SCES 2230: KIMIA FIZIK 2 (KINETIK)

TAHAP 2 SEMESTER KEDUA SESI 2006/2007

Exam NOV 2006

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4. Calculate the mean speed and most probable speed for oxygen molecule. If the collision taken place in every 0.13 second, given that diameter of molecule is 370 x 10^{-12} m, the collisional frequency 7.2 x 10^{9} s^{-1} $molecule^{-1}$, Calculate the number density of oxygen at 25 ^{o}C.

$$Z=\sqrt{2}\,\bar{v}\sigma\left(\frac{N}{V}\right);\; c_{ave}=\sqrt{\frac{8RT}{\pi M}}=444ms^{-1}$$

$$c_{mp}=\sqrt{\frac{2RT}{M}}=393.5ms^{-1}$$

NOTE Give full mark if student is using above values

$$7.2\times10^{9}=\sqrt{2}\times444\times\pi\left(370\times10^{-12}\right)^{2}\left(\frac{N}{V}\right)$$

$$\therefore\left(\frac{N}{V}\right)=\frac{7.2\times10^{9}}{\sqrt{2}\times444\times\pi\times\left(370\times10^{-12}\right)^{2}}=3\times10^{25}m^{-3}$$

5. Methyl acetate undergoes hydrolysis in an acid aqueous solution. The following data were obtained by taking aliquots of equal volume at intervals and titrated with standardized NaOH. Calculate the first order rate constant.

Time, s	339	1242	2745	4546	∞
Volume, mL	26.34	27.80	29.70	31.81	39.81

Else use this formula: $\ln\frac{(A-A_\infty)}{(A_0-A_\infty)}=-kt$

Concentration of methylacetate remaining is proportional to,
$[\text{Methylacetate}]_t = (39.81 - V_t)$.

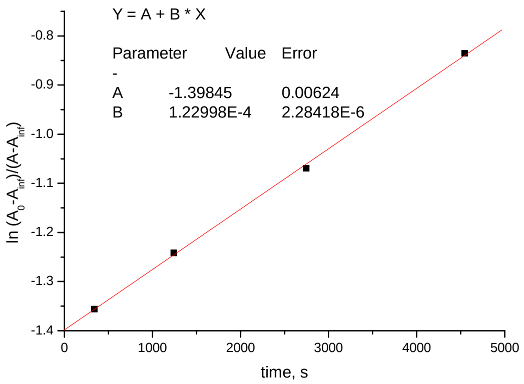
$\ln\frac{(A_0-A_\infty)}{(A-A_\infty)}=kt$, can derive into solving the problem such that,

ln (A_0 - A_∞) – ln (A – A_∞) = kt. Therefore can plot – ln (A – A_∞) versus t.

or $\ln\frac{(A_0-A_\infty)}{(A-A_\infty)}$ versus t, k is the slope.

Time, s	Volume, ml	ln(A0-A∞)/(A-A∞)
339	26.34	-1.35631
1242	27.8	-1.24159
2745	29.7	-1.06937
4546	31.81	-0.83529

Ans: k = 1.23×10^{-4} s^{-1} OR 1.32×10^{-4} s^{-1}.



6. Hydrogen peroxide reacts with thiosulfate ion as follows:

$$H_2O_2 + 2S2O_3^{2-} + 2H^+ \rightarrow 2H_2O + S_2O_6^{2-}$$

The initial concentrations:

$[H_2O_2]$= 0.036 mol dm^{-3};

$[S_2O_3^{2-}]$ = 0.0204 mol dm^{-3}.

The following data were obtained at 25 ^{o}C and pH 5.

Time, min	16	36	43	52
$[S_2O_3^{2-}]$, 10^{-3} mol dm^{-3}	10.30	5.18	4.16	3.13

Determine the order of reaction and the rate constant of the above reaction.

$$\ln\frac{[A]_0}{[A]} = kt$$

Second order reaction test: $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$

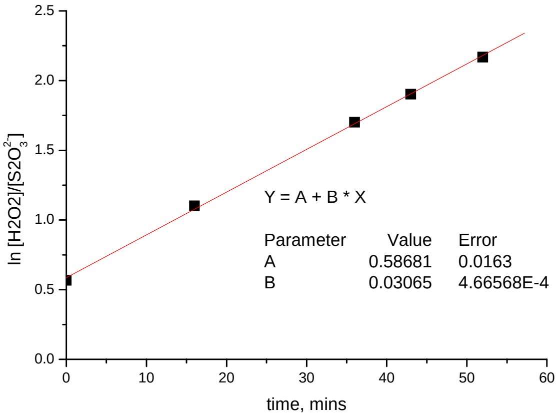
aA + bB → product, $\ln\frac{[A][B]_0}{[A]_0[B]} = kt\left(b[A]_0 - a[B]_0\right)$

Ans:By solving individually to determine the overall order of reaction.

1 mol H_2O_2 reacts with 2 mol of $S_2O_3^{2-}$, thus $[H_2O_2]$ at 16 second is,

$36.0 - \frac{20.40 - 10.3}{2} = 30.95$ mmol dm^{-3}. (Test first order). The reaction is first order with respect to $[H_2O_2]$ and $[S_2O_3^{2-}]$, the overall is second order.

t, min	0	16	36	43	52
$[S_2O_3^{2-}]$, mol dm^{-3}	0.0204	0.0103	0.00518	0.00416	0.00313
$[H_2O_2]$, mol dm^{-3}	0.036	0.03095	0.02839	0.02788	0.027365
$\ln\left(\frac{[H_2O_2]}{[S_2O_3^{2-}]}\right)$	0.568	1.1002	1.701	1.902	2.168



Thus slope of the graph is 0.031 min^{-1}.

Hence, slope = $k(2[H_2O_2] - 1[S_2O_3^{2-}])$

The rate constant, $k = \dfrac{0.031}{2 \times 0.0368 - 1 \times 0.0204}$ = 0.50 L mol^{-1} min^{-1}.

TUTORIAL: SCES 2230 Kimia Fizik 2.

1. Calculate the means speed and root-mean square speed of oxygen at 25 ^{o}C. Given gas constant = 8.314 J K mol^{-1}.
2. Use the means speed from question 1, calculate,
   Maxwell-boltzmann distribution of molecular velocity of O_2.
   Maxwellian probable distribution of speed.
   Probability density of oxygen.

3. With suitable diagram, describe
   collision diameter.
   Collision cross-section.

4. The decomposition of urea in 0.1 M HCl occurs according to reaction

$$NH_2CONH_2 + 2H_2O \longrightarrow 2NH_4^{+} + CO_3^{2-}$$

The first order rate constant for this reaction was measured as a function of temperature, with the following results:

Temperature, ^{o}C	k, mins^{-1}
61.0	0.713×10^{-5}
71.2	2.77×10^{-5}

Calculate the activation energy, E_a, and the pre-exponential coefficient factor, A for this reaction.

5. Kira halaju paling mungkin, halaju purata dan min ganda-dua halaju bagi oksigen pada 25 ^{o}C.

6. Kira ketumpatan yang mungkin bagi taburan halaju Maxwell gas oksigen pada 300 K pada Setiap 0 ms^{-1}, 300 ms^{-1} dan 600 ms^{-1}.

7. Kira halaju purata dan bagi methane, ethana dan propana pada 25 ^oC. Beri pandangan anda terhadap populasi taburan halaju tersebut.

8. Perkembangan tindakbalas didalam larutan berair telah di pantau dengan mengunakan alatan UV-ternampak spektofotometer seperti berikut,

Masa (s)	0	54	171	390	720	1010	1190
Serapan	1.67	1.51	1.24	0.847	0.478	0.301	0.216

Kira pemalar tidakbalas.

9. Kira halaju purata dan bagi methana pada 20, 30 dan 40 ^oC. Beri pandangan anda terhadap populasi taburan halaju tersebut.

10. Semasa kajian tindakbalas penguraian azomethana pada suhu 3003 oC dan tekanan 2.18×10^4 Pa, kepekatan azomathana dicatakan pada masa-masa tertentu seperti berikut,

Masa (minit)	0	30	60	90	120	150	180
[azomethana], $\times 10^{-3}$ mol dm^{-3}	8.70	6.52	4.89	3.67	2.75	2.06	1.55

Tentukan pemalar tidakbalas k dan $t_{½}$ seterusnya nyatakan tertib kadar tindakbalas.

11. Pemalar kadar tindakbalas untuk tertib kadar pertama penguraian satu larutan bahan organic telah diukur pada suhu-suhu yang berbeza,

K (s^{-1})	4.92×10^{-3}	21.6×10^{-3}	95.0×10^{-3}	0.326	1.15
T (^oC)	5.0	15	25	35	45

Kira tenaga pengaktifan penguraian tersebut.

12. Kira halaju purata dan bagi methana pada 20, 30 dan 40 ^oC. Beri pandangan anda terhadap populasi taburan halaju tersebut.

13. Sekiranya seorang pelajar mendapati pemguraian H_2O_2 adalah seperti berikut, tunjukkan bagaimana beliau menentukan tertib kadar tindakbalas dan apakah pemalar kadar tindakbalas bagi penguraian hydrogen peroksida.

[H_2O_2], mol dm^{-3}	*t*, min
0.300	0
0.22	1
0.107	5
0.065	10
0.047	15
0.037	20

14. Kira halaju purata dan seterusnya tentukan taburan halaju molekul Maxwell-boltzmann bagi molekul oksigen pada 20 °C.

15. Teknik pembauran gas adalah diantara cara pemisah isotop-isotop uranium. Sekiranya jisim molar $^{235}UF_6$ = 349 dan $^{235}UF_6$ = 352, kira v_{rms}. R = 8.314 J K mol^{-1}.

16. Pemalar kadar tindakbalas untuk tertib kadar pertama penguraian satu larutan bahan organic telah diukur pada suhu-suhu yang berbeza,

K (s^{-1})	4.92×10^{-3}	21.6×10^{-3}	95.0×10^{-3}	0.326	1.15

T (^oC)	5.0	15	25	35	45

Kira tenaga pengaktifan penguraian tersebut.

17. An unstable metabolite decomposed very rapidly in aqueous solution at pH 7. At all temperature in the range 15 to 37 ^oC, the decomposition proceeded with first order kinetics and the following values were obtained for its 1st order rate constant.

Temperature/^oC	*Rate constant, k/s^{-1}*
15	2.51×10^{-4}
20	4.57×10^{-4}
25	8.22×10^{-4}
30	1.445×10^{-3}
37	3.09×10^{-3}

Determine from this findings the energy of activation of the decomposition.

18. Berikut adalah nilai keseluruhan pemalar kadar tindakbalas menghad (k') yang diperolehi daripada penguraian Dimetil eter (DME),

[DME], mol dm^{-3}	0.00120	0.00189	0.00355	0.00542	0.00818
K', s^{-1}	2.48×10^{-4}	3.26×10^{-4}	4.61×10^{-4}	5.54×10^{-4}	6.29×10^{-4}

Guna keputusan diatas bagi membuktikan kesahihan teori Lindmann dan tentukan nilai menghad k' dalam keadaan tekanan tinggi.

19. Didalam ujikaji makmal terhadap penguraian metil asetat kepada asid asetik didalam larutan berasid pada suhu 30 ^oC, penentuan hasil tindakbalas dilakukan dengan menitratkan 5 ml contoh larutan pada masa-masa tertentu dengan 0.1 mol dm^{-3} NaOH didalam keadaan sesejuk ais. Berikut adalah keputusan ujikaji,

Masa, minit	5	10	20	30	45	60	80
Isipadu, ml	8.40	11.00	17.25	19.90	25.00	28.10	31.00

Selepas 80 minit larutan tersebut dipanaskan dan didapati 35.5 ml larutan 0.1 mol dm^{-3} NaOH diperlukan bagi penitratan 5 ml contoh larutan.

Tuliskan persamaan tindakbalas bagi ujikaji diatas. Seterusnya, dengan bantuan graf tentukan pemalar kadar tindakbalas dan separuh hayat. Nyatakan mengapa larutan tersebut perlu dipanaskan?

MODEL ANSWERS:

December 2006-03-23 Dr Misni Misran

1. Calculate the means speed and root-mean square speed and mean speed of oxygen at 25 ^oC. Given gas constant = 8.314 J K mol^{-1}.

2. Use the means speed from question 1, calculate,
   a. One dimensional Maxwell-boltzmann distribution of molecular velocity of O_2.

3. With suitable diagram, describe
   a. collision diameter.
   b. Collision cross-section.

4. Given that $\therefore \overline{E}_{trans} = \frac{3}{2}kT$, show that $v_{rms} = \sqrt{\frac{3RT}{M}}$

5. Calculate most probable speed for oxygen molecule at 298K. Given the gas constant is 8.314 JK^{-1} mol^{-1} and O = 16 g mol^{-1}. NOTE: your answer MUST be in SI unit.

6. If the oxygen gas molecule collides with another every 0.13 nanoseconds, given the diameter of oxygen molecule 370 x 10^{-12} m, the collision frequency is 7.2 x 10^{9} collisions per second per molecule, calculate the number density of oxygen at 298K. Use v_{mp} in question 2.

Answer to Class test (22/03/2006)

Q1. The Average (means) speed $\bar{c}$ is defined as $\bar{c} = \dfrac{c_1 + c_2 + ... + c_N}{N}$

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 298}{0.032\pi}} = 444.0ms^{-1}$$

Most probable speed,

$$c_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \times 298}{0.032}} = 393.5ms^{-1}.$$

Root-means-square-speed = $c_{rms} = \sqrt{\dfrac{3RT}{M}} = \sqrt{\dfrac{3 \times 8.314 \times 298}{0.032}} = 481.9ms^{-1}$

Q2. Maxwell boltzmann distribution of molecular speed,

O_2= 32×10^{-3} kg mol^{-1}. T=25 ^{o}C=273+25=298 K,

R=8.314 J K mol^{-1}. k=1.38×10^{-23}. kt=4.11×10^{-21} J.

The mass of one oxygen molecule = 0.032/6.022×10^{23}=5.31×10^{-26} kg.

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{\left(-mv_x^2 / 2kT\right)} = \left(\frac{5.31 \times 10^{-26}}{2\pi \times 4.11 \times 10^{-21}}\right)^{1/2} e^{\left(-5.31\times10^{-26}\times(293.5)^2 / 8.22\times10^{-21}\right)}$$

f(v_x) = $(2.056\text{x}10^{-6})^{0.5}$ $e^{(-0.5546)}$ =($1.434\text{x}10^{-3}$)(0.57323)= $8.235\text{x}10^{-4}$ s m^{-1}.

The decomposition of urea in 0.1 M HCl occurs according to reaction

$$NH_2CONH_2 + 2H_2O \longrightarrow 2NH_4^+ + CO_3^{2-}$$

The first order rate constant for this reaction was measured as a function of temperature, with the following results:

Temperature, ^{o}C	k, mins^{-1}
61.0	0.713 × 10^{-5}
71.2	2.77 × 10^{-5}

Calculate the activation energy, E_a, and the pre-exponential coefficient factor, A for this reaction.

Since, $k = Ae^{-E_a/RT} \Rightarrow \ln k = \ln A - \dfrac{E_a}{RT}$,

1/*T*, K^{-1}	ln *k*,
2.992 × 10^{-3}	-11.85
2.904 × 10^{-3}	2-10.49

WE can write, $\ln k_2 - \ln k_1 = -\dfrac{E_a}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

Therefore we obtain, $E_a = -\dfrac{R.(\ln k_2 - \ln k_1)}{{}^{1}\!/_{T_2} - {}^{1}\!/_{T_1}}$

$$E_a = -\frac{(8.314JK^{-1}mol^{-1}).(-10.49 + 11.85)}{(2.904 - 2.992) \times 10^{-3}K^{-1}} = 128.5kJmol^{-1}$$

Rearrange the equation to obtain ln *A*, $\ln A = \ln k + \dfrac{E_a}{RT}$

$$\ln A = -10.49 + \frac{128.5}{0.008314 \times 344.4} = -10.49 + 44.84 = 34.35$$

therefore, A = 8.28 × 10^{14} min^{-1} = 1.38 × 10^{13} s^{-1}.

Question: An unstable metabolite decomposed very rapidly in aqueous solution at pH 7. At all temperature in the range 15 to 37 ^{o}C, the decomposition proceeded with first order kinetics and the following values were obtained for its 1st order rate constant.

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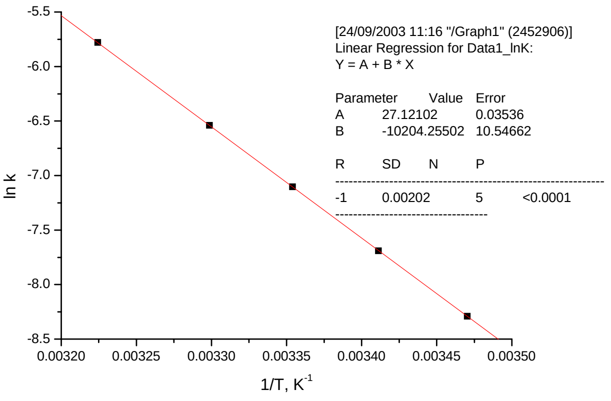
20	4.57×10^{-4}
25	8.22×10^{-4}
30	1.445×10^{-3}
37	3.09×10^{-3}

Determine from this findings the energy of activation of the decomposition.

Answer: $k = Ae^{-E_a/RT} \Rightarrow \ln k = \ln A - \dfrac{E_a}{RT}$

T, ^{o}C	k, s^{-1}	T, K	1/T, K^{-1}	**ln k**
15	2.51E-4	288.15	0.00347	-8.29006
20	4.57E-4	293.15	0.00341	-7.69083
25	8.22E-4	298.15	0.00335	-7.10377
30	0.00145	303.15	0.0033	-6.53965
37	0.00309	310.15	0.00322	-5.77958



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[24/09/2003 11:16 "/Graph1" (2452906)]
Linear Regression for Data1_lnK:
Y = A + B * X

Parameter       Value           Error
A               27.12102        0.03536
B               -10204.25502    10.54662

R       SD          N       P
------------------------------------------------------------
-1      0.00202     5       <0.0001
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$slope = -\frac{E_a}{R} =$ -10204.255, Therefore E_a = (10204.255×8.314) = 84.84 kJ mol^{-1}.