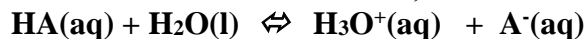


KEY

1. A 0.01 M solution of an acid has $\text{pH} = 4$ at 300 K. At a lower temperature, the pH of the acid solution is 3. On the axes below, sketch the line of $\ln(K)$ versus $(1/T)$ for this acid.



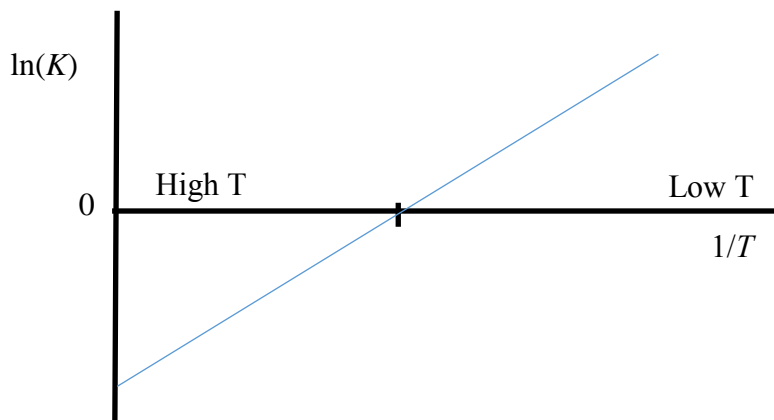
- a. $\text{pH} \downarrow$ this means $[\text{H}_3\text{O}^+] \uparrow$ when $T \downarrow$

Process is exothermic this means that slope is positive.

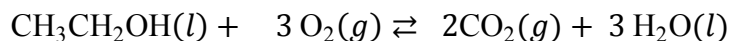
- b. $K \downarrow$ when $T \uparrow$

- c. $K(300\text{K}) = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{HA}] = 1 \cdot 10^{-6}$

$$K(T \downarrow) = 1 \cdot 10^{-4}$$



2. A fuel cell is made based on the combustion of ethanol. The fuel cell gas pressures are $p_{\text{O}_2} = 31.5 \text{ bar}$ and $p_{\text{CO}_2} = 0.0200 \text{ bar}$. For this combustion, $\Delta_r H^\circ = -1367.51 \text{ kJ/mol}$ and $\Delta_r S^\circ = -138.58 \text{ J/(K mol)}$. Calculate the total energy available for useful work from the combustion of 1.00 kg of ethanol (46.06 g/mol) in this fuel cell at 25 °C. (Answer: -29800kJ)



$$\Delta G^\circ = \Delta H^\circ_{\text{sys}} - T \Delta S^\circ_{\text{sys}} = -1367.51 \frac{\text{kJ}}{\text{mol}} - 298.15 \text{K} \cdot \left(-138.48 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \frac{1 \text{kJ}}{1000 \text{J}} = -1326.19 \frac{\text{kJ}}{\text{mol}}$$

$$Q = \frac{(p_{\text{CO}_2})^2}{(p_{\text{O}_2})^3} = 1.28 \cdot 10^{-8}$$

$$\Delta G = \Delta G^\circ + RT \ln Q = -1326.19 \frac{\text{kJ}}{\text{mol}} + R \cdot 298.15 \text{K} \ln Q = -1371.24 \frac{\text{kJ}}{\text{mol}}$$

$$\text{Total Energy} = -1371.24 \frac{\text{kJ}}{\text{mol}} \cdot \frac{1000.0 \text{g}}{46.06 \text{g/mol}} = -29770.79 \text{kJ} = -29800 \text{kJ}$$

3. The pH of water is 7.27 at 10.0 °C and 6.77 at 40.0 °C. Calculate the molar standard enthalpy and entropy change for the autoionization of water.

$$\text{At } T_1 = 283.15 \text{K} \quad K_{w1} = (10^{-7.27})^2 = 10^{-14.54} \quad ; \quad \text{At } T_2 = 313.15 \text{K} \quad K_{w2} = (10^{-6.77})^2 = 10^{-13.54}$$

$$\left[\begin{array}{l} -RT_1 \ln K_{w1} = \Delta H^\circ_{\text{sys}} - T_1 \Delta S^\circ_{\text{sys}} \\ -RT_2 \ln K_{w2} = \Delta H^\circ_{\text{sys}} - T_2 \Delta S^\circ_{\text{sys}} \end{array} \right.$$

$$\left[\begin{array}{l} -RT_1 \ln K_{w1} = \Delta H^\circ_{\text{sys}} - T_1 \Delta S^\circ_{\text{sys}} \\ -RT_2 \ln K_{w2} = \Delta H^\circ_{\text{sys}} - T_2 \Delta S^\circ_{\text{sys}} \end{array} \right.$$

$$-RT_1 \ln K_{w1} + RT_2 \ln K_{w2} = -T_1 \Delta S^\circ_{\text{sys}} + T_2 \Delta S^\circ_{\text{sys}} \quad ; \quad \Delta S^\circ = -78.52 \text{J/mol} \cdot \text{K}$$

And then solve for $\Delta H^\circ_{\text{sys}}$

$$\Delta H^\circ_{\text{sys}} = 56.58 \text{kJ/mol}$$

$$\text{Or: } \ln K_1 = -\frac{\Delta H_{sys}^\circ}{RT_1} + \frac{\Delta S_{sys}^\circ}{R} \quad \text{and} \quad \ln K_2 = -\frac{\Delta H_{sys}^\circ}{RT_2} + \frac{\Delta S_{sys}^\circ}{R}$$

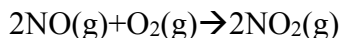
$$\ln K_1 - \ln K_2 = \left(-\frac{\Delta H_{sys}^\circ}{RT_1} + \frac{\Delta S_{sys}^\circ}{R}\right) - \left(-\frac{\Delta H_{sys}^\circ}{RT_2} + \frac{\Delta S_{sys}^\circ}{R}\right)$$

$$(\ln K_1 - \ln K_2) = \ln \frac{K_1}{K_2} = -\frac{\Delta H_{sys}^\circ}{RT_1} + \frac{\Delta H_{sys}^\circ}{RT_2} = \Delta H_{sys}^\circ \left(\frac{T_1 - T_2}{RT_1 T_2}\right);$$

$$\Delta H^\circ = \frac{\ln \frac{K_1}{K_2} \cdot T_1 \cdot T_2 \cdot R}{T_1 - T_2} = 56.58 \text{ kJ/mol}$$

$$\Delta S^\circ = (\ln K_1 + \frac{\Delta H_{sys}^\circ}{RT_1}) \cdot R = -78.52 \text{ J/mol} \cdot \text{K}$$

1. A study of the reaction below gave the following result:



Fill in the missing information in the table

	[NO]	[O ₂]	$-\frac{d[\text{NO}]}{dt}$ [M/s]	Reaction rate
Ex1	0.0125	0.0185	0.020	0.010
Ex2	0.0250	0.0185	0.080	0.040
Ex3	0.0250	0.0370	0.160	0.080
Ex4	0.0125	0.0370	0.040	0.020

To find **x** we need to compare the rate of experiment 1 to the rate of experiment 2:

NOTE: The rate constant does not change with experimental conditions: it is **constant**.

Concentration of NO changes but concentration of O₂ stays the same. [O₂]₁ = [O₂]₂

What order is the reaction in respect to [NO] **x = 2**

To find **y** we need to compare the rate of experiment 2 to the rate of experiment 3 (or 1 and 4):

NOTE: The rate constant does not change with experimental conditions: it is **constant**.

Concentration of O₂ changes but concentration of A stays the same. [NO]₃ = [NO]₂

What order is the reaction with respect to [O₂] **y = 1**

Write the rate law: **rate = k [NO]²[O₂]¹**

Overall rate order = **3**

What are the units of *this* **k**? $\frac{\left(\frac{\text{M}}{\text{s}}\right)}{\text{M}^x \cdot \text{M}^y} = \frac{\text{M}^{1-(x+y)}}{\text{s}} = \frac{1}{\text{M}^2 \text{s}}$

Calculate rate constant: $k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]^1} = 3.53 \cdot 10^3 \frac{1}{M^2 s}$

What is the reaction rate when $[\text{NO}] = [\text{O}_2] = 0.020M$

$\text{rate} = k [\text{NO}]^2 [\text{O}_2]^1 = 3.53 \cdot 10^3 \frac{1}{M^2 s} \cdot (0.020M)^2 \cdot (0.020M) = 2.8 \cdot 10^{-2} M/s$

For each reactant, circle which plot correlating concentration with time will give you a **straight line**, and what the **sign of the slope** will be.

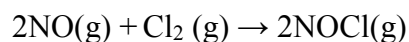
$[\text{NO}]$ vs. time $1/[\text{NO}]$ vs. time $\ln[\text{NO}]$ vs. time

Slope: positive = 2k negative zero

$[\text{O}_2]$ vs. time $1/[\text{O}_2]$ vs. time $\ln[\text{O}_2]$ vs. time

Slope: positive negative = -k zero

2. A study of the reaction below gave the following result:



	$[\text{NO}]$	$[\text{Cl}_2]$	$-\frac{d[\text{NO}]}{dt} [M/s]$	RXN rate
Ex1	1.2	2.5	0.6	0.3
Ex2	4.8	2.5	0.3	0.15
Ex3	1.2	5.0	0.18	0.9

What order is the reaction with respect to $[\text{NO}]$

To find x we need to compare the rate of experiment 1 to the rate of experiment 2:

NOTE: The rate constant does not change with experimental conditions: it is constant.

Concentration of NO changes but concentration of Cl₂ stays the same. $[\text{Cl}_2]_1 = [\text{Cl}_2]_2$

$\frac{\text{rate}_1}{\text{rate}_2} = \frac{0.3}{0.15} = \frac{k[\text{NO}]_1^x [\text{Cl}_2]_1^y}{k[\text{NO}]_2^x [\text{Cl}_2]_2^y} = \left(\frac{[\text{NO}]_1}{[\text{NO}]_2}\right)^x = \left(\frac{1.2}{4.8}\right)^x$

$2 = \left(\frac{1}{4}\right)^x \quad \log 2 = x \log(1/4) \quad x = \left(\frac{\log 2}{\log 1 - \log 4}\right) = \left(\frac{0.3}{-0.6}\right) = -\left(\frac{1}{2}\right) = -0.5$

What order is the reaction with respect to $[\text{Cl}_2]$

To find y we need to compare the rate of experiment 1 to the rate of experiment 3:

NOTE: The rate constant does not change with experimental conditions: it is constant.

Concentration of Cl₂ changes but concentration of NO stays the same. $[\text{NO}]_3 = [\text{NO}]_2$

$\frac{\text{rate}_3}{\text{rate}_1} = \frac{0.9}{0.3} = \frac{k[\text{NO}]_3^x [\text{Cl}_2]_3^y}{k[\text{NO}]_1^x [\text{Cl}_2]_1^y} = \left(\frac{[\text{Cl}_2]_3}{[\text{Cl}_2]_1}\right)^y = \left(\frac{5.0}{2.5}\right)^y ; \quad 3 = 2^y ; \quad \log(3) = y \log 2 ; \quad y = 1.6$

Fill in the table for reaction rate with respect to NO

Write the rate law: **rate = k $[\text{NO}]^{-0.5} [\text{Cl}_2]^{1.6}$**

Overall rate order: **x + y = 1.6 + (-0.5) = 1.1**

What are the units of *this* k? $M^{-0.1}/s$

3. Consider the chemical reaction: $3A + 4B \rightarrow 2C + 2D$. The experimentally determined rate law is $\text{Rate} = k[A]^2[B]$. When the initial concentrations are $[A]_i = 0.5 \text{ M}$ and $[B]_i = 0.01 \text{ M}$, the rate of consumption of B is $8 \times 10^{-5} \text{ M/s}$. Give the value of the rate constant, k , including the units.

$$\text{Rate} = -\frac{1}{4} \frac{d[B]}{dt} = k[A]^2[B]$$

$$-\frac{1}{4} * \left(-\frac{8 \times 10^{-5} \text{ M}}{\text{s}} \right) = k[5 \times 10^{-1} \text{ M}]^2 [1 \times 10^{-2} \text{ M}]$$

$$k = \frac{2 \times 10^{-5} \text{ M/s}}{25 \times 10^{-4} \text{ M}^3} = \frac{8 \times 10^{-3}}{\text{M}^2 \text{ s}}$$

4. Consider the chemical reaction: $3A + 4B \rightarrow 2C + 2D$. The experimentally determined rate law is $\text{Rate} = k[A][B]^2$. When the initial concentrations are $[A]_i = 0.3 \text{ M}$ and $[B]_i = 0.01 \text{ M}$, the rate of consumption of B is $6 \times 10^{-4} \text{ M/s}$. Give the value of the rate constant, k , including the units. (Answer: $5 \text{ M}^{-2} \text{ s}^{-1}$)
5. Consider the reaction $A + 2B \rightarrow D + C$. Three experiments were conducted and the initial reaction rate of each reaction was determined. For each of the reactants, find the appropriate order. (Answer: 1, 0.5)

Exp	Initial conc. (mol/L)		Initial Rate (mol/L·sec)
	[A]	[B]	
#1	1.0×10^{-3}	1.0×10^{-3}	3.2×10^{-7}
#2	1.0×10^{-3}	3.0×10^{-3}	9.6×10^{-7}
#3	4.0×10^{-3}	3.0×10^{-3}	1.9×10^{-6}

6. Consider the comproportionation reaction of bromate and bromide to make bromine gas. Four experiments were conducted and the initial reaction rate was determined.



Exp	Initial Concentrations (mol/L)			Initial Reaction Rate (mol/L·sec)
	$[\text{BrO}_3^-]$	$[\text{Br}^-]$	$[\text{H}_3\text{O}^+]$	
#1	0.10	0.10	0.01	1.0
#2	0.20	0.10	0.01	2.0
#3	0.10	0.30	0.01	3.0
#4	0.20	0.10	0.02	8.0

- a) Using the data, determine the order of the reaction with respect to H_3O^+ .

$$\frac{\text{rate}_4}{\text{rate}_2} = \frac{8.0}{2.0} = \frac{k[\text{H}_3\text{O}^+]_4^x}{k[\text{H}_3\text{O}^+]_2^x} = \left(\frac{[\text{H}_3\text{O}^+]_4}{[\text{H}_3\text{O}^+]_2} \right)^x = \left(\frac{0.02}{0.01} \right)^x \quad \mathbf{x=2}$$

b) What is the initial rate of formation of bromine gas in experiment #1? Br₂ (g)

$$\text{rxn rate} = \frac{1}{6} \frac{d[\text{Br}_2]}{dt}$$

$$\frac{d[\text{Br}_2]}{dt} = 6 \cdot \text{Initial Reaction Rate} = 6 \text{ mol/L}\cdot\text{se}$$

$$\text{Half Life } \frac{N_n}{N_0} = \left(\frac{1}{2}\right)^n ; t_{\text{pass}} = n \cdot t_{1/2} ; t_{1/2} = \frac{0.693}{k}$$

7. In a first order chemical reaction, the concentration of a reactant is observed to fall from 1.000 M to 0.250 M between $t = 6$ s and $t = 10$ s. What is the concentration (in M) at $t = 12$ s?

One half-life 1M → 0.5M

Two half life's 0.5M → 0.250M time spend was 10s-6s=4s for 2 half life's

$t_{1/2} = 2$ s at time 12s one more half-life must pass so the concentration is 0.125M

8. The first order reaction is 60% complete after 100 seconds. What is rate constant k and $t_{1/2}$ for this reaction?

60% complete 40% remains

$$\frac{N_n}{N_0} = \left(\frac{1}{2}\right)^n \quad \frac{40}{100} = \left(\frac{1}{2}\right)^n \quad \frac{4}{10} = \left(\frac{1}{2}\right)^n \quad n=1.3 ; t_{1/2} = t/n = 76.9\text{s}; \quad k = \frac{0.693}{t_{1/2}} = .013 \text{ 1/s}$$

9. Fluorine-18 has a half-life of 110 minutes. After 4 half-lives, how much time has elapsed? What percentage of your original F-18 remains? What percentage has decayed? (Answer: $t_{\text{pass}}=440$ minutes, remains=6.25% , decayed=93.75)

$$t_{1/2} = 110\text{min} \quad n=4 \quad t=440\text{s} \quad \frac{N_n}{N_0} = \left(\frac{1}{2}\right)^4 = 0.0625 \text{ remains}$$

10. You are trying to find the half-life of a new, meta-stable compound (X) created in your lab. You analyze the amount of X you have 30 minutes after initial production of X. You find you have 20% of the original amount. Approximately, what is $t_{1/2}$?

6 m. < $t_{1/2}$ < 7.5 m. 7.5 m. < $t_{1/2}$ < 10 m. 10 m. < $t_{1/2}$ < 15 m. 15 m. < $t_{1/2}$ < 30 m.

11. For another compound (Y), 94% of an original 100.0 g has decayed in 60.0 minutes. Express your answer to ONE SIGNIFICANT FIGURE.

(a) How many grams of Y is remaining? (Answer: 6g)

(b) How many half-lives have elapsed? (Answer: $n=4$ half-lives pass)

(c) What is the half-life of this compound? (Answer: $t_{1/2}=15$ min)

Things you should know when you leave Discussion today:

2. **Rate** = $\frac{\Delta[A]}{\Delta t}$; units: $\frac{M}{s}$

3. **Rate of chemical reactions depends on:**

- Temperature
- Catalysts
- Initial concentrations
- Magnitude of the rate constant

4. **Initial Reaction Rates:**

a. For a reaction: $aA + bB \rightarrow cC + dD$

b. Initial Reaction Rate = $-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$

c. Where $\frac{\Delta[A]}{\Delta t}$ is an individual rate of loss of A,

$$\frac{\Delta[B]}{\Delta t} = \frac{b}{a} \cdot \frac{\Delta[A]}{\Delta t}; \quad \frac{\Delta[C]}{\Delta t} = -\frac{c}{a} \frac{\Delta[A]}{\Delta t}$$

5. **Rate Law:**

- Differential Rate Law: rate versus concentration
 $aA + bB \rightarrow cC + dD$

$$\text{Rate} = k [A]^x [B]^y \quad \text{Where } k \text{ is a rate constant } k = \frac{\text{rate}}{[A]^x \cdot [B]^y}$$

Where x is the *order of the reaction* with respect to species A, and y is the *order of the reaction* with respect to species B.

- Comparing initial rates:

$$\frac{\text{rate } 1}{\text{rate } 2} = \frac{k[A]_1^x [B]_1^y}{k[A]_2^x [B]_2^y}$$

- Units of the rate constant depend on over all reaction order.**

$$k = \frac{\left(\frac{M}{s}\right)}{M^x \cdot M^y} = \frac{M^{1-(x+y)}}{s} \quad \text{where } (x+y) \text{ is the order of the overall reaction.}$$

6. **Integrated Rate Laws: see attached table for more information**

- Zero-Order:** $[R]_t - [R]_0 = -kt$

- First-Order:** $\ln \frac{[R]_t}{[R]_0} = -kt$

- Second-Order:** $\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt$

7. Half Life $\frac{N_n}{N_0} = \left(\frac{1}{2}\right)^n$; $t_{\text{pass}} = n \cdot t_{1/2}$; $t_{1/2} = \frac{0.693}{k}$