

CHEM 1120- 14.5 #4



[SPELL CARD]

Mole Fraction, χ_a

- A mole fraction is the fraction of the moles of one component in the total moles of all the components of the solution

$$\chi_a = \frac{\text{moles of substance } a}{\text{moles of substance } a + \text{moles of substance } b}$$

- Mole fraction has no units

- Mole percentage:
mol % = mole fraction (χ_a) $\times 100\%$

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CHEM 1120- 14.5 PROB 3

[SPELL CARD]

An aqueous solution of ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$ used as an automobile engine coolant) is 40.0% $\text{HOCH}_2\text{CH}_2\text{OH}$ by mass and has a density of 1.05 g/mL. What are the (a) molarity, (b) molality, and (c) mole fraction of $\text{HOCH}_2\text{CH}_2\text{OH}$ in this solution?

a. 40% -60 H_2O 100g Solution: $d=m/v$, $V=100g/1.013g/\text{mL}$, 95.24mL , .095L; MW= 62g/mol, $n=40g/62\text{g/mol}$, .645; M= $n/\text{Solute}/V$ Solution= 6.79M

b. $m=n/\text{Solute}/\text{mass Solvent}$ = 0.01075M

c. $n/\text{Solute } a/n/\text{Solute } a+b = .645/.645+3.33 = 16.2\%$

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CHEM 1120- 14.6



[TRAP CARD]

Colligative properties

- Properties whose value depends only on the **number of solute** particles and not on their structure or identity
 - Value depends on the concentration of the solution (typically m)
- The difference in the value of the property between the solution and the pure substance is generally related:
 - The different attractive forces
 - Solute particles occupying solvent molecules' positions

4 Colligative Properties of Solutions:

- Vapor Pressure (of the Solvent)
- Freezing Point Depression
- Boiling Point Elevation
- Osmotic Pressure

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CHEM 1120- 14.6.1 #1



[SPELL CARD]

Vapor Pressure of Solutions

- The pure solvent establishes a liquid-vapor equilibrium
- Addition of a *nonvolatile* solute reduces the rate of vaporization, decreasing the amount of vapor
- The solute particles replace some of the solvent molecules at the surface
- Eventually, equilibrium is re-established

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CHEM 1120- 14.6.1 #2

[SPELL CARD]

Vapor Pressure Lowering

- The vapor pressure of a **solvent** in a solution is
 - always lower than the vapor pressure of the pure solvent
- The vapor pressure of the **solution**
 - is directly proportional to the amount of the solvent in the solution

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[SPELL CARD]

Raoult's Law

- The vapor pressure of a volatile solvent above a solution is equal to its normal vapor pressure, P° , multiplied by its mole fraction in the solution

$$P_{\text{solvent in solution}} = \chi_{\text{solvent}} \cdot P^\circ$$

- The mole fraction of a solvent in solution is always less than 1, so vapor pressure of solution will always be less than the vapor pressure of the pure solvent

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CHEM 1120- 14.6 PROB 4



[SPELL CARD]

Most of the world's maple syrup supply is made in Quebec, Canada. The sap from maple trees is evaporated until the concentration of sugar (mostly sucrose) in the sap reaches 66% by weight. What is the vapor pressure (in atm) of a 66% aqueous solution of sucrose at 100 °C?

Assume the solution obeys Raoult's Law, the molar mass of syrup is 342 g/mol, and the vapor pressure of pure water at 100 °C is 1 atm.

66g Sucrose-34g H_2O ; p SOLUTE insulin-Xsolvent Pa; 66g Sucrose-1 mol Sucrose/342g = .193 mol Sucrose; 34g/1 mol $\text{H}_2\text{O}/18\text{g} = 1.89\text{mol H}_2\text{O}$; n=.193 mol + 1.89mol = 2.083 mol; $x_{\text{solvent}} = 1.89\text{mol}/2.083\text{mol} = .907$ or $P = .907$ atm

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CHEM 1120- 14.6.1 #4

[SPELL CARD]

Raoult's Law for Volatile Solute

- Both the solvent and the solute can evaporate, thus both molecules will be found in the vapor phase
- For an ideal solution,

$$P_{\text{total}} = P_{\text{solute}} + P_{\text{solvent}}$$
- Vapor pressure of solute **and** solvent are affected by their relative mole fraction

$$P_{\text{solute}} = \chi_{\text{solute}} \cdot P^\circ_{\text{solute}} \text{ and } P_{\text{solvent}} = \chi_{\text{solvent}} \cdot P^\circ_{\text{solvent}}$$

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CHEM 1120- 14.6.1 #5



[SPELL CARD]

From vapor pressure lowering...

- In *ideal systems*, vapor pressure lowering occurs at all temperatures
- Thus, the temperature required to boil the solution is higher than the boiling point of the pure solvent
- This also results in the temperature required to freeze the solution being lower than the freezing point of the pure solvent

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CHEM 1120- 14.6.2 #1

[SPELL CARD]

Boiling Point Elevation

- The boiling point of a solution is higher than the boiling point of the pure solvent
- The difference between the boiling point of the solution and the boiling point of the pure solvent is directly proportional to the *molality*

$$(BP_{\text{solution}} - BP_{\text{solvent}}) = \Delta T_b = m \cdot k_b$$

- The proportionality constant is called the boiling point elevation constant, k_b
 - The value of k_b depends on the solvent
 - The units of k_b are (degrees K or degrees C)/m

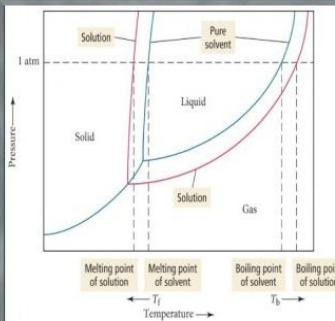
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CHEM 1120- 14.6.2 #2

[SPELL CARD]



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CHEM 1120- 14.6.3

[SPELL CARD]

Freezing Point Depression

- The freezing point of a solution is lower than the freezing point of the pure solvent
 - The melting point of the solid solution is also lower
- The difference between the freezing point of the solution and freezing point of the pure solvent is directly proportional to the molal concentration of solute particles

$$(FP_{\text{solvent}} - FP_{\text{solution}}) = \Delta T_f = m \cdot k_f$$

- The proportionality constant is called the freezing point depression constant, k_f
 - The value of k_f depends on the solvent
 - The units of k_f are (degrees K or degrees C)/m

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CHEM 1120- 14.6 PROB 5

[SPELL CARD]

Ethylene glycol [$\text{CH}_2(\text{OH})\text{CH}_2\text{OH}$] is a common ingredient in automobile antifreeze and fairly nonvolatile (boiling point = 197 °C). Calculate the (a) freezing point and (b) boiling point of a solution containing 685 g of ethylene glycol in 2075 g of water.

$$K_f = 1.86 \text{ }^{\circ}\text{C}/\text{m}$$

$$K_b = 0.52 \text{ }^{\circ}\text{C}/\text{m}$$

a. $T_f = mK_f; \text{MW ethgly} = 62.1 \text{ g/mol}; \text{mol. Solute} = 685 \text{ g}/62.1 \text{ g/mol} = 11.03 \text{ mol ethgly}; m = \text{mol. Solute}/\text{kg. Solvent} = 11.03 \text{ mol}/2.075 \text{ kg H}_2\text{O} = 5.32 \text{ mol/kg}; 5.32 \text{ mol} \cdot 1.86 \text{ }^{\circ}\text{C}/\text{m} = 9.90 \text{ }^{\circ}\text{C}$

b. $T_b = m \cdot 5.32 \text{ }^{\circ}\text{C}/\text{m}; 100 \text{ }^{\circ}\text{C} + 2.77 \text{ }^{\circ}\text{C} = 102.77 \text{ }^{\circ}\text{C}$

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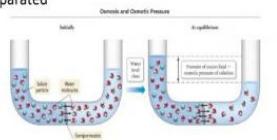
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CHEM 1120- 14.6.4 #1

[SPELL CARD]

Osmosis

- Osmosis** is the flow of solvent from a solution of low concentration into a solution of high concentration
- A semipermeable membrane allows solvent, but not solute, to flow through it. Solution can be separated



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CHEM 1120- 14.6.4 #2

[SPELL CARD]

Venus fly traps

- Turgor pressure** pushes the plasma membrane against the cell wall of plant cells
- In a venus fly trap, the pressure of a fly or other potential meal on surface hairs causes release of K^+ ions into the leaf tissues (osmotic pressure)
 - This makes the cells on one surface of the leaves wilt
 - The wilting surface is then slightly smaller than the unwilted, opposing leaf surface
 - Change in Turgor pressure allows the leaf to rapidly curl towards the wilted side



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CHEM 1120- 14.6.4 #3

[SPELL CARD]

- The amount of pressure needed to keep osmotic flow from taking place is called the **osmotic pressure**

- The osmotic pressure, Π , is directly proportional to the molarity of the solute particles

$$-\bar{R} = 0.08206 \text{ (atm} \cdot \text{L})/(\text{mol} \cdot \text{K})$$

$$\Pi = MRT$$

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CHEM 1120- 14.6 PROB 6

[SPELL CARD]

Calculate the osmotic pressure of seawater at 15°C if we assume that the salt concentration in seawater is equal to 0.55 M $\text{NaCl}_{(\text{aq})}$

$$15^\circ\text{C} = 288.15 \text{ K}; n = 288.15 \cdot 0.55 \text{ M} \text{ NaCl} \cdot 0.08206 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol} \\ n = 13 \text{ atm}$$

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CHEM 1120- 14.7 #1

[SPELL CARD]

Van't Hoff Factors

- Ionic compounds produce multiple solute particles for each formula unit
- The theoretical van't Hoff factor, i , is the ratio of moles of solute particles to moles of formula units dissolved
- The measured van't Hoff factors are generally less than the theoretical values as a result of ion pairing in solution
 - Therefore, the measured van't Hoff factors often cause ΔT to be lower than you might expect

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

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CHEM 1120- 14.7 #2

[SPELL CARD]

Van't Hoff Factors

$$(BP_{\text{solution}} - BP_{\text{solvent}}) = \Delta T_b = i \cdot m \cdot k_b$$

$$(FP_{\text{solvent}} - FP_{\text{solution}}) = \Delta T_f = i \cdot m \cdot k_f$$

$$\Pi = iMRt$$

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CHEM 1120- 15.2



[SPELL CARD]

Factors affecting reaction rate

- Generally, the greater the concentration of reactant molecules, the faster the reaction
 - This increases the frequency of reactant molecule contact
 - Liquids \rightarrow molarity
 - Gases \rightarrow partial pressure
- Increasing temperature increases the reaction rate for most reactions

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CHEM 1120- 14.7 PROB 7

[SPELL CARD]

The osmotic pressure of a 0.0100 M potassium iodide (KI) solution at 25 °C is 0.465 atm. Determine the experimental van't Hoff factor for KI at this concentration.

$$0.465 \text{ atm} = 298.15 \text{ K} \cdot 0.08206 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol} \cdot 1.90058206$$

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CHEM 1120- 15.1

[SPELL CARD]

Chemical kinetics

- The speed of a chemical reaction is called its **reaction rate**
- The reaction rate is a measure of how fast the reaction makes products / uses reactants
- The ability to quantify and control the speed of a chemical reaction is important

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[SPELL CARD]

- Average rate
 - The change in measured concentrations in any particular time period
 - Linear approximation of a curve
- Instantaneous rate
 - The change in concentration at any one particular time
 - Slope at one point of a curve
 - determined by taking the slope of a line tangent to the curve at that particular point
 - In calculus: first derivative of the function

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CHEM 1120- 15.4 #3

[SPELL CARD]

Disappearance/formation rates and stoichiometry



Two moles of A disappear for each mole of B that is formed.

$$\text{rate} = -\frac{1}{2} \frac{\Delta [A]}{\Delta t} = \frac{\Delta [B]}{\Delta t}$$



$$\text{rate} = -\frac{1}{a} \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \frac{\Delta [B]}{\Delta t} = \frac{1}{c} \frac{\Delta [C]}{\Delta t} = \frac{1}{d} \frac{\Delta [D]}{\Delta t}$$

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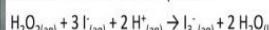
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CHEM 1120- 15.4 PROB 1

[SPELL CARD]

Consider this balanced equation:



In the first 10.0 seconds of the reaction, the concentration of I^- drops from 1.000 M to 0.868 M.

- Calculate the average rate of the reaction in this time interval
- Determine the rate of change in the concentration of H^+ during this time interval

a. Rate = $-1/3 [I]_f - [I]_i / t = -(0.868M - 1.00M) / 10.0s = 4.40 \times 10^{-3} \text{ M/s}$

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CHEM 1120- 15.4

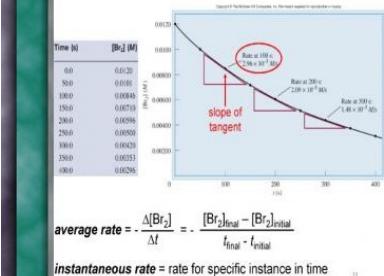
[SPELL CARD]

Chemical kinetics

- The speed of a chemical reaction is called its **reaction rate**
- The reaction rate is a measure of how fast the reaction makes products / uses reactants
- The ability to quantify and control the speed of a chemical reaction is important

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[SPELL CARD]



$$\text{average rate} = -\frac{\Delta [Br_2]}{\Delta t} = -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

$$\text{instantaneous rate} = \text{rate for specific instance in time}$$

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[SPELL CARD]

Some recapping...

- Reporting rate of reaction in terms of disappearance or appearance of one species is ambiguous
- A chemical reaction proceeds at a specific rate, regardless of which species we monitor experimentally
- Rate of reaction is
 - Not determined by concentration of products
 - Not necessarily controlled by concentration of reactants

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[SPELL CARD]

The Rate Law is different!

The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.



$$\text{Rate} = k[A]^x[B]^y$$

Reaction is x th order in AReaction is y th order in BReaction is $(x+y)$ th order overall

Reaction order = Sum of reactant exponents

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[SPELL CARD]

- ### Zero Order reactions: $A \rightarrow \text{product}$
- If a reaction is zero order, the rate of the reaction does not change with changing concentration
 - Doubling [A] will have no effect on the reaction rate
 - Rate law:
 - $\text{Rate} = k[A]^0 = k$
 - Rate constant (k) units:
 - $\text{Rate} = \text{M/sec}, k = \text{M/sec (M sec}^{-1}\text{)}$

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[SPELL CARD]

- ### First order reactions: $A \rightarrow \text{product}$
- If a reaction is first order, the rate is directly proportional to the reactant concentration
 - Doubling [A] will double the rate of the reaction
 - Rate law:
 - $\text{Rate} = k[A]^1 = k[A]$
 - Rate constant (k) units:
 - Since $\text{Rate} = \text{M/sec}, k = \text{sec}^{-1}$

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[SPELL CARD]

Finding the Rate Law: The Initial Rate Method

- The rate law must be determined experimentally
- The rate law shows how the rate of a reaction depends on the concentration of the reactants
- Changing the initial concentration of a reactant may therefore affect the initial rate of the reaction

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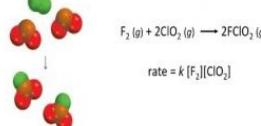
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[SPELL CARD]

Things to remember for Rate Laws

- Rate laws are always determined experimentally
- Reaction order is always defined in terms of reactant (not product) concentrations
- The order of a reactant is not related to the stoichiometric coefficient of the reactant in the balanced chemical equation



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[SPELL CARD]

Reaction order

- The exponent on each reactant in the rate law is called the order with respect to that reactant
- The sum of the exponents on the reactants is called the overall order of the reaction
- If the rate law for the reaction $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$ is as follows:
 - $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$
 - Remember: Rate law does not always agree with stoichiometry
 - The reaction is
 - second order with respect to $[\text{NO}]$
 - first order with respect to $[\text{O}_2]$
 - The reaction is third order overall

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[SPELL CARD]

- ### Second order reactions: $A \rightarrow \text{product}$
- If a reaction is second order, the rate is directly proportional to the square of the reactant concentration
 - Doubling [A] will quadruple the rate of the reaction
 - Rate law:
 - $\text{Rate} = k[A]^2$
 - Rate constant (k):
 - Since $\text{Rate} = \text{M/sec}, k = \text{M}^{-1} \cdot \text{sec}^{-1}$

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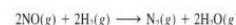
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CHEM 1120- 15.4 PROB 2



[SPELL CARD]

The reaction of nitric oxide with hydrogen at 1280°C is



From the following data collected at this temperature, determine

- the rate law
- units of the rate constant
- the value of the rate constant
- the rate of the reaction when $[\text{NO}] = 12.0 \times 10^{-3} \text{ M}$ and $[\text{H}_2] = 6.0 \times 10^{-3} \text{ M}$

Experiment	$[\text{NO}] (\text{M})$	$[\text{H}_2] (\text{M})$	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.25×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

From exp. z/1 of NO: Rate2/Rate1=5/1.25*4, $2x=4 \Rightarrow x=2$
From exp. y/2 of H2: Rate3/Rate2=10/5*2, $y=1$

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[SPELL CARD]

Integrated rate laws

- For any reaction, for example,



the rate law depends on the concentration of A

- Applying calculus to integrate the rate law gives another equation

- This shows the relationship between the concentration of A and the time of the reaction

- This is the integrated rate law

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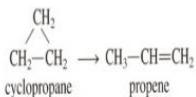
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CHEM 1120- 15.5 PROB 3

[SPELL CARD]

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4} \text{ s}^{-1}$ at 500°C.



- (a) If the initial concentration of cyclopropane was 0.25 M, what is the concentration after 8.8 min? Done

- (b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M?

a. $\ln[A] - kt = \ln[A_0] - 8.8\text{min} \cdot 6.7 \times 10^{-4} \text{ s}^{-1}$; $\ln(A) = -6.7 \times 10^{-4} \text{ s}^{-1} \cdot 8.8\text{min} + \ln(0.25)$

b. $\ln(0.15) = -6.7 \times 10^{-4} \text{ s}^{-1} \cdot t + \ln(0.25)$; $t = \frac{\ln(0.25) - \ln(0.15)}{-6.7 \times 10^{-4} \text{ s}^{-1}}$; $t = 13 \text{ min}$

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CHEM 1120- 15.5.1 #2

[SPELL CARD]

First-order reactions

$$A \longrightarrow \text{product} \quad \text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k[A]^1 = k[A]$$

$$k = \frac{\text{rate}}{[A]} = \frac{M/\text{s}}{M} = 1/\text{s} \text{ or } \text{s}^{-1}$$

$[A]$ is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t = 0$

$$[A] = [A]_0 e^{-kt}$$



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



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[SPELL CARD]

$\ln[A]_0 - kt$

First order

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

$$\ln[A] = (-k)t + \ln[A]_0$$

$$y = mx + b$$

Slope = $-k$

Time

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CHEM 1120- 15.5.2 #2

[SPELL CARD]

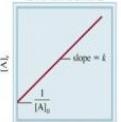
Second-Order Reactions

$$A \longrightarrow \text{product} \quad \text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k[A]^2$$

$$k = \frac{\text{rate}}{[A]^2} = \frac{M/\text{s}}{M^2} = 1/(M \cdot \text{s})$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad [A] \text{ is the concentration of A at any time } t \\ [A]_0 \text{ is the concentration of A at time } t=0$$

$$t_{1/2} = \frac{1}{k[A]_0} \quad \text{--- slope} = k$$



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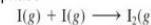
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CHEM 1120- 15.5 PROB 4

[SPELL CARD]

Iodine atoms combine to form molecular iodine in the gas phase



This reaction follows second-order kinetics and has the high rate constant $7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 23°C.

- (a) If the initial concentration of I was 0.086 M, calculate the concentration after 2.0 min.

- (b) Calculate the half-life of the reaction (in seconds) if the initial concentration of I is 0.42 M.

$1/(A) = 1/(0.086\text{M}) \cdot 7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \cdot 2.0\text{min}; 1/(A) = 8.4 \times 10^{-1}\text{M}^{-1}$

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CHEM 1120- 15.5.2 #3

[SPELL CARD]

Zero-Order Reactions

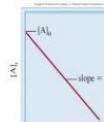
$$A \longrightarrow \text{product} \quad \text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k[A]^0 = k$$

$$k = \frac{\text{rate}}{[A]^0} = M/\text{s}$$

$$[A] = [A]_0 - kt \quad [A] \text{ is the concentration of A at any time } t \\ [A]_0 \text{ is the concentration of A at time } t = 0$$

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

$$t_{1/2} = \frac{[A]_0}{2k}$$



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CHEM 1120- 15.5 #1



[TRAP CARD]

Relationship between Order and Half-Life

- For a **zero order reaction**, the lower the initial concentration of the reactants, the shorter the half-life
 $-t_{1/2} = [A]_0/2k$
- For a **first order reaction**, the half-life is independent of the concentration
 $-t_{1/2} = \ln(2)/k$ or $0.693/k$
- For a **second order reaction**, the half-life is inversely proportional to the initial concentration. Increasing the initial concentration shortens the half-life
 $-t_{1/2} = 1/[k(A)_0]$

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[TRAP CARD]

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_0 - kt = [A]_t$	$y\text{-intercept} = [A]_0$ $\text{Slope} = -k$ $A_t = [A]_0 - \frac{[A]_0}{2} = \frac{1}{2}[A]_0$	$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k}[A]_0$
1	Rate = $k[A]^1$	s^{-1}	$\ln([A]_0) = -kt + \ln([A]_t)$ $\frac{[A]_t}{[A]_0} = e^{-kt}$	$y\text{-intercept} = \ln([A]_0)$ $\text{Slope} = -k$ $A_t = [A]_0 e^{-kt} = [A]_0 e^{-\frac{1}{2}(0.693)}$	$t_{1/2} = \frac{0.693}{k}$
2	Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_0} = kt + \frac{1}{[A]_t}$	$y\text{-intercept} = \frac{1}{[A]_0}$ $\text{Slope} = k$ $A_t = \frac{1}{k[A]_0} + \frac{1}{k[A]_0}$	$t_{1/2} = \frac{1}{k[A]_0} + \frac{1}{k[A]_0}$

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[SPEL CARD]

What influences the rate constant?

- Concentration of reactants:**
 - Increased frequency of collisions
 - Defined by rate law
- Energy of collisions**
 - Breaking bonds in reactants
 - Forming new bonds in products
 - Unimolecular versus multimolecular
- Orientation of colliding molecules**

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[SPEL CARD]

What influences the rate constant? (cont.)

- Temperature:**
 - Increased T increases kinetic energy of molecules
 - Increases # of molecular collisions
- Activation Energy (E_a):**
 - Minimum energy of molecular collisions required
 - Break reactant bonds or form product bonds
- These factors incorporated into rate constant k by Arrhenius Equation**

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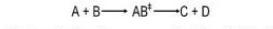
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CHEM 1120- 15.6.1 #1



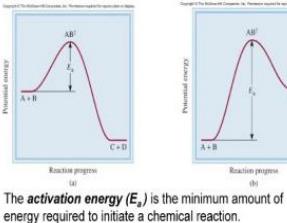
[SPEL CARD]

Chemistry is reactions!



Exothermic Reaction

Endothermic Reaction



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CHEM 1120- 15.6.1 #2



[SPEL CARD]

Activation Energy and the Activated Complex

- There is an energy barrier to almost all reactions
- The **activation energy** is the amount of energy needed to convert reactants into the **activated complex**
 - The activated complex is usually called the **transition state**
- The transition state is a chemical species with partially broken and partially formed bonds

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CHEM 1120- 15.6.2 #1



[SPEL CARD]

Effect of temperature on rate

- Changing the temperature changes the rate constant of the rate law
- This relationship is given by $k = A \cdot e^{(-E_a/RT)}$
- where
 - T is temperature in kelvins
 - R is the gas constant in energy units, 8.314 J/(K · mol)
 - E_a is the activation energy, the extra energy needed to overcome the transition state barrier
 - A is a constant referred to as the frequency factor
 - The rate that the reactant energy approaches the activation energy

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CHEM 1120- 15.6.2 #2



[SPEL CARD]

Arrhenius equation (one more time)

$$k = A \cdot e^{(-E_a/RT)}$$

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Rate constant (k) and T are observable experimentally

We usually use them to get E_a from experiment

Solve Arrhenius equation in terms of E_a !

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[SPEL CARD]

Collision theory

- For an intermolecular reaction to take place, the reacting molecules must collide with each other
- Once molecules collide, they may react together or they may not, depending on two factors:
 - The reacting molecules must have sufficient kinetic energy to form the activated complex
 - The reacting molecule must collide in the proper orientation for new bonds to form

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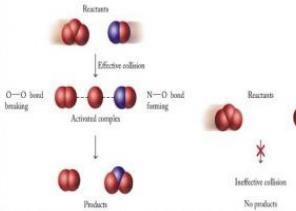
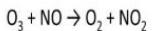
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[SPELL CARD]

Molecular Orientation



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CHEM 1120- 15.6 PROB 5

[SPELL CARD]

The rate constant of a first-order reaction is $3.46 \times 10^{-2} \text{ s}^{-1}$ at 298 K.

What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

$$k_1 = 3.46 \times 10^{-2} \text{ s}^{-1} \quad k_2 = ?$$

$$T_1 = 298 \text{ K} \quad T_2 = 350 \text{ K}$$

$$\ln(K_2/K_1) = E_a / R^*(1/T_1 - 1/T_2)$$

$$\ln(x/3.46E-2) = 5.02E4(1/298.1 - 1/350); K_2 = .702\text{s}^{-1}$$

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CHEM 1120- 15.7 #2

[SPELL CARD]

Reaction mechanisms definitions

- Reaction Mechanism:** Proposed set of steps that describe how a reaction occurs
- Elementary Step:** Molecular-level view of single process in a chemical reaction
- Intermediate:** Species produced in one step of a reaction mechanism and consumed in a later step
- Molecularity:** the number of reactant ions, atoms, or molecules involved in an elementary step

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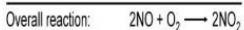
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CHEM 1120- 15.7 #5

[SPELL CARD]

The **molecularity of a reaction** is the number of molecules reacting in an elementary step.

- Unimolecular reaction** – elementary step with 1 molecule
- Bimolecular reaction** – elementary step with 2 molecules
- Termolecular reaction** – elementary step with 3 molecules



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CHEM 1120- 15.6 PROB 5

[SPELL CARD]

CHEM 1120- 15.7 #1

[SPELL CARD]

Reaction mechanisms

- Writing chemical reactions tells us **what**, but nothing about **how**
 - Balanced chemical equation tells us the overall chemical change
 - Activation energy is the first step to understanding **how**
- Describing the series of reactions that occurs to produce the overall observed reaction is called a **reaction mechanism**
- Knowing the rate law of the reaction helps us understand the sequence of reactions in the mechanism

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[SPELL CARD]

An Example of a Reaction Mechanism

- Overall reaction: $\text{H}_2(g) + 2 \text{ICl}(g) \rightarrow 2 \text{HCl}(g) + \text{I}_2(g)$
- Mechanism:
 - $\text{H}_2(g) + \text{ICl}(g) \rightarrow \text{HCl}(g) + \text{HI}(g)$
 - $\text{HI}(g) + \text{ICl}(g) \rightarrow \text{HCl}(g) + \text{I}_2(g)$
- The two reactions in this mechanism are the **elementary steps**
 - They cannot be broken down into simpler steps
 - The molecules interact directly in this manner without any other steps
- Materials that are products in an early mechanism step but reactants in a later step are called **intermediates**

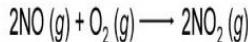
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N_2O_2 is detected during the reaction!



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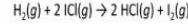
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CHEM 1120- 15.7 #6

[SPELL CARD]

Rate laws for elementary steps

- Each elementary step in the mechanism has its own activation energy and own rate law
- The rate law of an elementary step can be deduced from the chemical equation of that step
- But the rate law for an overall reaction must be determined experimentally



$$\begin{aligned} 1) \text{H}_2(g) + \text{ICl}(g) &\rightarrow \text{HCl}(g) + \text{HI}(g) & \text{Rate} = k_1[\text{H}_2][\text{ICl}] \\ 2) \text{HI}(g) + \text{ICl}(g) &\rightarrow \text{HCl}(g) + \text{I}_2(g) & \text{Rate} = k_2[\text{HI}][\text{ICl}] \end{aligned}$$

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CHEM 1120- 15.7 #7

[SPELL CARD]

Rate Laws and Elementary Steps

The **rate-determining step** is the **slowest** step in the sequence of steps leading to product formation.

Unimolecular reaction $\text{A} \rightarrow \text{products}$ rate = $k[\text{A}]$

Bimolecular reaction $\text{A} + \text{B} \rightarrow \text{products}$ rate = $k[\text{A}][\text{B}]$

Bimolecular reaction $\text{A} + \text{A} \rightarrow \text{products}$ rate = $k[\text{A}]^2$

Writing plausible reaction mechanisms:

- The sum of the elementary steps **must** give the overall balanced equation for the reaction.
- The rate-determining step should predict the same rate law that is determined experimentally.

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[SPELL CARD]

TABLE 15.3 Rate Laws for Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	1	Rate = $k[A]$
$A + A \rightarrow \text{products}$	2	Rate = $k[A]^2$
$A + B \rightarrow \text{products}$	2	Rate = $k[A][B]$
$A + A + A \rightarrow \text{products}$	3 [rare]	Rate = $k[A]^3$
$A + A + B \rightarrow \text{products}$	3 [rare]	Rate = $k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	3 [rare]	Rate = $k[A][B][C]$

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[SPELL CARD]

Rate-determining step

- Some controversy about this when studied in detail
- DOI: 10.1002/cap.201100157
The Rate-Determining Step is Dead. Long Live the Rate-Determining State!
Sebastian Kosuch^{a,b} and Jan M. L. Martin^{b,c}
- The concept of the rate-determining step can break down when studying complex reactions
 - Step with highest activation energy will have the smallest rate constant and slowest rate of reaction

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[SPELL CARD]

Review of criteria for a full reaction mechanism

- Sum of elementary steps must be consistent with the stoichiometry of the overall reaction
- Rate law is based on molecularity of rate-determining step
- Rate law from rate-determining step must be consistent with rate law derived from experimental data

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[SPELL CARD]

Catalysis

- A Catalyst** is a substance added to a reaction that increases the rate of the reaction but is not consumed
- Homogeneous catalysis** is when catalyst and reacting species are the *same* phase
 - Typical inorganic catalysis
 - Biochemistry
- Heterogeneous catalyst** is when catalyst and reacting species are different phases
 - Catalysis on metal surfaces

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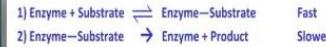
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[SPELL CARD]

Enzymes: bio-catalysis

- Most biological reactions require a catalyst to proceed at a reasonable rate
- Protein molecules that catalyze biological reactions are called **enzymes**
- Enzymes work by adsorbing the substrate (sometimes called "ligand") onto an **active site** that orients the substrate for reaction



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[SPELL CARD]

Equilibrium is a state in which there are no observable changes as time goes by

Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal, and
- the concentrations of the reactants and products remain constant



Physical equilibrium



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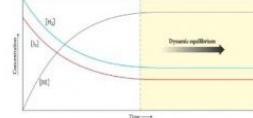
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[SPELL CARD]

Dynamic equilibrium

- Dynamic equilibrium** is the condition when the rates of the forward and reverse reactions are equal
 - The forward reaction slows and the reverse reaction accelerates, eventually they reach the same rate
- At equilibrium, the concentrations of all the chemicals remain constant because the chemicals are being consumed and formed at the same rate



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[SPELL CARD]

Attention!

- The rates of the forward and reverse reactions are equal at equilibrium
- That does **not** mean the concentrations of reactants and products are equal!
- Some reactions reach equilibrium only after almost all the reactant molecules are consumed:
 - The position of equilibrium favors the products
- Other reactions reach equilibrium when only a small percentage of the reactant molecules are consumed:
 - The position of equilibrium favors the reactants

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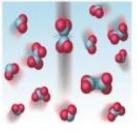
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CHEM 1120- 16.3.1

[SPELL CARD]

Definitions

- The Law of mass action shows that for a reversible reaction at equilibrium (and at a specific T), the concentration ratio of products/reactants are constant
- This constant is called the **equilibrium constant** (K)



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CHEM 1120- 16.3.3 #2

[SPELL CARD]

What does the value of K imply when it is less than 1?

- When the value of $K \ll 1$, at equilibrium there will be many more reactant molecules present than product molecules
- When $K < 1$, the position of equilibrium always favors reactants



$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$\text{Red} + \text{Blue} \rightleftharpoons \text{Red Blue}$$

$$K = \frac{[NO]^2}{[N_2][O_2]} = 4.9 \times 10^{-3}$$

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CHEM 1120- 16.3.6

[SPELL CARD]

K and stoichiometry

- When the coefficients of an equation are multiplied by a factor, the equilibrium constant is raised to that factor
- The equilibrium constant expression for the reaction $aA + bB \rightleftharpoons cC$ $K_1 = \frac{[C]^c}{[A]^a \times [B]^b}$
- The equilibrium constant expression for the reaction $2aA + 2bB \rightleftharpoons 2cC$ $K_2 = \frac{[C]^{2c}}{[A]^{2a} \times [B]^{2b}}$ or $K_2 = \left(\frac{[C]^c}{[A]^a \times [B]^b} \right)^2$
- Therefore, $K_1 = K_2^n$

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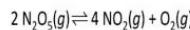
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CHEM 1120- 16.3.2

[SPELL CARD]

Writing Equilibrium Constant Expressions

For the reaction,



the expression for the equilibrium constant, K , is as follows:

$$K = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

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CHEM 1120- 16.3.4

[SPELL CARD]

TABLE 16.1 Initial and Equilibrium Concentrations for the Reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 445 °C

Initial Concentrations	Equilibrium Concentrations		Equilibrium Constant as Defined by the Law of Mass Action	
	[H ₂]	[I ₂]		
0.50	0.50	0.0	0.11	0.11
0.0	0.0	0.50	0.055	0.39
0.50	0.50	0.50	0.165	0.165
1.0	0.50	0.0	0.53	0.033
0.50	1.0	0.0	0.033	0.53

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CHEM 1120- 16.3.3 #1

[SPELL CARD]

What does the value of K imply when it is greater than 1?

- When the value of $K > 1$, at equilibrium there will be many more product molecules present than reactant molecules



$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

$$\text{Red} + \text{Blue} \rightleftharpoons \text{Red Blue}$$

$$K = \frac{[HBr]^2}{[H_2][Br_2]} = 1.9 \times 10^9$$

- When $K > 1$, the position of equilibrium always favors products

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CHEM 1120- 16.3.5

[SPELL CARD]

K and reverse reactions

- When the reaction is written in reverse, the equilibrium constant, K , is inverted
- The equilibrium constant expression for the reaction $aA + bB \rightleftharpoons cC + dD$ (forward) $K_{\text{forward}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- The equilibrium constant expression for the reaction $cC + dD \rightleftharpoons aA + bB$ (reverse) $K_{\text{reverse}} = \frac{[A]^a[B]^b}{[C]^c[D]^d}$

$$\text{Therefore, } K_{\text{forward}} = 1/K_{\text{reverse}}$$

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CHEM 1120- 16.3.6

[SPELL CARD]

K and stoichiometry

- When the coefficients of an equation are multiplied by a factor, the equilibrium constant is raised to that factor
- The equilibrium constant expression for the reaction $aA + bB \rightleftharpoons cC$ $K_1 = \frac{[C]^c}{[A]^a \times [B]^b}$
- The equilibrium constant expression for the reaction $2aA + 2bB \rightleftharpoons 2cC$ $K_2 = \left(\frac{[C]^c}{[A]^a \times [B]^b} \right)^2$
- Therefore, $K_1 = K_2^n$

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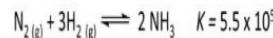
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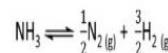
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[SPELL CARD]

The chemical equation and equilibrium constant for the synthesis of ammonia at 25 °C is



What is the equilibrium constant for the following reaction at 25 °C?



$[NH_3]/[N_2][H_2]^3 \cdot kf = 5.5e5; kr \cdot [H_2]^3[N_2]/[NH_3]^2; kr = 1/5.5E5 \cdot \text{Sqr} \frac{1.8E-6}{1.3E-3}$

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CHEM 1120- 16.4

[SPELL CARD]

Equilibrium Constant for an Overall Reaction

- Similar to the use of Hess's Law of constant heat summation:



- If the reaction is expressed as the sum of two or more reactions, K_c for the overall reaction is given by the **product** of the equilibrium constants of the individual reactions

$$K(3) = K(1) \times K(2)$$

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[SPELL CARD]

Equilibrium Constants for Reactions Involving Gases

- The concentration of a gas in a mixture is proportional to its partial pressure
- Therefore, the equilibrium constant can be expressed as the ratio of the partial pressures of the gases
- For $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$, the equilibrium constant expressions are as follows:

$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \quad \text{or} \quad K_p = \frac{P_c^c \times P_d^d}{P_a^a \times P_b^b}$$

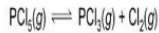
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[SPELL CARD]

The equilibrium constant K_p for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine



is found to be 1.05 at 250°C. If the equilibrium partial pressures of PCl_3 and Cl_2 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?

k=1.05--kp+ pCl3*pOz/PpCl5; 1.05*.463*pCl3/.875=1.98 atm
Chnge n=1; kp-kc(RT)Chnge n-- kp/RT-kc;
1.05/.0821*523.15*.0245*kC

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[SPELL CARD]

Equilibrium in the gas phase

- Ideal Gas Law:

- $PV = nRT \rightarrow P = (n/V)RT$
- n/V is moles per liter (molarity: M)
- $K_p = K_c(RT)^{\Delta n}$
- $\Delta n = \text{number of moles of gaseous products minus the number of moles of gaseous reactants}$
- The difference in stoichiometric constants:
 $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$
- $\Delta n = (c + d) - (a + b)$
- $R = \text{gas constant}; T = \text{temperature}$

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