar{H}_f^\circ \text{NO} + \Delta \bar{H}_f^\circ \text{Cl}_2)$

$$\Delta \bar{H}_r^\circ = 2 \times 51,7 - (2 \times 90,25 + 0)$$

$$\Delta \bar{H}_r^\circ = 103,4 - 180,5$$

$$\Delta \bar{H}_r^\circ = -77,1 \text{ kJ/mol (Processo exotérmico)}$$

$$\Delta \bar{S}_r^\circ = 2 \cdot S_{\text{NOCl}}^\circ - (2 \cdot S_{\text{NO}}^\circ + S_{\text{Cl}_2}^\circ)$$

$$\Delta \bar{S}_r^\circ = 2 \times 261,6 - (2 \times 210,65 + 222,965)$$

$$\Delta \bar{S}_r^\circ = 532,2 - 642,965$$

$$\Delta \bar{S}_r^\circ = -110,765 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta \bar{G}_n^{\circ} = \Delta \bar{H}_n^{\circ} - T \Delta \bar{S}_n^{\circ}$$

$$T = 298 \text{ K}$$

$$\Delta \bar{G}_n^{\circ} = -77.100 - 298 \times (-119,765)$$

$$\Delta \bar{G}_n^{\circ} = -77.100 + 35.690$$

$$\Delta \bar{G}_n^{\circ} = -41.410 \text{ J/mol}$$

CONSTANTE TERMODINÂMICA DE EQUILÍBRIO

$$\Delta \bar{G}_n^{\circ} = -RT \ln K$$
$$K_p = e^{-\Delta \bar{G}_n^{\circ}/RT}$$

$$R = 8,314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{ou } K_p = \exp(41410 / (298 \times 8,314))$$

$$K_p = e^{16,71} \approx 1,79 \times 10^7$$

c) Eq. de Van't Hoff

$$\left( \frac{d \ln K_p}{dT} \right)_P = \frac{\Delta \bar{H}_r^\circ}{RT^2}$$

Em um intervalo reduzido de  $T$  onde

$$\Delta \bar{H}_r^\circ \approx \text{CONST TEMOS}$$

$$\ln \left( \frac{K_p(T_2)}{K_p(T_1)} \right) = \left( \frac{\Delta \bar{H}_r^\circ}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

No caso  $\Delta \bar{H}_r^\circ = -77.100 \text{ J/mol}$

$$R = 8,314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$T_1 = 298 \text{ K}$$

$$T_2 = 80 + 273 = 353$$

$$\ln K_p(T_2) = \ln K_p(T_1) - \frac{77.100}{8.314} \left( \frac{1}{298} - \frac{1}{353} \right)$$

$5,23 \times 10^{-4}$

$$\ln K_p(T_2) = 16,71 - 4,85$$

$$K_p(T_2) = e^{11,86}$$

$$K_p(T_2) = 1,4 \times 10^5$$

## CONCLUSÃO

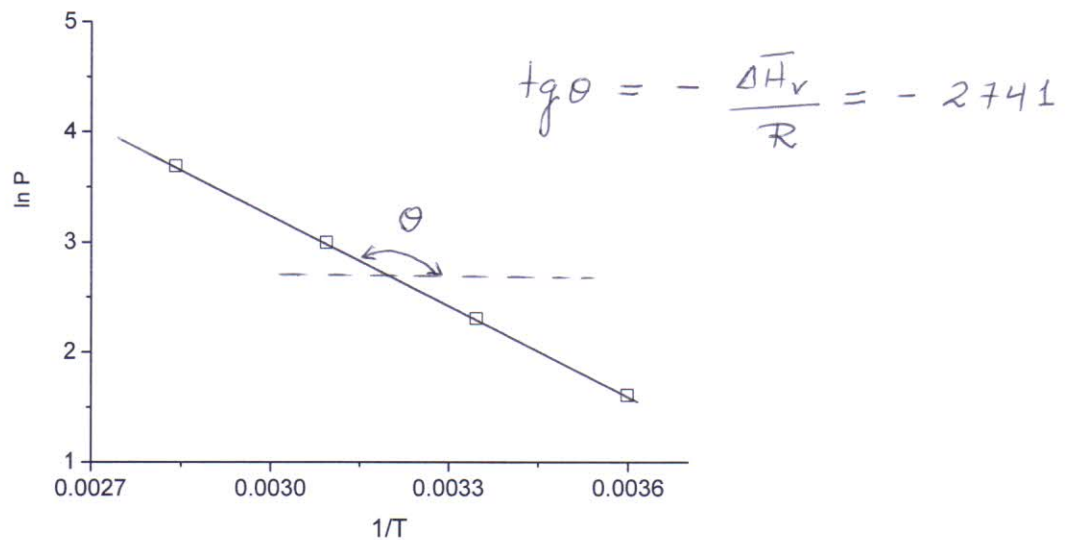
$$K_p(353) < K_p(298)$$

Sendo a reação exotérmica, o aumento na temperatura resulta na diminuição da constante de equilíbrio (ou seja desloca o equilíbrio no sentido dos reagentes ou menos produtos (Princípio de Le Chatelier))

2) Usando a equação de Clapeyron na forma integrada:

$$\ln\left(\frac{P_2}{P_1}\right) = - \frac{\Delta \bar{H}_v}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1)$$

a) GRÁFICO DE  $\ln P \times 1/T$  tem como coeficiente angular



Assim a entalpia de vaporização do  $\text{NH}_3$

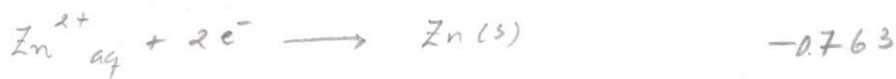
é dado por  $\Delta \bar{H}_v = 2741 R$  ;  $R = 8,314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\Delta \bar{H}_v = 22788 \text{ J/mol}$$

b) Ponto de ebulição normal  $T_{eb} \Rightarrow P = 1 \text{ atm}$   
 Considerando o ponto (5 atm, 277,8) temos por

$$(1) \quad \ln\left(\frac{5}{1}\right) = - 2741 \cdot \left( \frac{1}{277,8} - \frac{1}{T_{eb}} \right) = 1,609$$

$$\underline{T_{eb} = 238,85 \text{ K} \quad (-34,3^\circ \text{C})}$$



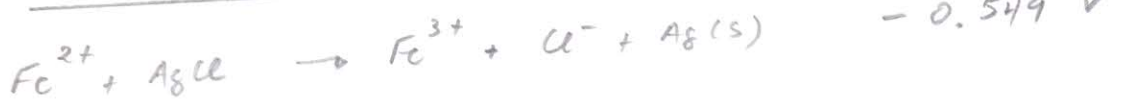
$$\epsilon = \epsilon^{\circ} - \frac{0,05916}{2} \log \frac{[Ag^+]^2}{[Zn^{2+}]}$$

$$\epsilon = -1,562 - \frac{0,05916}{2} \cdot \log \frac{(10^{-2})^2}{0,1}$$

$$\epsilon = -1,562 + 0,08874 \Rightarrow$$

$$\epsilon = -1,473 \text{ Volts}$$

(reac espontânea)



$$\epsilon = \epsilon^{\circ} - 0,05916 \cdot \log \frac{a_{Cl^-} \cdot a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

$$\epsilon = -0,549 - 0,05916 \log \frac{0,002 \cdot 0,1}{1}$$

$$\epsilon = -0,549 + 0,2366$$

$$\epsilon = -0,3124 \text{ Volts}$$

Nas espontânea.



$\epsilon^{\circ}$  in Volts  
+ 1,216



+ 0,098

1,314 volts



$$\epsilon = \epsilon^{\circ} - \frac{0,05916}{2} \cdot \lg \frac{a_{\pm} \text{ZnO}_2^{2-}}{(a_{\pm} \text{OH}^-)^2}$$

$$\epsilon = 1,314 - \frac{0,05916}{2} \cdot \lg \frac{0,1}{1}$$

$$\epsilon = 1,346 \text{ volts} \quad \text{Espontânea}$$

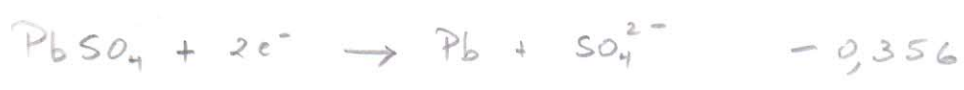
$$2) \quad \varepsilon^{\circ} = \frac{RT}{nF} \ln K_{eq}$$

$$25^{\circ}\text{C} \Rightarrow \log K_{eq} = \frac{n \varepsilon^{\circ}}{0,05916}$$



$$\log K_{eq} = \frac{2 \cdot 0,497}{0,05916}$$

$$K_{eq} = 6,3 \times 10^{16}$$



$$\log K_{eq} = \frac{2 \times (-0,230)}{0,05916}$$

$$K_{eq} = 1,7 \times 10^{-8}$$



$$5) r = k [\text{NO}]^x [\text{Cl}_2]^y$$

suma de reacciones

$$\frac{v_f}{v_i} = 8 = 2^x \cdot 2^y \quad (1)$$

$$\left. \begin{array}{l} 2 = 2^y \\ x = 2 \end{array} \right\} \Rightarrow r = k [\text{NO}]^2 [\text{Cl}_2]^2$$

$$6) -\frac{d[\text{Fe}^{2+}]}{dt} = k' [\text{Fe}^{2+}] \quad ; \quad k' = k P(\text{O}_2)$$

$$k' = 3,7 \times 10^{-3} \text{ L mol}^{-1} \text{ atm h}^{-1} \cdot 0,2 \text{ atm} = 7,4 \times 10^{-4}$$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{0,693}{3,7 \times 10^{-3} \cdot 0,2} \Rightarrow \boxed{t_{1/2} = 936 \text{ horas}}$$

$$[\text{Fe}^{2+}] = [\text{Fe}^{2+}]_0 e^{-k't}$$

$$0,01 = 0,1 \cdot e^{-7,4 \times 10^{-4} t}$$

$$-2,302 = -7,4 \times 10^{-4} t$$

$$t = 3,112 \times 10^3 \text{ h}$$

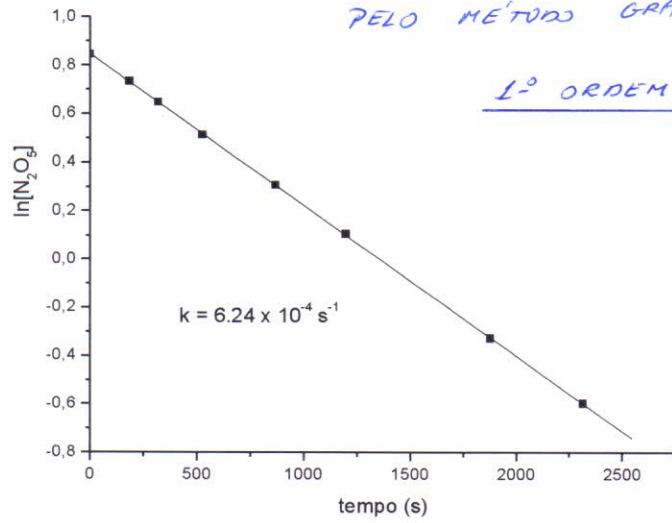
$$\underline{t \approx 130 \text{ dias}}$$

7)

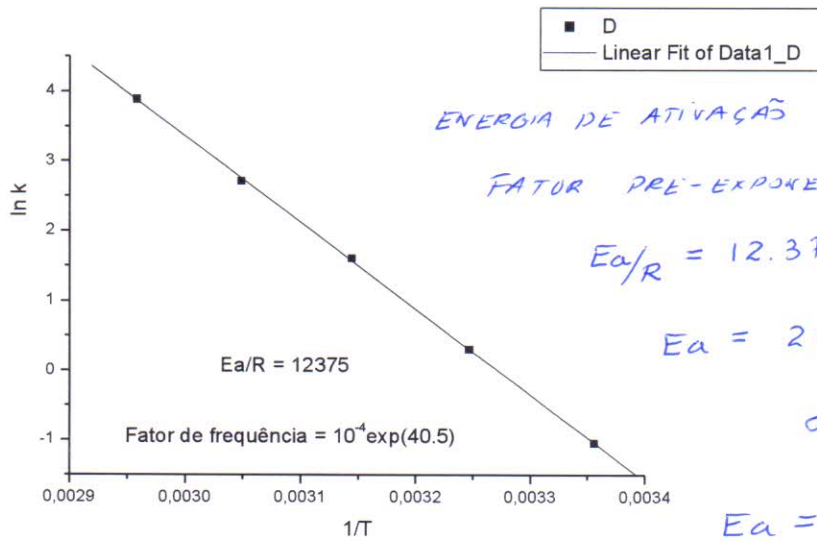
CÁLCULO DA CONSTANTE VELOCIDADE DE REAÇÃO

PELO MÉTODO GRAFICO:

1º ORDEM GRAFICO LINEAR



8)



ENERGIA DE ATIVAÇÃO  $E_a$  e

FATOR PRE-EXPONENCIAL

$$E_a/R = 12.375$$

$$E_a = 24600 \text{ cal/mol}$$

ou

$$E_a = 102,9 \text{ kJ/mol}$$

$$A = 3.9 \times 10^{13} \text{ s}^{-1}$$