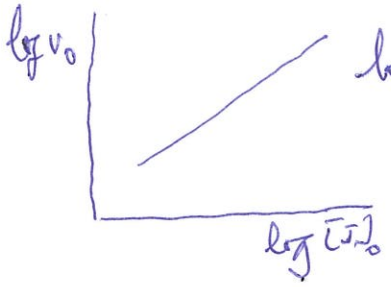
PROBLEMAS DE CINÉTICA QUÍMICA

(1)

$J_0 / 10^{-3}\ mol.L^{-1}$	5×10^{-3}	8.2×10^{-3}	17×10^{-3}	30×10^{-3}
$v_0 / mol.L^{-1}.s^{-1}$	3.6×10^{-7}	9.6×10^{-7}	41×10^{-7}	130×10^{-7}
$\log v_0$	-6.4437	-6.0177	-5.387	-4.886
$\log J_0$	-2.30	-2.086	-1.7695	-1.523

$$\log v_0 = \log K + \alpha \log [J]_0$$



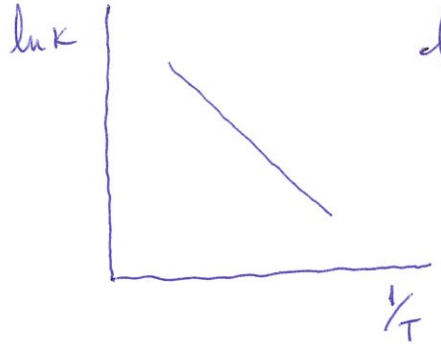
$\log v_0 = 2.005 \log J_0 - 1.8429$ c/ $R^2 \approx 1$

$\alpha = 2$ (2ª ordem) ; $K = 10^{-1.84} \sim 1.44\times10^{-2}$ $mol^{-1}.L.s^{-1}$

(2)

T/K	300	350	400	450	500
$K / mol^{-1}.L.s^{-1}$	7.9×10^{6}	3.7×10^{7}	7.9×10^{7}	1.7×10^{8}	3.2×10^{8}
$1/T\ (K^{-1})$	3.33×10^{-3}	2.86×10^{-3}	2.5×10^{-3}	2.22×10^{-3}	2×10^{-3}
$\ln K$	15.88	17.43	18.18	18.95	19.58

$$\ln K = \ln A - \frac{E_a}{RT}$$



$\ln K = 25.015 - 2715.6 \times \frac{1}{T}$

$R^2 \approx 0.99$

logo $\ln A = 25$ ou $A \approx 7.34\times10^{10}\ M^{-1}s^{-1}$

$-\frac{E_a}{R} = -2715.6$

$E_a \approx 22.6\ kJ/mol$

(3) $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$ logo $\frac{1}{0.056} = \frac{1}{0.22} + k \times 1.22 \times 10^4$

$k = \frac{13.31}{1.22 \times 10^4} \approx 1.1 \times 10^{-3}\ mol^{-1} \cdot L \cdot s^{-1}$

(4) $2A \rightarrow B$

t/min	0	10	20	30	40	∞
$[B]/mol \cdot L^{-1}$	0	0.089	0.153	0.200	0.230	0.312
$[A]_0$	0.624	0.446	0.318	0.224	0.164	0

$v = k[A] = -\frac{1}{2}\frac{d[A]}{dt} = \frac{d[B]}{dt}$

$\frac{d[A]}{dt} = -2k[A]$

$\ln[A] - \ln[A]_0 = -2kt$

$\ln[A] = -0.4763 - 0.0335t$ logo $k = 1.675 \times 10^{-2}\ min^{-1} \times \frac{1}{60}$

$k = 2.3 \times 10^{-4}\ s^{-1}$

(5) $K_1 = A \exp\left(-\frac{E_a}{RT_1}\right)$ e $K_2 = 1.1 \times K_1$

$\frac{K_2}{K_1} = \frac{1.1\,K_1}{K_1} \exp\left(-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$

$\ln 1.1 = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\frac{1}{T_2} - \frac{1}{T_1} \approx -9 \times 10^{-6}$ e $\frac{1}{T_1} = 0.0335$

$T_2 \approx 298.6\ K$

(6)

t/min	0	30	60	90	120	150	180
$[\,]$	8.7×10^{-3}	6.52	4.89	3.67	2.75	2.06	1.55

a) $\ln[A] = \ln[A]_0 - kt$

$\ln[A] = -4.7454 - 9.6\times10^{-3}t$

$R^2 \approx 1$, logo $k \approx 9.6\times10^{-3}\ min^{-1}$ (1ª ordem)

b) Para 1ª ordem o tempo de meia vida é $t_{1/2} = \frac{\ln 2}{k}$

$t_{1/2} \approx 72$ min o que confere com o valor interpolado da tabela

(7)

$K_1 = A\exp\left(-\frac{Ea}{R}\times\frac{1}{293}\right)$

$K_2 = 2K_1 = A\exp\left(-\frac{Ea}{R}\times\frac{1}{303}\right)$

$\frac{K_2}{K_1} = \frac{2K_1}{K_1} = \exp\left(-\frac{Ea}{R}\times\left(\frac{1}{303}-\frac{1}{293}\right)\right)$

$\ln 2 = -\frac{Ea}{R}\times(-1.13\times10^{-4})$

$Ea = \frac{\ln 2 \times R}{1.13\times10^{-4}} \approx 51\ kJ/mol$

(8) $$v = \frac{d[C_6H_5N_2^+]}{dt} = k_3[ONBr][C_6H_5NH_2]$$

$$\frac{d[ONBr]}{dt} = 0 = k_2[H_2NO_2^+][Br^-] - k_3[ONBr][C_6H_5NH_2]$$

$$\frac{d[H_2NO_2^+]}{dt} = 0 = k_1[H^+][HNO_2] - k_1'[H_2NO_2^+] - k_2[H_2NO_2^+][Br^-]$$

estado estacionário!

$$[ONBr] = \frac{k_2[H_2NO_2^+][Br^-]}{k_3[C_6H_5NH_2]} \quad e \quad [H_2NO_2^+] = \frac{k_1[H^+][HNO_2]}{k_1' + k_2[Br^-]}$$

$$\text{logo } [ONBr] = \frac{k_2 k_1[H^+][HNO_2][Br^-]}{k_3[C_6H_5NH_2](k_1' + k_2[Br^-])}$$

$$v = k_3[ONBr][C_6H_5NH_2] = \frac{k_3 k_2 k_1}{k_3} \times \frac{[H^+][Br^-][HNO_2][C_6H_5NH_2]}{[C_6H_5NH_2](k_1' + k_2[Br^-])}$$

$$0 = \frac{k_2 k_1[H^+][Br^-][HNO_2]}{k_1' + \underbrace{k_2[Br^-]}_{\sim 0}}$$ Passo lento!

$$\text{logo } v = k[H^+][Br^-][HNO_2] \quad c/ \quad k = \frac{k_2 k_1}{k_1'}$$

(9)

t/min	0	5	10	15
[A]	1.5×10^{-3}	1.24×10^{-3}	1×10^{-3}	8.3×10^{-4}
1/[A]	6.67×10^{2}	8.06×10^{2}	1×10^{3}	1.2×10^{3}

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

2ª ordem

$y = 648.3 + 39.16\,x$ e $R^2 \approx 0.99$

$k = 39.16\ mol^{-1}.L.min^{-1} \times \frac{1\ min}{60\ s}$

$k \approx 0.65\ mol^{-1}.L.s^{-1}$

(10)

$$2O_3 \rightarrow 3O_2 \qquad v = k_b[O_3][O]$$

$$\frac{d[O]}{dt} = 0 = k_a[O_3] - k_a'[O_2][O] - k_b[O][O_3]$$

$$[O] = \frac{k_a[O_3]}{k_a'[O_2] + k_b[O_3]}$$

$$v = \frac{k_a k_b [O_3]^2}{k_a'[O_2] + k_b[O_3]}$$

$k_a'[O_2] \sim 0$

$$v = k_c[O_3]^2$$