



CHAPTER 0

RATE OF REACTION

0.1 A is the reactant of two different reactions. Plot the data below in order to compare the rate of the two reaction.

	Reaction I	Reaction II
Time, s	[A] (M)	[A] (M)
0	100	100
1	7×10^{-1}	36.78
2	4×10^{-3}	13.53
3	3×10^{-5}	4.90
4	2×10^{-7}	1.80

0.2 Use the data below to identify reactants and products in a reaction.

Time, s	[A] (M)	[B] (M)
0	0	3
1	2×10^{-2}	2.4
2	3×10^{-2}	2.0
3	6×10^{-2}	1.64
4	8×10^{-2}	1.34

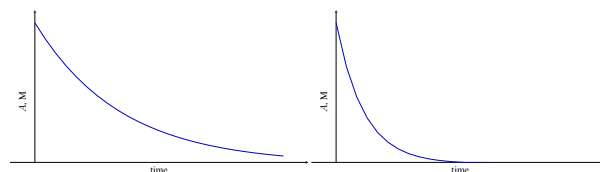
0.3 Use the data below to identify reactants and products in a reaction.

Time, s	[A] (M)	[B] (M)
0	2	0
1	1.996	4×10^{-3}
2	1.992	8×10^{-3}
3	1.988	1.2×10^{-2}
4	1.984	1.6×10^{-2}

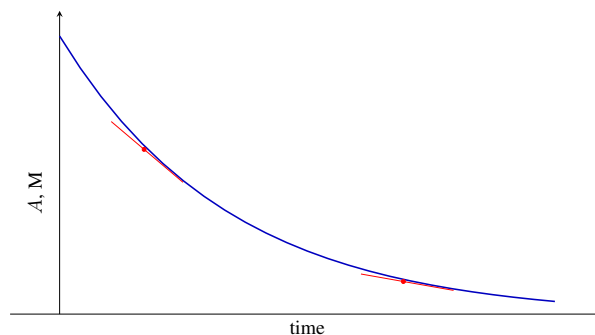
0.4 Use the data below to identify reactants and products in a reaction.

Time, s	[A] (M)	[B] (M)
0	4	0
1	3.6	2×10^{-3}
2	2.2	2×10^{-3}
3	1.3	2×10^{-2}
4	0.8	2×10^{-2}

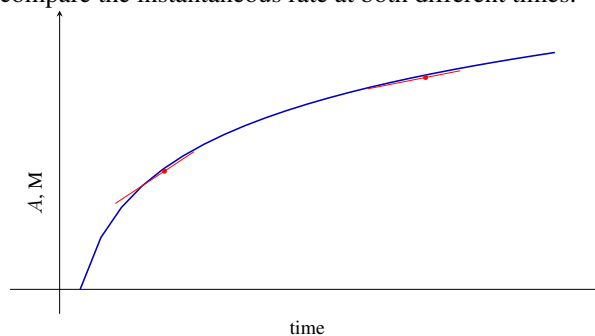
0.5 The concentration plots below represent two different reaction. Indicate which has the fastest initial reaction rate.



0.6 Using the concentration vs. time plot shown below, compare the instantaneous rate at both different times.



0.7 Using the concentration vs. time plot shown below, compare the instantaneous rate at both different times.





0.8 For a given reaction the differential rate is measured for a set of species. Given the numerical values indicated next, identify the specie as reactant or product: (a) $r_A=0.3\text{M/s}$ (b) $r_B=-0.1\text{M/s}$ (c) $r_C=-1.2\text{M/s}$ (d) $r_D=0.6\text{M/s}$

0.9 For the reaction below: $2a + 3b \longrightarrow 4c + 5d$ and given that the rate of disappearance of b is $r_B=-0.3\text{M/s}$, calculate: (a) the rate of disappearance of A, r_A (b) the rate of appearance of C, r_C (c) the rate of appearance of D, r_D (d) the rate of reaction r

0.10 For the reaction below: $2a + 2b \longrightarrow 3c + d$ and given that the rate of appearance of d is $r_D=0.2\text{M/s}$, calculate: (a) the rate of disappearance of A, r_A (b) the rate of disappearance of B, r_B (c) the rate of appearance of C, r_C (d) the rate of reaction r

RATE LAWS

0.11 Given the following rate law

$$r=0.04[A]^2[B][C]^3$$

indicate: (a) the reaction order of A (b) the reaction order of B (c) the reaction order of C (d) the overall reaction order (e) the value of the reaction constant including its units

0.12 Given the following rate law

$$r=0.4[\text{Cl}_2][\text{F}_2]^2$$

indicate: (a) the reaction order of Cl_2 (b) the reaction order of F_2 (c) the overall reaction order (d) the value of the reaction constant including its units

0.13 Given the following rate law

$$r=k[A]^4[B]^2[C]^2$$

indicate the impact on the rate of the following: (a) to double [A] (b) to triple [B] (c) to double [C]

0.14 Given the following rate law

$$r=k[A][B]^2[C]$$

indicate the impact on the rate of the following: (a) to double [B] (b) to triple [A] (c) to quadruple [C]

0.15 Given the following rate constant values, identify the reaction order: (a) $k=3 \times 10^{-4} \text{ L/(s}\cdot\text{mol)}$ (b) $k=0.03 \text{ M/s}$ (c) $k=3 \times 10^{-5} \text{ 1/(s}\cdot\text{M}^2)$

0.16 Given the following rate constant values, identify the reaction order: (a) $k=0.04 \text{ M/s}$ (b) $k=0.00 \text{ 1/s}$ (c) $k=0.09 \text{ s/M}$

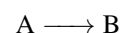
0.17 Identify the following rate laws as integral or differential, and given a form obtain the corresponding other type of form (i.e. if the integral form is given then obtain the differential form) (a) $r = 0.0023$, $[A]_0=0.3$ (b) $\ln([A]) = -0.045 \cdot t + 0.45$ (c) $r = 0.3[A]^2$, $[A]_0=25$

0.18 Identify the following rate laws as integral or differential, and given a form obtain the corresponding other type of form (i.e. if the integral form is given then obtain the differential form) (a) $[A] = 0.045 - 0.34 \cdot t$ (b) $r = 0.9[A]^1$, $[A]_0=1.49$ (c) $\frac{1}{[A]} = 0.3 + 0.04 \cdot t$

0.19 Compute the half-life for the following reactions: (a) a first order reaction with $k=0.234 \text{ 1/s}$ (b) a zeroth-order reaction with $k=0.34 \text{ M/s}$ and initial concentration 0.1M (c) a second-order reaction with $k=0.067 \text{ M/s}$ and initial concentration 0.01M

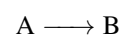
THE DIFFERENTIAL AND INTEGRAL METHODS OF OBTAINING RATE LAWS

0.20 Use the data below to calculate the rate law of the following reaction:



Experiment	$r \text{ (M/s)}$	$[A], \text{ (M)}$
1	0.03	1
2	0.12	2

0.21 Use the data below to calculate the rate law of the following reaction:



Experiment	$r \text{ (M/s)}$	$[A], \text{ (M)}$
1	5×10^{-3}	0.5
2	5×10^{-3}	0.6



0.22 Use the data below to calculate the rate law of the following reaction:



Experiment	r (M/s)	$[A]$, (M)
1	0.03	0.1
2	0.30	0.2

0.23 Use the data below to calculate the rate law:

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.1	0.02	2.08×10^{-5}
2	0.1	0.04	8.32×10^{-5}
3	0.2	0.01	1.04×10^{-5}
4	0.4	0.01	2.08×10^{-5}

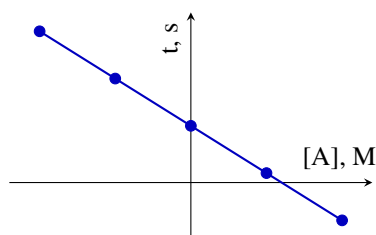
0.24 Use the data below to calculate the rate law:

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.1	0.02	1.03×10^{-3}
2	0.1	0.04	2.08×10^{-3}
3	0.2	0.01	1.04×10^{-3}
4	0.4	0.01	2.08×10^{-3}

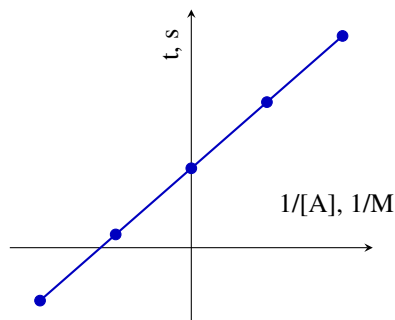
0.25 Use the data below to calculate the rate law:

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.1	0.02	1.03×10^{-3}
2	0.1	0.04	2.08×10^{-3}
3	0.2	0.01	1.04×10^{-3}
4	0.4	0.01	2.08×10^{-3}

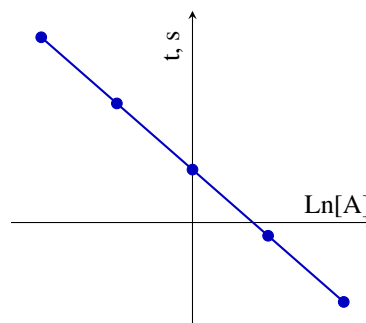
0.26 The plot below resulting from integral method represent a perfect line with $r^2=0.99$. Indicate the order of the reaction.



0.27 The plot below resulting from integral method represent a perfect line with $r^2=0.99$. Indicate the order of the reaction.

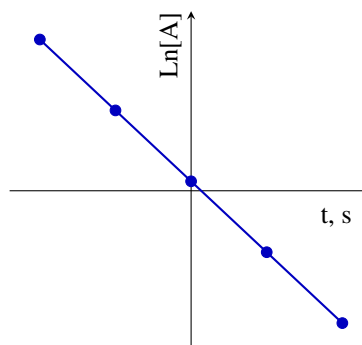


0.28 The plot below resulting from integral method represent a perfect line with $r^2=0.99$. Indicate the order of the reaction.

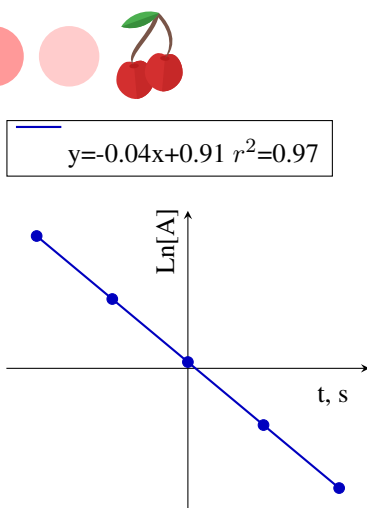


0.29 The following plots results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law.

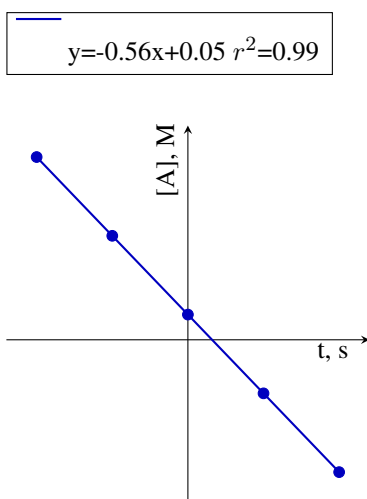
$$y = -0.34x + 0.1 \quad r^2 = 0.99$$



0.30 The following plots results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law.



0.31 The following plots results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law.



0.32 Using the following data, calculate the order and rate constant and write down the rate law.

t (s)	$[A]$, (M)
5	0.952
10	0.625
15	0.465
20	0.370
25	0.308
35	0.230

0.33 Using the following data, calculate the order and rate constant and write down the rate law.

t (s)	$[A]$, (M)
0	9.90×10^{-2}
5	4.97×10^{-2}
10	3.32×10^{-2}
15	2.49×10^{-2}
20	1.66×10^{-2}
25	1.43×10^{-2}

0.34 Calculate the rate law for the following reaction using the given data: $2 \text{ClO}_2 + 2 \text{I}^- \longrightarrow 2 \text{ClO}_2^- + \text{I}_2$

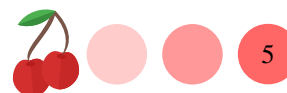
t (s)	$[\text{ClO}_2]$, (M)
0	4.77×10^{-4}
1	3.31×10^{-4}
2	3.91×10^{-4}
3	3.53×10^{-4}
5	2.89×10^{-4}
10	1.76×10^{-4}
30	2.40×10^{-5}
50	3.20×10^{-6}

0.35 Calculate the rate law for the following reaction using the given data: $\text{CH}_3\text{COOCH}_3 + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{CH}_3\text{OH}$

t (s)	$[\text{CH}_3\text{COOCH}_3]$, (M)
0	1.00×10^{-2}
3	7.40×10^{-3}
4	6.83×10^{-3}
5	6.34×10^{-3}
10	4.63×10^{-3}
20	3.04×10^{-3}
30	2.24×10^{-3}

0.36 Calculate the rate law for the following reaction using the given data: $2 \text{NO}_2 \longrightarrow 2 \text{NO} + \text{O}_2$

t (s)	$[\text{NO}_2]$, (M)
0	1.00×10^{-2}
60	6.83×10^{-3}
120	5.18×10^{-3}
180	4.18×10^{-3}
240	3.50×10^{-3}
300	3.01×10^{-3}
360	2.64×10^{-3}



0.37 Calculate the rate law for the following reaction using the given data: $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$

t (s)	$[\text{HI}]$, (M)
0	1
1000	0.11
2000	0.061
3000	0.041
4000	0.031

0.38 Calculate the rate law for the following reaction using the given data: $\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$

t (s)	$[\text{H}_2]$, (M)
0	1
1	0.43
2	0.27
3	0.20
4	0.16

0.39 Calculate the rate law for the following reaction using the given data: $\text{C}_3\text{H}_5 \longrightarrow \text{C}_3\text{H}_6$

t (s)	$[\text{C}_3\text{H}_5]$, (M)
0	1.5×10^{-3}
5	1.24×10^{-3}
10	1.0×10^{-3}
15	0.83×10^{-3}

0.40 Calculate the rate law for the following reaction using the given data: $2\text{P} + \text{Q} \longrightarrow \text{W}$

t (s)	$[\text{P}]$, (M)
9	1.077×10^{-3}
13	1.068×10^{-3}
18	1.055×10^{-3}
22	1.046×10^{-3}
25	1.039×10^{-3}

0.41 Calculate the rate law for the following reaction using the given data: $2\text{O}_3 \longrightarrow 3\text{O}_2$

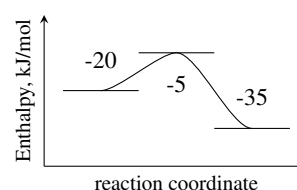
t (h)	$[\text{O}_3]$, (M)
5	0.952
10	0.625
15	0.465
20	0.37
25	0.308
35	0.23

0.42 Calculate the rate law for the following reaction using the given data: $2\text{X} \longrightarrow \text{Y} + \text{Z}$

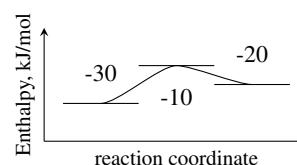
t (s)	$[\text{X}]$, (M)
5	0.0990
10	0.0497
15	0.0332
20	0.0249
25	0.0200
30	0.0166
35	0.0143
40	0.0125

COLLISION THEORY

0.43 For the energy profile below, indicate the activation energy and the reaction energy. Does this diagram corresponds to an exothermic or endothermic reaction?



0.44 For the energy profile below, indicate the activation energy and the reaction energy. Does this diagram corresponds to an exothermic or endothermic reaction?

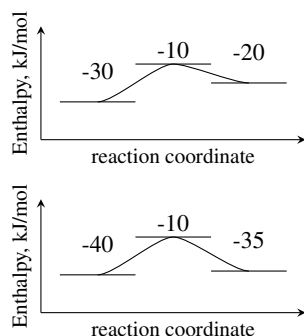




0.45 Sketch an energy profile in which reactants are located at -10kJ/mol , the activation energy is 15kJ/mol and the energy of reaction is 10kJ/mol .

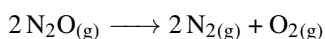
0.46 Sketch an energy profile in which reactants are located at -15kJ/mol , the activation energy is 10kJ/mol and the energy of reaction is -10kJ/mol .

0.47 Compare both energy profiles top and bottom and indicate: (a) What reaction proceeds faster (b) What reaction exchanges more energy



0.48 The reaction energy of a process, going from reactants into products, is 10kJ/mol and its activation energy is 15kJ/mol . Calculate the reaction energy and the activation energy of the reverse process, starting from products and going to reactants. Is the direct reaction exothermic or endothermic. How about the reverse process?

0.49 The rate constant for the gas-phase decomposition of N_2O has the following temperature dependence:

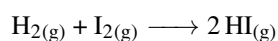


has the following temperature dependence:

$T \text{ (K)}$	$k, (\text{s}^{-1})$
1500	1.1×10^{-15}
1400	1.4×10^{-13}
1300	6.9×10^{-13}
1200	1.5×10^{-12}

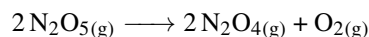
Indicate the reaction order, and compute the activation energy in (kJ/mol) and the frequency factor.

0.50 For the gas-phase reaction between hydrogen and iodine



the rate constant at 500K was found to be $9.36 \times 10^{-7} \text{ l}/(\text{M}\cdot\text{s})$ and the rate constant at 600K was found to be $5.69 \times 10^{-4} \text{ l}/(\text{M}\cdot\text{s})$. Calculate the activation energy in kJ/mol and the frequency factor of the reaction.

0.51 For the decomposition of dinitrogen pentoxide



the rate constant at 500K is 345.43 s^{-1} and at different temperature, the rate constant is 24.84 s^{-1} . Given that the activation energy of this reaction is 103.03 kJ/mol , calculate the second temperature value.

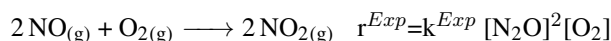
0.52 For a given reaction, when temperature increases from 100K to 200K , its rate constant triples. Calculate the activation energy for this process.

REACTION MECHANISMS

0.53 For the following elemental reaction steps indicate the molecularity and give the rate law:

- $\text{N}_2\text{O} \longrightarrow \text{NO} + \text{O}$
- $\text{N}_2\text{O} + \text{O} \longrightarrow \text{N}_2 + \text{O}_2$
- $2\text{NO} \longrightarrow \text{N}_2\text{O}_2$
- $\text{N}_2\text{O}_2 + \text{H} \longrightarrow \text{N}_2\text{O} + \text{HO}$

0.54 The experimental rate law for the reaction of nitrogen monoxide and molecular oxygen given by the following reaction

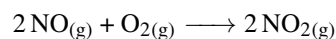


is second order with respect to dinitrogen oxide and first order with respect to oxygen. A plausible mechanism would be:

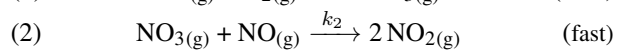
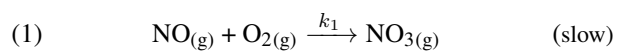
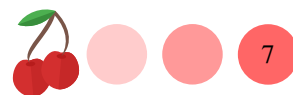
- $\text{NO}_{(\text{g})} + \text{NO}_{(\text{g})} \xrightleftharpoons[k_{-1}]{k_1} \text{N}_2\text{O}_{2(\text{g})}$
- $\text{N}_2\text{O}_{2(\text{g})} + \text{O}_{2(\text{g})} \xrightarrow{k_2} 2\text{NO}_{2(\text{g})} \quad (\text{slow})$

Calculate: (a) the molecularity of each reaction step (b) the rate law for each reaction step (c) identify all intermediates (d) justify whether the suggested mechanism is valid and if so give k^{Exp} in terms of the rate constants in the mechanism

0.55 A possible mechanism for the reaction of nitrogen monoxide and molecular oxygen to produce nitrogen dioxide given by the following reaction



could be:



Calculate: (a) the molecularity of each reaction step
(b) the rate law for each reaction step (c) identify all intermediates (d) give the experimental rate law



Answers **0.1** Reaction I is faster **0.2** B is the reactants and A the product **0.3** A is the reactants and B the product **0.4** A is the reactants and B neither reactant or product **0.5** The plot on the right **0.6** $r_{left} > r_{right}$ **0.7** $r_{left} > r_{right}$ **0.8** (a) $r_A = 0.3 \text{ M/s}$ (product) (b) $r_B = -0.1 \text{ M/s}$ (reactant) (c) $r_C = -1.2 \text{ M/s}$ (reactant) (d) $r_D = 0.6 \text{ M/s}$ (product) **0.9** (a) - 0.2 M/s (b) +0.4 M/s (c) +0.5 M/s (d) 0.1 M/s **0.10** (a) - 0.4 M/s (b) - 0.4 M/s (c) +0.6 M/s (d) 0.2 M/s **0.11** (a) second order (b) first order (c) third order (d) sixth order (e) 0.04 s/M^5 **0.12** (a) first order (b) second order (c) third order (d) 0.4 s/M^2 **0.13** (a) 16 times faster (b) 9 times faster (c) 4 times faster **0.14** (a) 4 times faster (b) 3 times faster (c) 4 times faster **0.15** (a) second order (b) zeroth order (c) third order **0.16** (a) zeroth order (b) first order (c) second order **0.17** (a) $r = 0.0023$, $[A]_0 = 0.3$ (b) $\ln([A]) = -0.045 \cdot t + 0.45$ (c) $r = 0.3[A]^2$, $[A]_0 = 25$ **0.18** (a) $[A] = 0.045 - 0.34 \cdot t$ (b) $r = 0.9[A]^1$, $[A]_0 = 1.49$ (c) $\frac{1}{[A]} = 0.3 + 0.04 \cdot t$ **0.19** (a) 2.96 s (b) 0.15 s (c) 1492 s **0.20** $r = 0.03[A]^2$ **0.21** $r = 0.005$ **0.22** $r = 0.15[A]$ **0.23** $r = 0.52[A]^1[B]^2$ **0.24** $r = 0.52[A][B]$ **0.25** $r = 0.52[A][B]$ **0.26** zeroth-order **0.27** second order **0.28** first order **0.29** $r = 0.34[A]^1$, $[A]_0 = 1.1 \text{ M}$ **0.30** No rate law can be derived **0.31** $r = 0.56$, $[A]_0 = 0.05 \text{ M}$ **0.32** $r = 0.11[A]^2$, $[A]_0 = 2 \text{ M}$ **0.33** $r = 2.45[A]^2$, $[A]_0 = 0.13 \text{ M}$ **0.34** $r = 0.098[\text{ClO}_2]$, $[\text{ClO}_2]_0 = 4.5 \times 10^{-4} \text{ M}$ **0.35** $r = 11.51[\text{CH}_3\text{COOCH}_3]^2$, $[\text{CH}_3\text{COOCH}_3]_0 = 9.9 \times 10^{-3} \text{ M}$ **0.36** $r = 0.77[\text{NO}_2]^2$, $[\text{NO}_2]_0 = 0.01 \text{ M}$ **0.37** $r = 7.69 \times 10^{-3}[\text{HI}]^2$, $[\text{HI}]_0 = 0.7 \text{ M}$ **0.38** $r = 7.69 \times 10^{-3}[\text{H}_2]^2$, $[\text{H}_2]_0 = 0.7 \text{ M}$ **0.39** $r = 4.5 \times 10^{-5}$, $[\text{C}_3\text{H}_6]_0 = 1.48 \times 10^{-3} \text{ M}$ **0.40** $r = 2.39 \times 10^{-6}$, $[\text{P}]_0 = 1.09 \times 10^{-3} \text{ M}$ **0.41** $r = 0.109[\text{O}_3]^2$, $[\text{O}_3]_0 = 1.99 \text{ M}$ **0.42** $r = 1.99[\text{X}]^2$, $[\text{X}]_0 = 6.15 \text{ M}$ **0.43** $E_a = 15 \text{ kJ/mol}$; $\Delta H = -15 \text{ kJ/mol}$; exothermic **0.44** $E_a = 20 \text{ kJ/mol}$; $\Delta H = 10 \text{ kJ/mol}$; endothermic **0.45** Reactants (-10); TS (5); products (-0) **0.46** Reactants (-15); TS (-5); products (-25) **0.47** (a) top goes faster (b) top consumes more energy **0.48** $E_a = 5 \text{ kJ/mol}$; $\Delta H = -10 \text{ kJ/mol}$; direct endothermic; reverse exothermic **0.49** Order one; $E_a = 252.05 \text{ kJ/mol}$; $A = 5.52 \times 10^{12} \text{ s}^{-1}$ **0.50** Order one; $E_a = 159.88 \text{ kJ/mol}$; $A = 4.73 \times 10^{10} \text{ s}^{-1}$ **0.51** 452 K **0.52** 1.8 kJ/mol **0.53** (a) molecularity=1; $r = k[\text{N}_2\text{O}]$ (b) molecularity=2; $r = k[\text{N}_2\text{O}][\text{O}]$ (c) molecularity=2; $r = k[\text{NO}]$ (d) molecularity=2; $r = k[\text{N}_2\text{O}_2][\text{H}]$ **0.54** (a) (2;2) (b) $0 = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2]$; $r_2 = k_2[\text{N}_2\text{O}_2][\text{O}_2]$ (c) N_2O_2 (d) $\frac{k_2 \cdot k_1}{k_{-1}}$ **0.55** (a) 2; 2 (b) $r_1 = k_1[\text{NO}]^2[\text{O}_2]$; $r_2 = k_2[\text{NO}_3][\text{NO}]$ (c) NO_3 (d) $r^{\text{Exp}} \sim r^{\text{slow}} = k_1[\text{NO}]^2[\text{O}_2]$