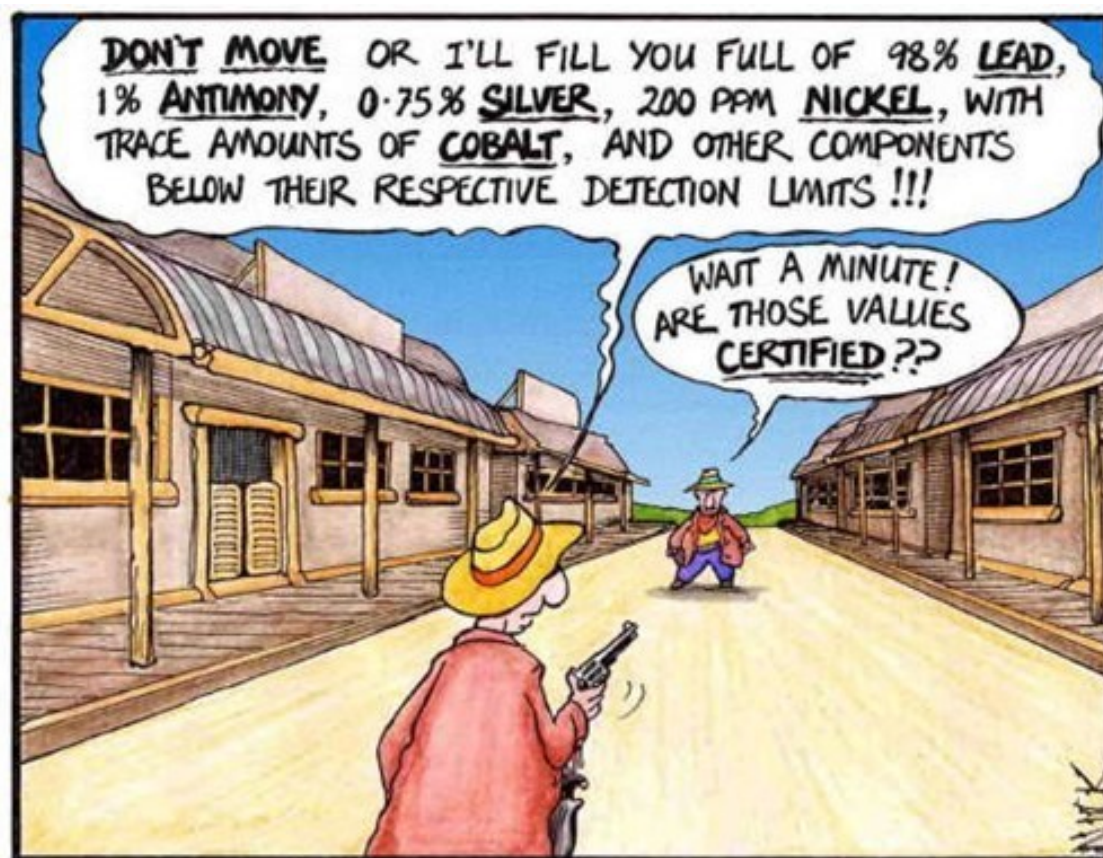


# WELCOME!

## Analytical Chemistry

### CHEM 2354



ANALYTICAL CHEMISTS IN THE WILD WEST

SCHOOLFAILBLOG.ORG

# Analytical Chemistry

CHEM 2354, Winter 2015

## Schedule:

Tuesday	LEC	10:00-11:30	Montpetit Hall (MNT)	Room: 202
Thursday	LEC	08:30-10:00	Montpetit Hall (MNT)	Room: 202
Tuesday	DGD	14:30-15:30	Hagen Hall (HGN)	Room: 302
Thursday	DGD	14:30-15:30	Social Science Building (FSS)	Room: 2005
Monday	LAB	14:30-18:30	Marion Hall (MRN)	Room: 301
Monday	LAB	08:30-12:30	Marion Hall (MRN)	Room: 301

**Lecture Instructor:** Professor Maxim Berezovski

## Office:

Address: D'lorio Hall room 201

Phone: 613-562-5800 ext. 1898

e-mail: Maxim.Berezovski@uottawa.ca

web page: <http://mysite.science.uottawa.ca/mberezov/>

## Office Hours:

15:30-17:30 Tuesdays & Thursdays (after DGDs)

*I am in my office many other times during the week and am always willing to speak with you if you find me in or make an appointment.*

**Lab Instructor:** Prof. Heshel Teitelbaum, [Heshel.Teitelbaum@uottawa.ca](mailto:Heshel.Teitelbaum@uottawa.ca)

All questions about labs will be transferred to Dr. Teitelbaum.

# Course Calendar

Date	Chapter	Lecture Topic	Mark
13-Jan	0, 1	Measurements	
15-Jan	2, 3	Tools & Errors	
15-20 Jan	Assignment 1 (online, based on ch. 0-3)		10 pts (2%)
20-Jan	4	Statistics	
22-Jan	5	Calibration	
22-27 Jan	Assignment 2 (online, based on ch. 4, 5)		10 pts (2%)
27-Jan	6	Titrations	
29-Jan	7	Gravimetric & Combustion Analysis	
29-Jan - 3-Feb	Assignment 3 (online, based on ch. 6, 7)		10 pts (2%)
3-Feb	8	Monoprotic Acid/Base	
5-Feb	9	Buffers	
5-10 Feb	Assignment 4 (online, based on ch. 8, 9)		10 pts (2%)
10-Feb	10	Acid/Base Titration	
12-Feb	11	Polyprotic Acid/Base	
16-22 Feb	Reading week		
19-24 Feb	Assignment 5 (online, based on ch. 10, 11)		10 pts (2%)
24-Feb	12	Activity & Ionic Strength	
26-Feb	13	EDTA Titration	
1-Mar	Midterm Exam (offline, closed book, ch.0-13, MNT202, 12:30 PM – 2:30 PM)		100 pts (20%)
3-Mar	14	Electrode Potentials	
5-Mar	15	Electrodes & Potentiometry	
5-10 Mar	Assignment 6 (online, based on ch. 14, 15)		10 pts (2%)
10-Mar	16	Redox Titration	
12-Mar	17	Instrumental Methods in Electrochemistry	
12-17 Mar	Assignment 7 (online, based on ch. 16, 17)		10 pts (2%)
17-Mar	18	Spectrophotometry	
19-Mar	19	Luminescence	
19-24 Mar	Assignment 8 (online, based on ch. 18, 19)		10 pts (2%)
24-Mar	20	Atomic Spectroscopy	
26-Mar	21	Principles of Chromatography	
26-31 Mar	Assignment 9 (online, based on ch. 20)		5 pts (1%)
31-Mar	21	Liquid Chromatography	
2-Apr	22	Gas Chromatography	
7-Apr	22	Mass Spectrometry	
9-Apr	23	Electrophoresis	
7-14 Apr	Assignment 10 (online, based on ch. 21, 22, 23)		15 pts (3%)
Laboratory (6 experiments, reports-due to the end of each lab, except lab 2)			100 pts (20%)
TBA	Final Exam (offline, closed book, all chapters)		200 pts (40%)
Class Activity			Bonus 15 pts
Practice Assignments			Bonus 2 pts
<b>Total: 500 pts (100%) + 17 pts (3.4%, extra points)</b>			

# ***Required Items:***

1. Textbook: “Exploring Chemical Analysis” 5/e Daniel C. Harris, Freeman & Co., New York

<http://www.macmillanhighered.com/Catalog/product/exploringchemicalanalysis-fifthedition-harris>

[http://www.amazon.ca/Exploring-Chemical-Analysis-Daniel-Harris/dp/1429295767/ref=sr\\_1\\_1?ie=UTF8&qid=1418084415&sr=8-1&keywords=Exploring+Chemical+Analysis](http://www.amazon.ca/Exploring-Chemical-Analysis-Daniel-Harris/dp/1429295767/ref=sr_1_1?ie=UTF8&qid=1418084415&sr=8-1&keywords=Exploring+Chemical+Analysis)

2. Solutions Manual for Exploring Chemical Analysis (optional)

3. Sapling Learning Online Account (\$38.25)

<http://www2.saplinglearning.com/higher-education>

4. Lecture Tools Online Account (\$0)

[https://my.lecturetools.com/users/generic\\_invite/e7b9fa8da9ee41d619e9d7b34ac51161](https://my.lecturetools.com/users/generic_invite/e7b9fa8da9ee41d619e9d7b34ac51161)

5. Lab Manual

6. Safety glasses and a lab coat

7. 2 bound notebooks (hard cover or spiral bound), a calculator, a permanent marker, a ruler

# Introduction to Analytical Chemistry

## *Background*

### 1.) **Definition:**

ANALYTICAL CHEMISTRY: The Science of Chemical Measurements.

### 2.) **Types of Questions Asked in Analytical Chemistry**

a.) What is in the sample? (qualitative analysis)

b.) How much is in the sample? (quantitative analysis)

### 3.) **Techniques used in Analytical Chemistry:**

a.) Wet Chemical Methods: titrations, color-forming reactions, precipitations, etc.

b.) Instrumental Methods: spectrometry, chromatography, mass spectrometry.



**What is it ?**

**How much is there?**

**How pure is it?**

**What are the impurities?**

**The table shows the extent to which industrial employers think students should have experience with various analytical techniques, as determined by the 2014 survey.**

<b>Group 1 (&gt;66%)</b>	<b>Group 2 (33–66%)</b>	<b>Group 3 (&lt;33%)</b>
UV–vis absorption, potentiometer (pH measurement), GC, HPLC, IR absorption, atomic absorption, autotitration	MS, optical microscopy, flame atomic emission, microwave digestion, X-ray fluorescence	NMR, CHN analysis, CE, molecular fluorescence, gel electrophoresis, ICPMS, ICP-optical emission spectroscopy, surface analysis, electrochemical techniques, thermal methods

# The Analytical Process

## 1.) **Formulating the Question:**

Translate General Question into Specific Question

*Is this coffee strong? → What is the concentration of caffeine?*

## 2.) **Selecting Analytical Procedures:**

a.) Choose procedure to measure caffeine

- (i) Sample preparation
- (ii) Uncertainty in measurement
- (iii) Limit of detection
- (iv) Availability, time, cost

b.) If necessary, develop new procedure

## 3.) **Sampling:**

a.) Select representative material to analyze

- (i) don't use the entire sample
- (ii) consistency in sample collection



Kazuki Yamamoto is a Japanese barista who constructs eye-popping works of 3D art using just foam and coffee.



**Try Asking for One of These at Starbucks**

**Within the six years Yamamoto has been working at a coffee shop in Osaka, he's racked up more than 100,000 Twitter followers obsessed with his latte art.**

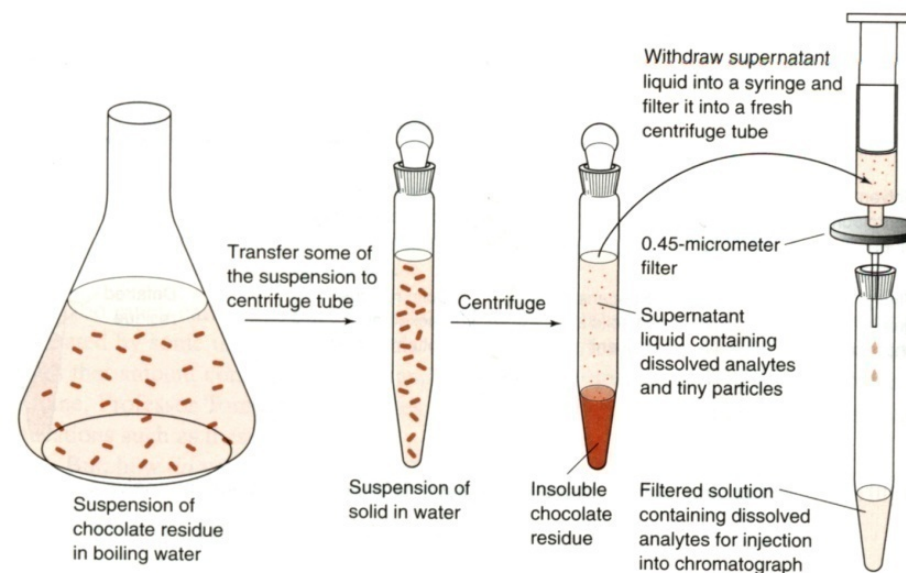
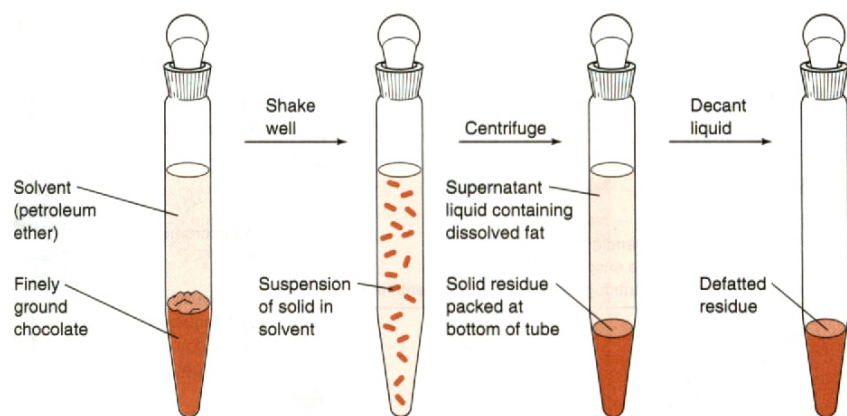
# Introduction to Analytical Chemistry

## The Analytical Process

### 4.) Sample Preparation:

a.) convert sample into form suitable for chemical analysis

- (i) Remove species that interfere with analysis
- (ii) Dissolve sample
- (iii) Concentrate sample



# Introduction to Analytical Chemistry

## The Analytical Process

### 5.) Analysis:

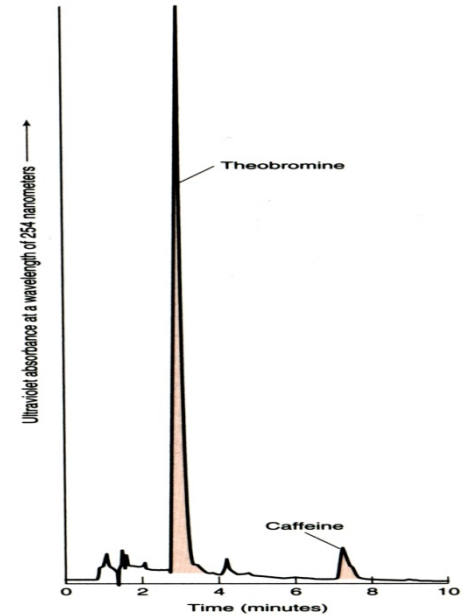
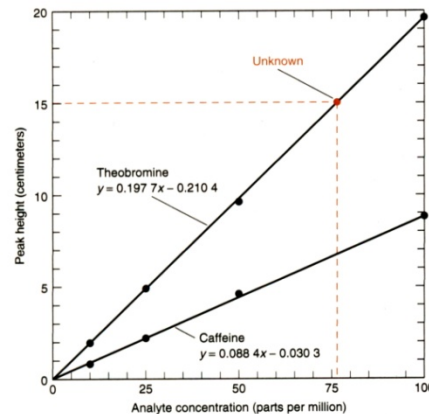
a.) measure concentration of analyte in several identical **aliquots** (portions)

(i) Replicate measurements → uncertainty in the analysis

- Avoid large errors
- Reliability of measurement

(ii) Calibration Curve

- Measure response for *known samples*



### 6.) Report and Interpretation of Results

### 7.) Drawing Conclusions

a) How the Report is used

# Units and Concentrations

*To a large extent, analytical chemistry is a science of measurement and measurements require minimizing errors*

## Units of Measurement

### 1.) **SI (International System of Units)** from the French Le Système International d'Unités:

- a.) International units of measurement (metric units)
- b.) ALL SI units are based on certain fundamental quantities

**Table 1-1** Fundamental SI units

Quantity	Unit (symbol)	Definition
Length	meter (m)	One meter is the distance light travels in a vacuum during $\frac{1}{299\,792\,458}$ of a second.
Mass	kilogram (kg)	One kilogram is the mass of the prototype kilogram kept at Sèvres, France.
Time	second (s)	One second is the duration of 9 192 631 770 periods of the radiation corresponding to a certain atomic transition of $^{133}\text{Cs}$ .
Electric current	ampere (A)	One ampere of current produces a force of $2 \times 10^{-7}$ newtons per meter of length when maintained in two straight, parallel conductors of infinite length and negligible cross section, separated by 1 meter in a vacuum.
Temperature	kelvin (K)	Temperature is defined such that the triple point of water (at which solid, liquid, and gaseous water are in equilibrium) is 273.16 K, and the temperature of absolute zero is 0 K.
Luminous intensity	candela (cd)	Candela is a measure of luminous intensity visible to the human eye. One cd is the luminous intensity in a given direction of a source that emits monochromatic radiation of frequency $540 \times 10^{12}$ hertz and of which the radiant intensity in that direction is $\frac{1}{683}$ watt per steradian.
Amount of substance	mole (mol)	One mole is the number of atoms in exactly 0.012 kg of $^{12}\text{C}$ (approximately $6.022 \times 10^{23}$ ).
Plane angle	radian (rad)	There are $2\pi$ radians in a circle.
Solid angle	steradian (sr)	There are $4\pi$ steradians in a sphere.

# Units and Concentrations

## Units of Measurement

### 1.) SI Units:

c.) To indicate multiples or fractions of units, various prefixes are used

### Example:

$$3.2 \times 10^{-11} \text{ s} = 32 \times 10^{-12} \text{ s} = 32 \text{ ps}$$

Prefix	Symbol	Factor
Mega	M	$10^6$
Kilo	k	$10^3$
Hecto	h	$10^2$
Deca	da	$10^1$
Deci	d	$10^{-1}$
Centi	c	$10^{-2}$
Milli	m	$10^{-3}$
Micro	$\mu$	$10^{-6}$
Nano	n	$10^{-9}$
Pico	p	$10^{-12}$
Femto	f	$10^{-15}$
Atto	a	$10^{-18}$



# Units and Concentrations

## *Units of Measurement*

- 1.) **SI Units:**  
 d.) conversions to SI units  
 e.) **Liter is commonly used for volume instead of m<sup>3</sup>**

Quantity	Unit	Symbol	SI equivalent
Volume	liter	L	*10 <sup>-3</sup> m <sup>3</sup>
	milliliter	mL	*10 <sup>-6</sup> m <sup>3</sup>
Length	angstrom	Å	*10 <sup>-10</sup> m
	inch	In.	*0.0254 m
Mass	pound	lb	*0.45359237 kg
	metric ton		*1000 kg
Force	dyne	dyn	*10 <sup>-5</sup> N
Pressure	bar	bar	*10 <sup>5</sup> Pa
	atmosphere	atm	*101325 Pa
	torr	Torr	133.322 Pa
Energy	pound/in <sup>2</sup>	psi	6894.76 Pa
	erg	erg	*10 <sup>-7</sup> J
	electron volt	eV	1.602176462x10 <sup>-19</sup> J
Power	calorie, thermochemical	cal	*4.184 J
	Calorie (British)	Cal	*1000 cal = 4.184 kJ
	British thermal unit	Btu	1055.06 J
Temperature	horsepower		745.700 W
Temperature	Centigrade (= Celsius)	°C	*K - 273.15
	Fahrenheit	°F	*1.8(K - 273.15) + 32

# Units and Concentrations

## Units of Measurement

### 2.) Expressions of Concentration:

a.) Molarity (moles/L, or M):

#### Most common unit of concentration

- Number of moles of a substance per liter of total solution.
- Recall: 1 mole (mol) of a substance =  $6.022\ 141\ 29 \times 10^{23}$  units (atoms, molecules, ions, etc).
- Molecular weight (MW) or molecular mass: the mass of a substance that contains 1 mole.
- $1\text{L} = (0.1\text{ m})^3 = 10^{-3}\text{ m}^3$
- Expressed by squared brackets as in  $[\text{H}^+]$

Molality (moles/kg or  $m$ ):

- Number of moles of a substance per kilogram of solvent (not total solution).
- Molality does not change when temperature changes.

$$M = \frac{d \times m}{1 + m \times \text{MW}}$$

$$m = \frac{M}{d - M \times \text{MW}}$$

$d$  – density of solvent in g/L



DO IT WITH MOLES

Celebrate “Mole Day” at 6:02 am on October 23 (10/23) every year

$$1 \text{ mol/L} = 1 \text{ mol/dm}^3 = 1 \text{ mol dm}^{-3} = 1 \text{ M} = 1000 \text{ mol/m}^3$$

Name	Abbreviation	Concentration	Concentration (SI unit)
millimolar	mM	$10^{-3} \text{ mol/dm}^3$	$10^0 \text{ mol/m}^3$
micromolar	$\mu\text{M}$	$10^{-6} \text{ mol/dm}^3$	$10^{-3} \text{ mol/m}^3$
nanomolar	nM	$10^{-9} \text{ mol/dm}^3$	$10^{-6} \text{ mol/m}^3$
picomolar	pM	$10^{-12} \text{ mol/dm}^3$	$10^{-9} \text{ mol/m}^3$
femtomolar	fM	$10^{-15} \text{ mol/dm}^3$	$10^{-12} \text{ mol/m}^3$
attomolar	aM	$10^{-18} \text{ mol/dm}^3$	$10^{-15} \text{ mol/m}^3$
zeptomolar	zM	$10^{-21} \text{ mol/dm}^3$	$10^{-18} \text{ mol/m}^3$

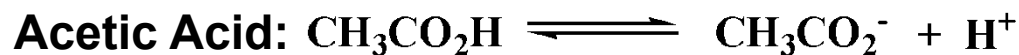
# Units and Concentrations

## *Units of Measurement*

### 2.) **Expressions of Concentration:**

#### b.) Formality (F):

- (i) Concentrations expressed in M describe the actual concentration of a given chemical species in solution.
- (ii) Some chemicals when placed in solution will dissociate or converted to multiple forms
  - **Example:**



- (iii) Not convenient to refer to the concentrations of each individual form.
- (iv) Instead, concentration of total substance originally added to the solution is used.
  - **Formal concentration or Formality given in (mol/L)**
  - **Note: For compounds with a single form in solution, M = F**

# Units and Concentrations

## Units of Measurement

### 2.) Expressions of Concentration:

#### c.) Percent Composition:

- (i) **Weight Percent (wt/wt or w/w):** Concentration expressed in terms of mass of substance versus the total mass of the sample.

$$\text{Weight percent} = \frac{\text{mass of substance}}{\text{mass of total solution or total sample}} \times (100)$$

- (ii) **Volume Percent (vol/vol or v/v):** Concentration expressed in terms of volume of substance versus the total volume of the sample.

$$\text{Volume percent} = \frac{\text{volume of substance}}{\text{volume of total solution or total sample}} \times (100)$$

- (iii) **Weight-Volume Percent (wt/vol or w/v):** Concentration expressed in terms of mass of substance versus the total volume of the sample.

$$\text{weight - volume percent} = \frac{\text{mass of substance}}{\text{volume of total solution or total sample}} \times (100)$$



# Units and Concentrations

## *Units of Measurement*

### 2.) **Expressions of Concentration:**

#### d.) Percent Composition:

(iv) **Instead of expressing concentrations as a percentage, express in terms of:**

- **parts per thousand (ppt) –  $\times 10^3$**
- **parts per million (ppm) –  $\times 10^6$**
- **parts per billion (ppb) –  $\times 10^9$**

**If a DILUTE solution has a concentration of 1 ppm, it would be approximately 1 mg/L or 1  $\mu\text{g/mL}$  (valid if  $d_{\text{mix}} = 1.0 \text{ g/mL}$ )**

### 3.) **Solution Preparation:**

#### a.) Dilution of a Solution:

$$M_c V_c = M_d V_d$$

**where:**

$M_c$  = Molarity of substance in the concentrated solution

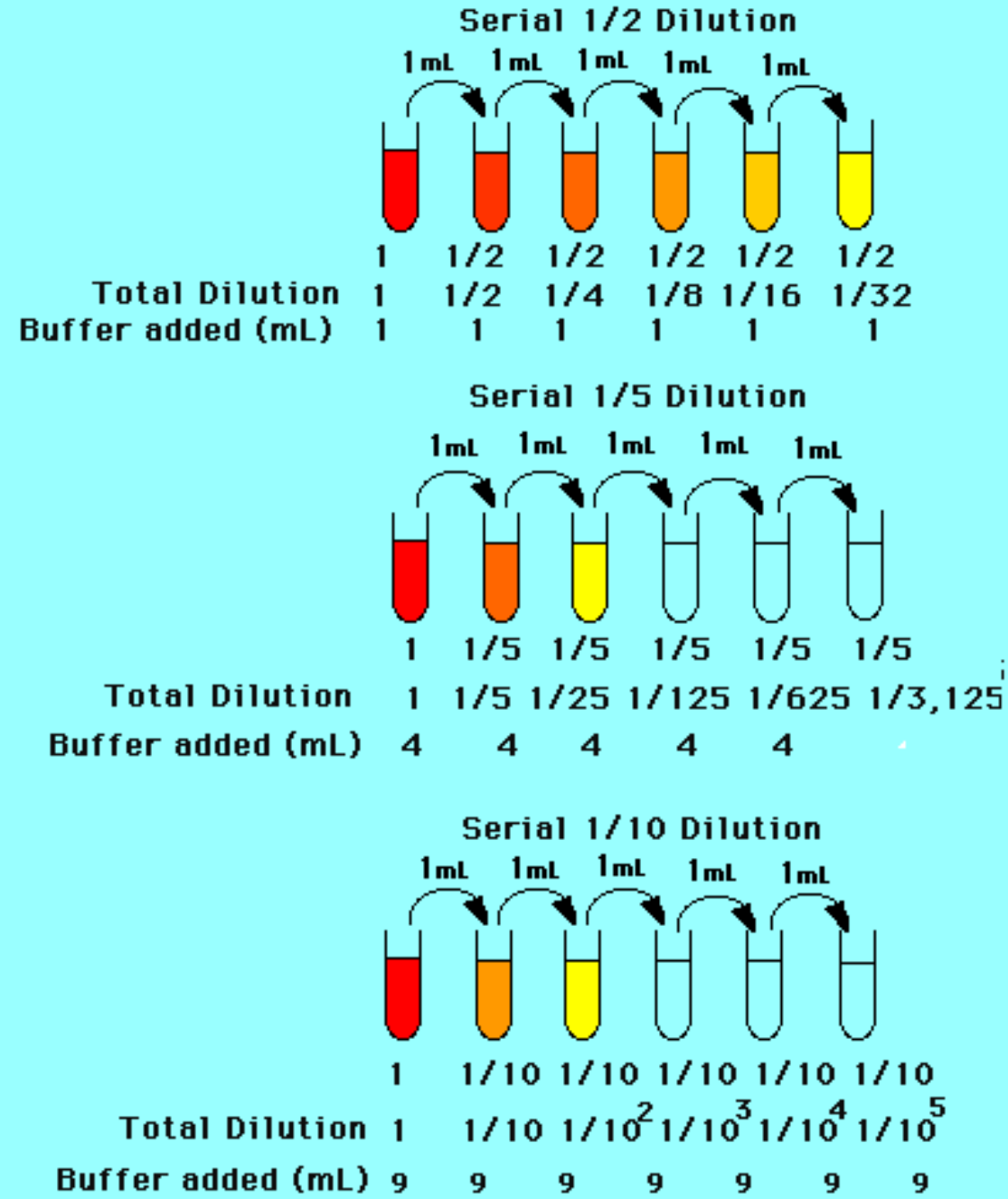
$V_c$  = volume of concentrated solution used

$M_d$  = desired Molarity of the diluted solution

$V_d$  = total volume of final diluted solution

**Serial dilution** is the stepwise dilution of a substance in solution. Usually the dilution factor at each step is constant, resulting in a geometric progression of the concentration in a logarithmic fashion.

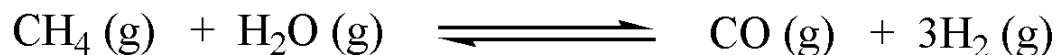
Serial dilutions are used to accurately create highly diluted solutions as well as solutions for experiments resulting in concentration curves with a logarithmic scale.



# Chemical Equilibrium

## Introduction

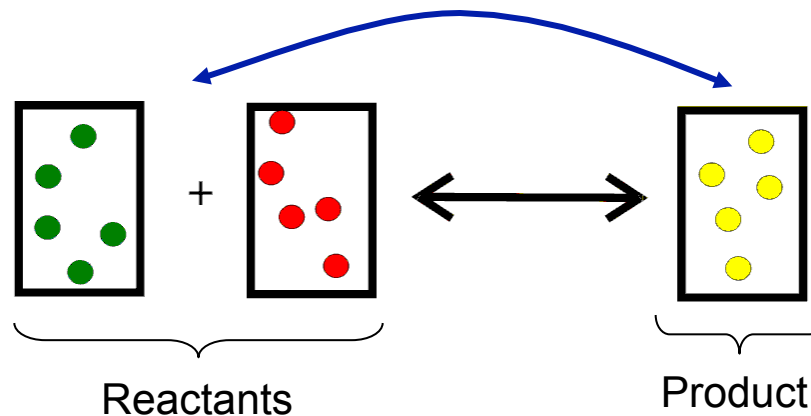
- 1.) **Equilibria govern diverse phenomena**
  - **Protein folding, acid rain action on minerals to aqueous reactions**
- 2.) **Chemical equilibrium applies to reactions that can occur in both directions:**



- **reactants are constantly forming products and vice-versa**
- **At the beginning of the reaction, the rate that the reactants are changing into the products is higher than the rate that the products are changing into the reactants.**
- **When the net change of the products and reactants is zero the reaction has reached equilibrium.**

First, system reaches equilibrium

Then, system continually exchanges products and reactants, while maintaining equilibrium distribution.

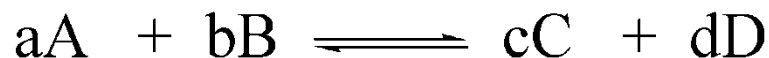


***At equilibrium the amount of reactants and products are constant, but not necessarily equal***

# Chemical Equilibrium

## *Equilibrium Constant*

- 1.) The relative concentration of products and reactants at equilibrium is a constant.
- 2.) Equilibrium constant ( $K$ ):
  - For a general chemical reaction



*Equilibrium constant:* 
$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

**Where:**

- small superscript letters are the stoichiometry coefficients
- $[A]$  concentration chemical species A relative to standard state

# Chemical Equilibrium

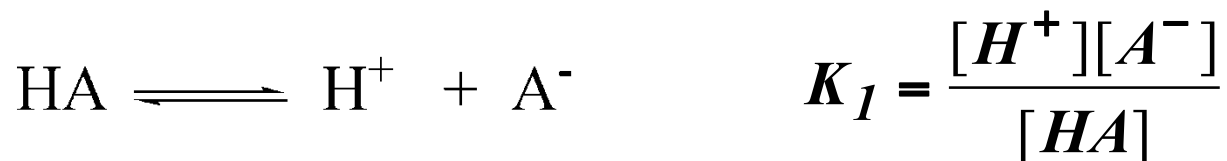
## *Equilibrium Constant*

### 2.) Equilibrium constant ( $K$ ):

- A reaction is favored when  $K > 1$
- $K$  has no units, dimensionless
  - Concentration of solutes should be expressed as moles per liter (M).
  - Concentrations of gases should be expressed in bars.
    - ▶ express gas as  $P_{\text{gas}}$ , emphasize pressure instead of concentration
    - ▶ 1 bar =  $10^5$  Pa; 1 atm = 1.01325 bar
  - Concentrations of pure solids, pure liquids and solvents are omitted
    - ▶ are unity
    - ▶ standard state is the pure liquid or solid

### 3.) Manipulating Equilibrium Constants

Consider the following reaction:



*Reversing the reaction results in a reciprocal equilibrium reaction:*

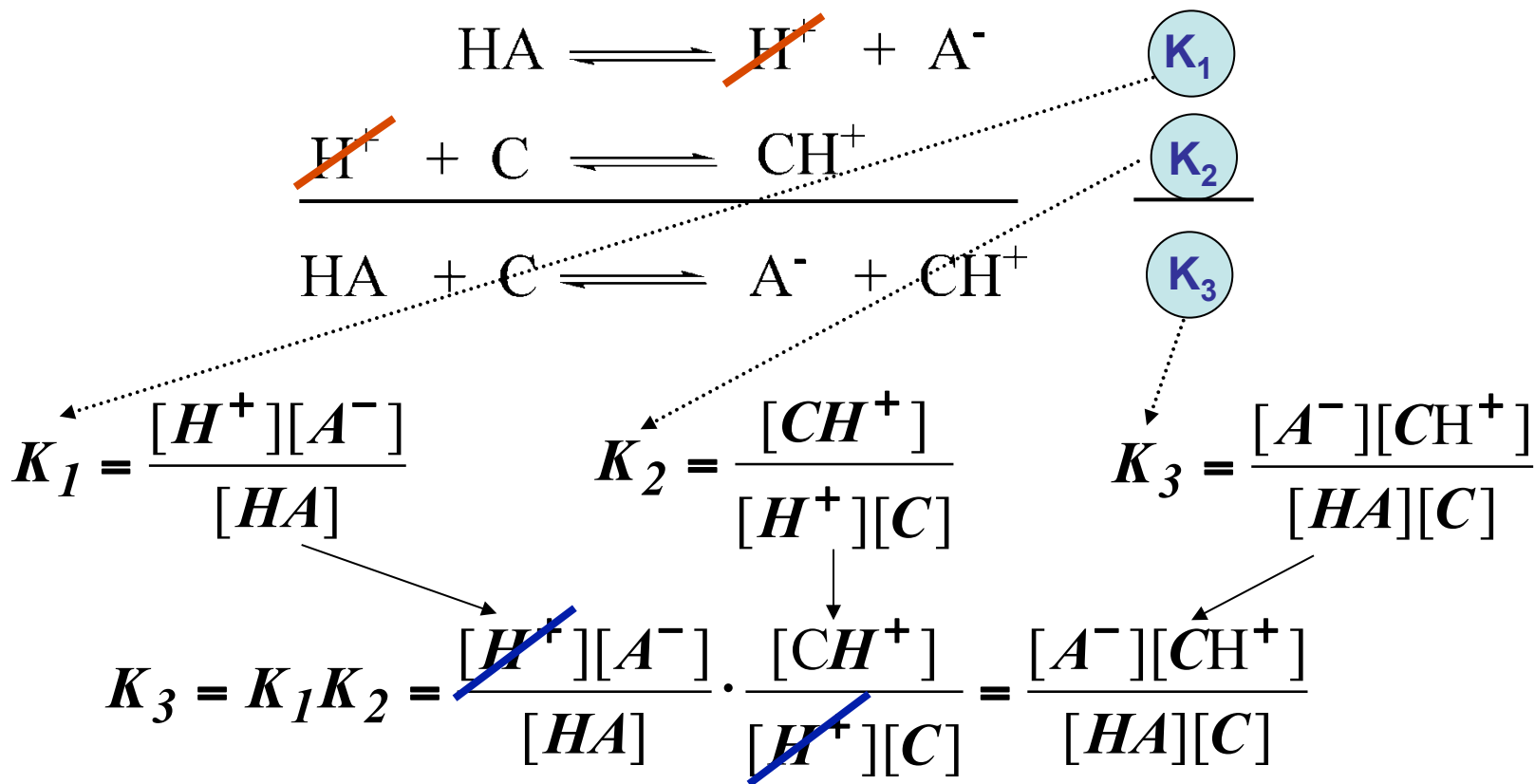


# Chemical Equilibrium

## Equilibrium Constant

### 3.) Manipulating Equilibrium Constants

*If two reactions are added, the new K is the product of the two individual K values:*



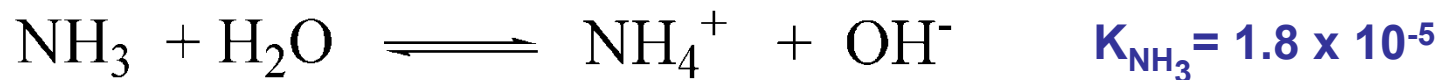
# Chemical Equilibrium

## Equilibrium Constant

### 3.) Manipulating Equilibrium Constants

➤ Example:

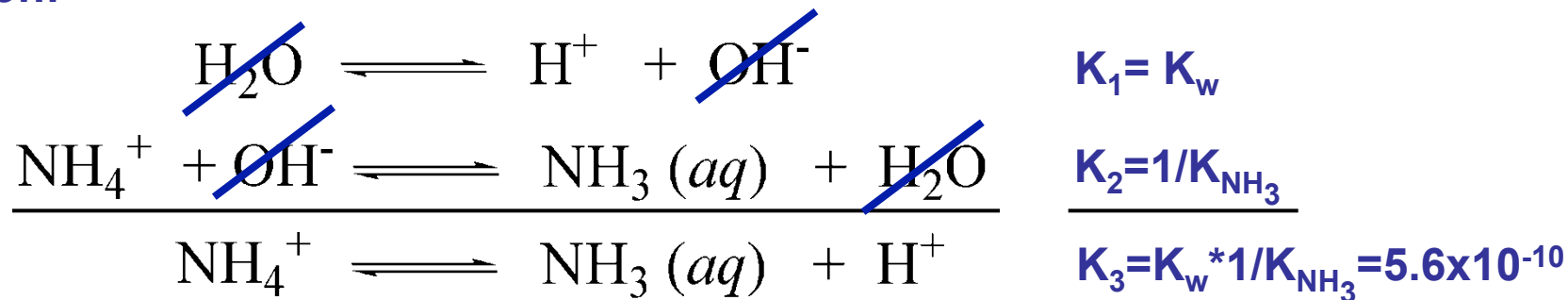
Given the reactions and equilibrium constants:



Find the equilibrium constant for the reaction:



Solution:



# Chemical Equilibrium

## *Le Châtelier's Principal*

### 1.) What Happens When a System at Equilibrium is Perturbed?

#### ➤ Le Châtelier's Principal:

- If a system in equilibrium is disturbed, the direction in which the system proceeds back to equilibrium is such that the disturbance is partially offset.

**Consider this reaction:**  $\text{CO (g)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$

**At equilibrium:**



**Add excess CO(g):**



To return to equilibrium (balance), some (*not all*) CO and H<sub>2</sub> are converted to CH<sub>3</sub>OH

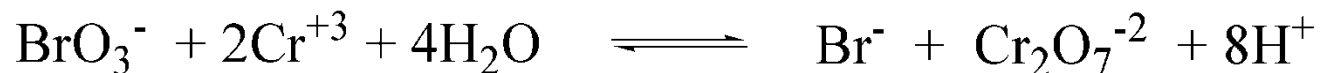
***If all added CO was converted to CH<sub>3</sub>OH, then reaction would be unbalanced by the amount of product***

# Chemical Equilibrium

## *Le Châtelier's Principal*

### 2.) Example:

Consider this reaction:



$$K = \frac{[\text{Br}^-][\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^8}{[\text{BrO}_3^-][\text{Cr}^{3+}]^2} = 1 \times 10^{11} \text{ at } 25^\circ \text{C}$$

At one equilibrium state:

$$[\text{H}^+] = 5.0 \text{ M} \quad [\text{Cr}_2\text{O}_7^{2-}] = 0.10 \text{ M} \quad [\text{Cr}^{3+}] = 0.0030 \text{ M}$$

$$[\text{Br}^-] = 1.0 \text{ M} \quad [\text{BrO}_3^-] = 0.043 \text{ M}$$

# Chemical Equilibrium

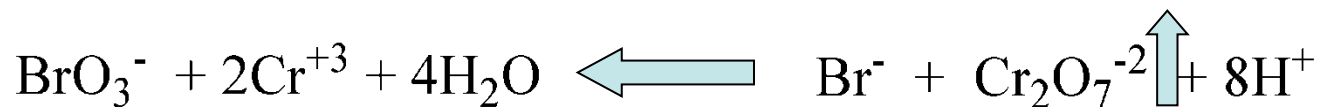
## *Le Châtelier's Principal*

### 2.) Example:

What happens when:

$[\text{Cr}_2\text{O}_7^{2-}]$  *increased from 0.10 M to 0.20 M*

According to Le Châtelier's Principal, reaction should go back to left to off-set dichormate on right:



Use reaction quotient (Q), Same form of equilibrium equation, but not at equilibrium:

$$Q = \frac{[\text{Br}^-][\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^8}{[\text{BrO}_3^-][\text{Cr}^{3+}]^2} = \frac{(1.0)(0.20)(5.0)^8}{(0.043)(0.0030)^2} = 2 \times 10^{11} > K$$

# Chemical Equilibrium

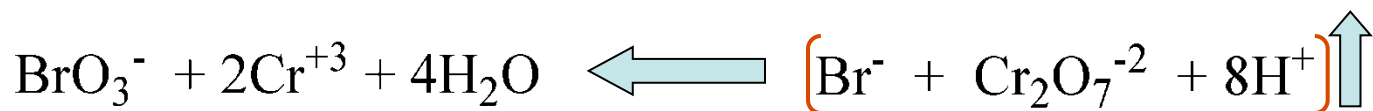
## *Le Châtelier's Principal*

### 2.) Example:

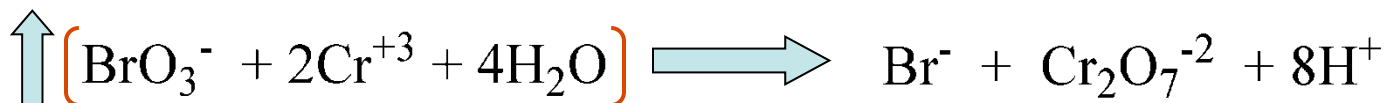
Because  $Q > K$ , the reaction must go to the left to decrease numerator and increase denominator.

Continues until  $Q = K$ :

1. If the reaction is at equilibrium and products are added (or reactants removed), the reaction goes to the left



2. If the reaction is at equilibrium and reactants are added ( or products removed), the reaction goes to the right



# Chemical Equilibrium

## *Le Châtelier's Principal*

### 3.) Affect of Temperature on Equilibrium

**Combine Gibbs free energy and Equilibrium Equations:**

$$\begin{aligned}K &= e^{-\Delta G^\circ / RT} = e^{-(\Delta H^\circ - T\Delta S) / RT} \\ &= e^{-\left(\Delta H^\circ / RT + \Delta S / R\right)} \\ &= e^{-\Delta H^\circ / RT} \cdot e^{\Delta S^\circ / R}\end{aligned}$$

**Only Enthalpy term is temperature dependent:**

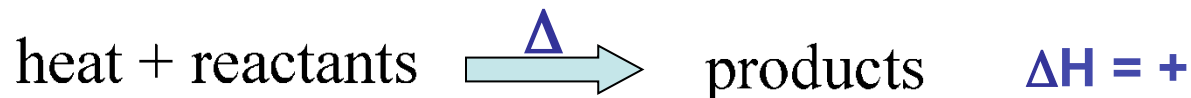
$$K(T) \propto e^{-\Delta H^\circ / RT}$$

# Chemical Equilibrium

## *Le Châtelier's Principal*

### 3.) Affect of Temperature on Equilibrium

1. Equilibrium constant of an endothermic reaction ( $\Delta H^\circ = +$ ) increases if the temperature is raised.



2. Equilibrium constant of an exothermic reaction ( $\Delta H^\circ = -$ ) decreases if the temperature is raised.

