School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Durban

General Principles of Chemistry – CHEM110

Tutorial 11 – 9th May and 11th May 2012

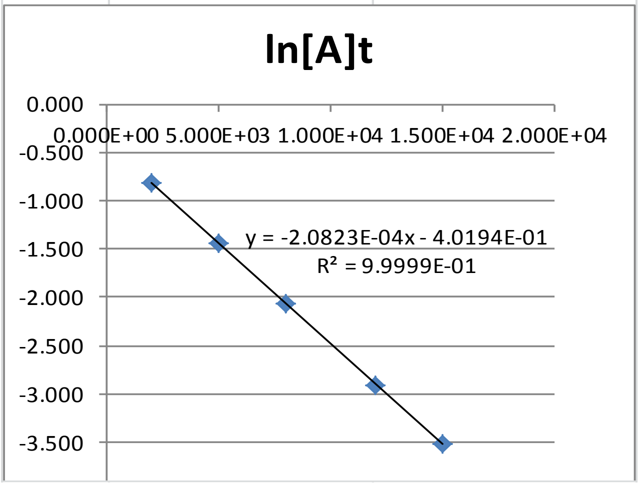
1. From the following data for the first-order gas-phase isomerisation of CH_3NC at 215 °C, calculate the first-order rate constant for the reaction.

Time (s)	Pressure CH_3NC (kPa)
0	0.661
2000	0.441
5000	0.237
8000	0.126
12000	0.0549
15000	0.0295

Solution

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

Time (s)	Pressure CH_3NC (kPa)	ln[A]t
0	0.661	-0.414001439
2000	0.441	-0.818710404
5000	0.237	-1.439695138
8000	0.126	-2.071473372
12000	0.0549	-2.90224193
15000	0.0295	-3.523365016



Note: If they use a table to calculate the answer they will get it wrong, they must use a graph

a) From the above data for the first-order gas-phase isomerization of of CH_3NC at 215 °C, calculate the half-life for the reaction.

$\ln 0.5 = -kt_{1/2}$

or

$$\frac{\ln 2}{k} = t_{1/2} \; or \; \frac{0.693}{k} = t_{1/2}$$

$$\frac{\ln 2}{2.0823 \times 10^{-4}} = 3328.757$$

Answer = 3.33×10^3 s

2. Understanding the high-temperature behaviour of nitrogen oxides is essential for controlling pollution generated in automobile engines. The decomposition of nitric oxide (NO) to N_2 and O_2 is second order with a rate constant of 0.0796 M^{-1} s^{-1} at 737 °C and 0.0815 M^{-1} s^{-1} at 947 °C.

a) Calculate the activation energy for the reaction.

$k = A\, e^{-Ea/RT}$

Only way to work out the solution is using a graphical method because we are not given the frequency factor (A)

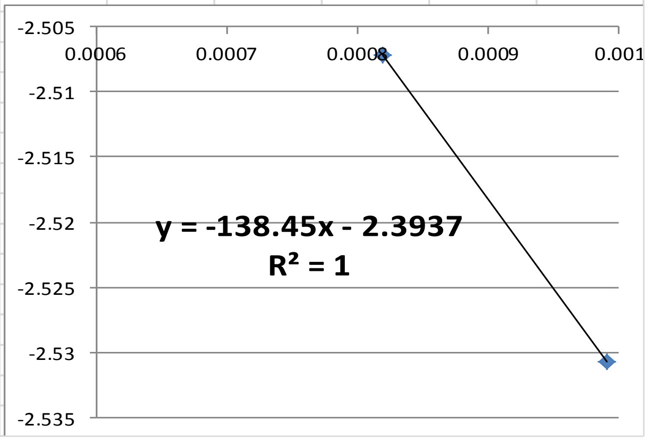
$\ln k = -E_a / RT + \ln A$

$$\frac{E_a}{R} = 138.45$$

$$E_a = 138.45K \times 8.314\ (JK^{-1}mol^{-1}) = 1151.0733$$

Ans = 1.15 kJ/mol

K	ln K	T (°C)	T (K)	1/T
0.0796	-2.53074	737	1010.15	0.00099
0.0815	-2.50715	947	1220.15	0.00082



3. Consider the gas-phase reaction between nitric oxide and bromine at 273 °C.

4. 2 NO(g) + Br_2(g) → 2 NOBr(g)

The following data for the initial rate of appearance of NOBr were obtained:

Experiment	[NO] (M)	[Br_2] (M)	Initial Rate (M/s)
1	0.10	0.20	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

a) Determine the rate law.

Using exp 1 &2:

$$\frac{150}{24} = \frac{(0.25)^n}{(0.1)^n}$$

$$6.25 = (2.5)^n$$

Students will only see 0, 1 & 2 order reactions, so process of elimination…

Thus n = 2 (with respect to [NO])

$$\frac{60}{24} = \frac{(0.50)^n}{(0.2)^n}$$

$$2.5 = (2.5)^n$$

Thus n = 1 (with respect to [Br_2])

Answer: The rate law is:

Rate = k $[NO]^2[Br_2]$

b) Calculate the average value of the rate constant for the appearance of NOBr from the four data sets.

Experiment	[NO] (M)	[Br_2] (M)	Initial Rate (M/s)	K
1	0.10	0.20	24	12000
2	0.25	0.20	150	12000
3	0.10	0.50	60	12000
4	0.35	0.50	735	12000

Answer = 12000 M^{-2} s^{-1}

c) How is the rate of appearance of NOBr related to the rate of disappearance of Br_2?

i) The rate of appearance of NOBr is half the rate of disappearance of Br_2

ii) The rate of disappearance of Br_2 is half the rate of appearance of NOBr

iii) The rate of disappearance of Br_2 is equal to the rate of appearance of NOBr

iv) All three statements are correct

Answer = ii