# Problems Ch.2

**2.1.** A reaction has the stoichiometric equation A + B = 2R. What is the order of reaction?

solution:

We require experimental kinetics data to answer this question, because order of reaction need not to match the stoichiometry, most oftenly it doesn't.

If this reaction is elementary, the order of reaction is 2. And rate expression is,

$$-r_A = K\, C_A\, C_B$$

**2.2.** Given the reaction $2NO_2 + \frac{1}{2} O_2 = N_2O_5$, what is the relation between the rates of formation and disappearance of the three reaction components?

solution:

$2NO_2 + \frac{1}{2} O_2 \rightarrow N_2O_5$ what rates of reaction and relation between them?

$$-r_{NO_2} = \frac{1}{V}\frac{dN_{NO_2}}{dt}, \quad -r_{O_2} = \frac{1}{V}\frac{dN_{O_2}}{dt}$$

$$r_{N_2O_5} = \frac{1}{V}\frac{dN_{N_2O_5}}{dt}$$

$$\frac{-rNO_2}{2} = \frac{-rO_2}{1/2} = \frac{-rN_2O_5}{1}$$

**2.3.** A reaction with stoichiometric equation $\frac{1}{2}$ A + B = R + $\frac{1}{2}$ S has the following rate expression $-r_A = 2C_A^{0.5}C_B$

What is the rate expression for this reaction if the stoichiometric equation is written as A + 2B = 2R + S?

solution:

It does not affect how we write the stoichiometry equation. The rate of reaction remains unchanged,

$$-r_A = 2\, C_A^{0.5}\, C_B$$

**2.5.** For the complex reaction with stoichiometry A + 3B → 2R + S and with second-order rate expression

$$-r_A = k_1[A][B]$$

are the reaction rates related as follows: $r_A = r_B = r_R$? If the rates are not so related, then how are they related? Please account for the signs, + or −.

Homework…

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**2.6.** A certain reaction has a rate given by

$$-r_A = 0.005C_A^2, \qquad \text{mol/cm}^3 \cdot \text{min}$$

If the concentration is to be expressed in mol/liter and time in hours, what would be the value and units of the rate constant?

solution:

Given rate expression: $r_A = 0.005C_A^2 \; \frac{mol}{cm^3.min}$

Change the unit $-r_{A} = 0.005C_A^2 \frac{mol}{(10^{-3})lit * \frac{1}{60}hr}$

$$-r_A = 300C_A^2 \quad \frac{mol}{lit.hr}$$

Value of rate constant =300

unit=?

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**2.7.** For a gas reaction at 400 K the rate is reported as

$$-\frac{dp_A}{dt} = 3.66 p_A^2, \qquad \text{atm/hr}$$

**(a)** What are the units of the rate constant?
**(b)** What is the value of the rate constant for this reaction if the rate equation is expressed as

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = kC_A^2, \qquad \text{mol/m}^3\cdot\text{s}$$

solution:

2.7 a) We are given $-\frac{dp_A}{dt} = k_p p_A^2$ (where $-\frac{dp_A}{dt}$ is in atm/hr, $k_p$ = 3.66, and $p_A^2$ is in $(atm)^2$)

Balancing dimensions we find $k_p = 3.66\,(atm)^{-1}(hr)^{-1}$ ⟵ a)

b) For an ideal gas $p_A V = n_A RT$ or $p_A = C_A RT$

thus $-\frac{dp_A}{dt} = 3.66\, p_A^2$ … becomes … $-\frac{d(C_A RT)}{dt} = 3.66\,(C_A RT)^2$

or $-\frac{dC_A}{dt} = \underbrace{\left[3.66\,(atm)^{-1} hr^{-1}\right] RT}_{\text{new rate constant} = k'} C_A^2$

where $k' = 3.66 \frac{1}{atm \cdot hr} \cdot \frac{(1\,atm)(22.4\,l)}{(1\,mol)(273°K)} \cdot (400°K) = 120\,(hr)^{-1}(mol/l)^{-1}$ ⟵ b)

- R = 0.082 L x atm x $K^{-1}$ x $mol^{-1}$
- R = 62.36 L x torr x $K^{-1}$ x $mol^{-1}$
- R = 62.36 L x mmHg x $K^{-1}$ x $mol^{-1}$
- R = 8.315 L x kPa x $K^{-1}$ x $mol^{-1}$

**2.9.** The pyrolysis of ethane proceeds with an activation energy of about 300 kJ/mol. How much faster is the decomposition at 650°C than at 500°C?

solution:

Activation energy = 300 $\frac{KJ}{mol}$

$T_1 = 650\ C^\circ = 923\ K$

$T_2 = 500\ C^\circ = 773\ K$

How much the rate in $T_1$ faster than rate in $T_2$ =?

$$\frac{-r_{T_1}}{-r_{T_2}} = \frac{e^{-\frac{E}{RT_1}}}{e^{-\frac{E}{RT_2}}} \Rightarrow \frac{-r_{T_1}}{-r_{T_2}} = e^{-\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$\frac{-r_{T_1}}{-r_{T_2}} = e^{-\frac{300000\ J/mol}{8.314\ J/mol.K} * \left[\frac{1}{923} - \frac{1}{773}\right]}$$

= 1953 Time faster

$$\ln\frac{r_2}{r_1} = \ln\frac{k_2}{k_1} = \frac{\mathbf{E}}{\mathbf{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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**2.10.** A 1100-K *n*-nonane thermally cracks (breaks down into smaller molecules) 20 times as rapidly as at 1000 K. Find the activation energy for this decomposition.

Homework…

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**2.12.** The maximum allowable temperature for a reactor is 800 K. At present our operating set point is 780 K, the 20-K margin of safety to account for fluctuating feed, sluggish controls, etc. Now, with a more sophisticated control system we would be able to raise our set point to 792 K with the same margin of safety that we now have. By how much can the reaction rate, hence, production rate, be raised by this change if the reaction taking place in the reactor has an activation energy of 175 kJ/mol?

Homework…

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**2.11.** In the mid-nineteenth century the entomologist Henri Fabre noted that French ants (garden variety) busily bustled about their business on hot days but were rather sluggish on cool days. Checking his results with Oregon ants, I find

| Running speed, m/hr | 150 | 160 | 230 | 295 | 370 |
|---|---|---|---|---|---|
| Temperature, °C | 13 | 16 | 22 | 24 | 28 |

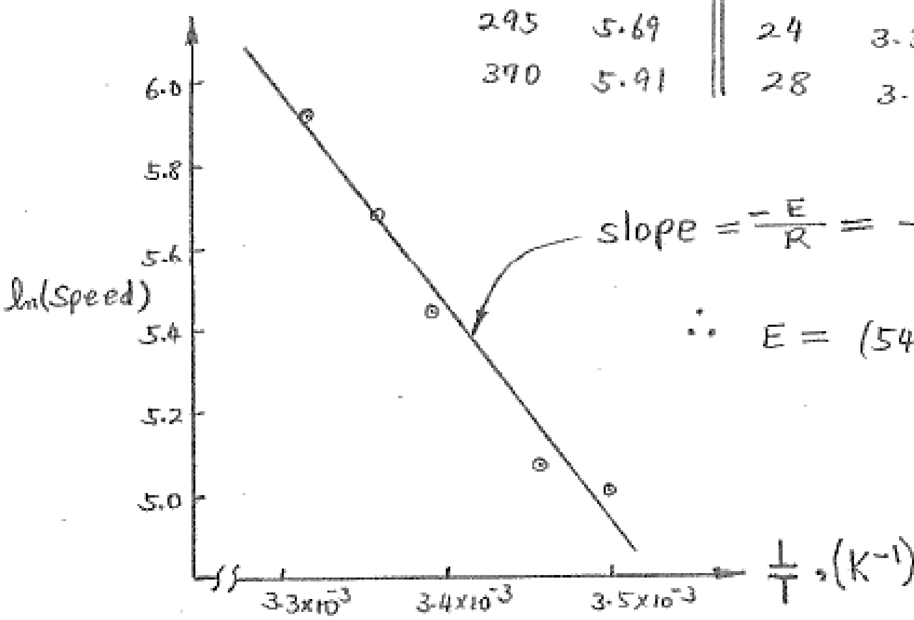
What activation energy represents this change in bustliness?

solution:

$$\ln\frac{r_2}{r_1} = \ln\frac{k_2}{k_1} = \frac{\mathbf{E}}{\mathbf{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

2.11

| Speed | ln S | T | $\left(\frac{1}{T}\right)\times 10^3$ |
|---|---|---|---|
| 150 | 5.01 | 13 | 3.4965 |
| 160 | 5.07 | 16 | 3.4602 |
| 230 | 5.44 | 22 | 3.3898 |
| 295 | 5.69 | 24 | 3.3670 |
| 370 | 5.91 | 28 | 3.3220 |




slope $= \frac{-E}{R} = -5420$

$\therefore$ $E = (5420)(8.314) = 45062\ J$

$\cong 45\ kJ$

**2.15.** On doubling the concentration of reactant, the rate of reaction triples. Find the reaction order.

solution:

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$$-r_A = k C_A^n \qquad C_{A2} = 2 C_{A1} \qquad r_2 = 3 r_1$$

$$\frac{r_2}{r_1} = \frac{k C_{A2}^n}{k C_{A1}^n} \Rightarrow \frac{3 r_1}{r_1} = \left(\frac{2 C_{A1}}{C_{A1}}\right)^n$$

$$3 = 2^n \Rightarrow (2)^{1.585} = 2^n$$

$$\Rightarrow n = 1.585$$

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**2.16.**

| | | | |
|---|---|---|---|
| $C_A$ | 4 | 1 | 1 |
| $C_B$ | 1 | 1 | 8 |
| $-r_A$ | 2 | 1 | 4 |

**2.17.**

| | | | |
|---|---|---|---|
| $C_A$ | 2 | 2 | 3 |
| $C_B$ | 125 | 64 | 64 |
| $-r_A$ | 50 | 32 | 48 |

For the stoichiometry A + B → (products) find the reaction orders with respect to A and B.

solution:

$$-r_A = k C_A^n C_B^m$$

$$50 = k (2)^n (125)^m \quad \text{---} (1)$$

$$32 = k (2)^n (64)^m \quad \text{---} (2)$$

$$48 = k (3)^n (64)^m \quad \text{---} (3)$$

divided (1) an (2)

$$\frac{50}{32} = \frac{k (2)^n}{k (2)^n} * \frac{(125)^m}{(64)^m}$$

$$\therefore \frac{25}{16} = \left(\frac{25^{1.5}}{16^{1.5}}\right)^m \Rightarrow \left(\frac{25}{16}\right)^1 = \left(\frac{25}{16}\right)^{1.5 m}$$

$$\therefore m = \frac{1}{1.5} = 0.6$$

divided (2) an (3)

$$\frac{32}{48} = \frac{k}{k} * \frac{(2)^n}{(3)^n} * \frac{(64)^m}{(64)^m} \Rightarrow \left(\frac{2}{3}\right)^1 = \left(\frac{2}{3}\right)^n \Rightarrow \therefore n = 1$$

$$\therefore -r_A = k C_A^1 C_B^{0.6}$$