101- chem
GENERAL CHEMISTRY-1

First Mid Term
(15 marks)

Second Mid Term
(15 marks)

Lab
(30 marks)

Mid term
(30 marks)

Final
(100 marks)

Course# and Name: Chem-101, General chemistry-I

Semester credit hours: 4.0 credit. Second Term 1436-1437

Total Contact Hours: 39 hr. theory (Sun,Tue, Thurs 10-11)
+ 24 hr. lab

101-Chem

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Total Contact Hours: **14 weeks x 3 hrs Theory**
(Sun, Tues, Thurs 10-11)
14x 2 hrs Lab (Mon 10-12)

Mid Term Exam: (First mid-term: Tues, 21/5, 12-1)
(Second mid-term: Tues, 27/6,12-1)

General Chemistry-1

Book: Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop

Chapter	Subject
1	**Chapter 1: The Mole and Stoichiometry (7 hrs)**
2	**Chapter 2: Properties of Gases (6 hrs)**
3	**Chapter 3: Energy and Thermodynamics (7 hrs)**
4	**Chapter 4: Chemical Kinetics (4 hrs)**
5	**Chapter 5: Properties of Solutions (5 hrs)**
6	**Chapter 6: Chemical Equilibrium (7 hrs)**
7	**Chapter 7: Acids and Bases (3 hrs)**

Chapter 1
The Mole and Stoichiometry

Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop

International System of Units (SI)

- Standard system of units
- Metric
- Seven Base Units

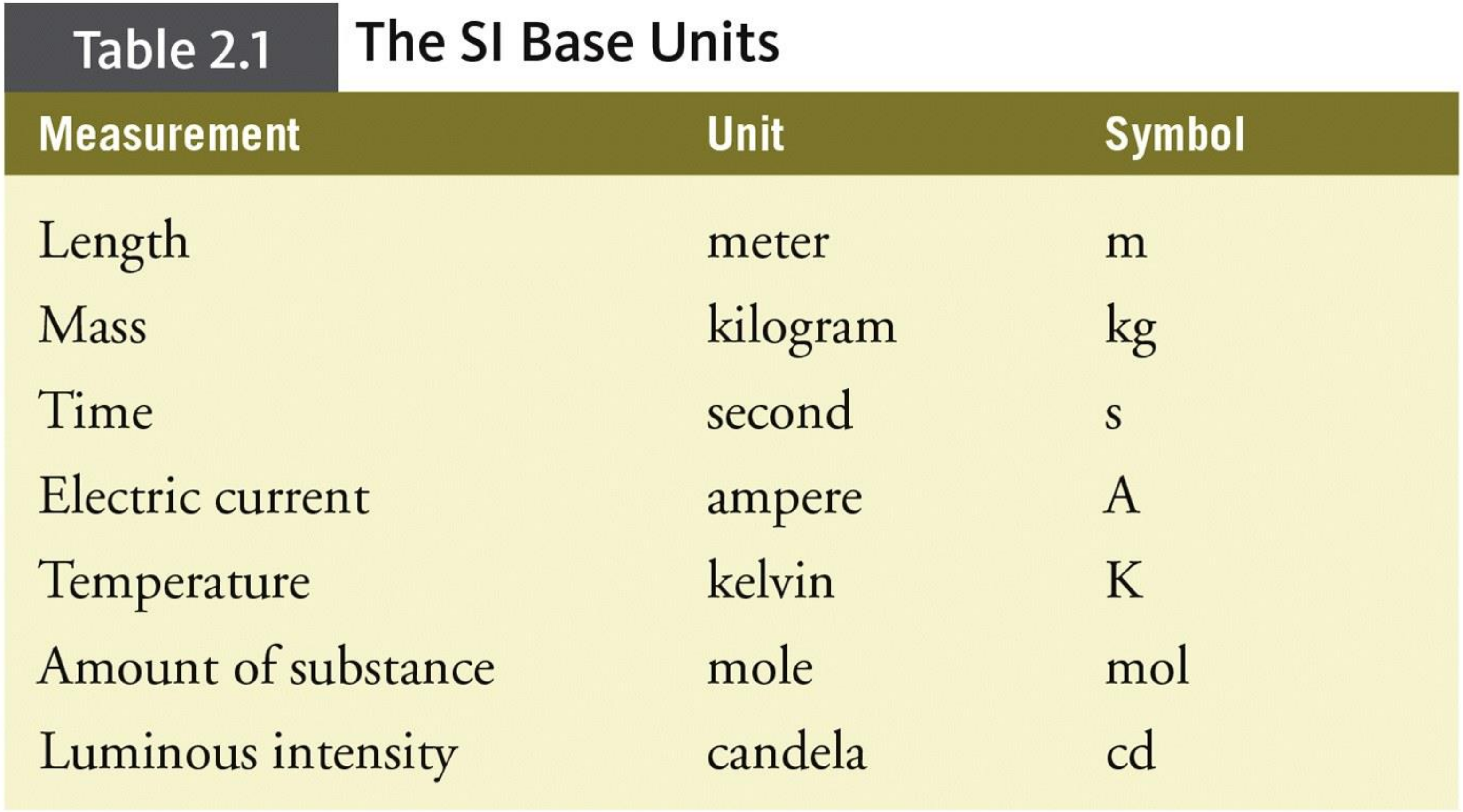

Table 2.1 The SI Base Units

Measurement	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

Your Turn!

The SI unit of **length** is the

A. millimeter
B. meter
C. yard
D. centimeter
E. foot

Decimal Multipliers

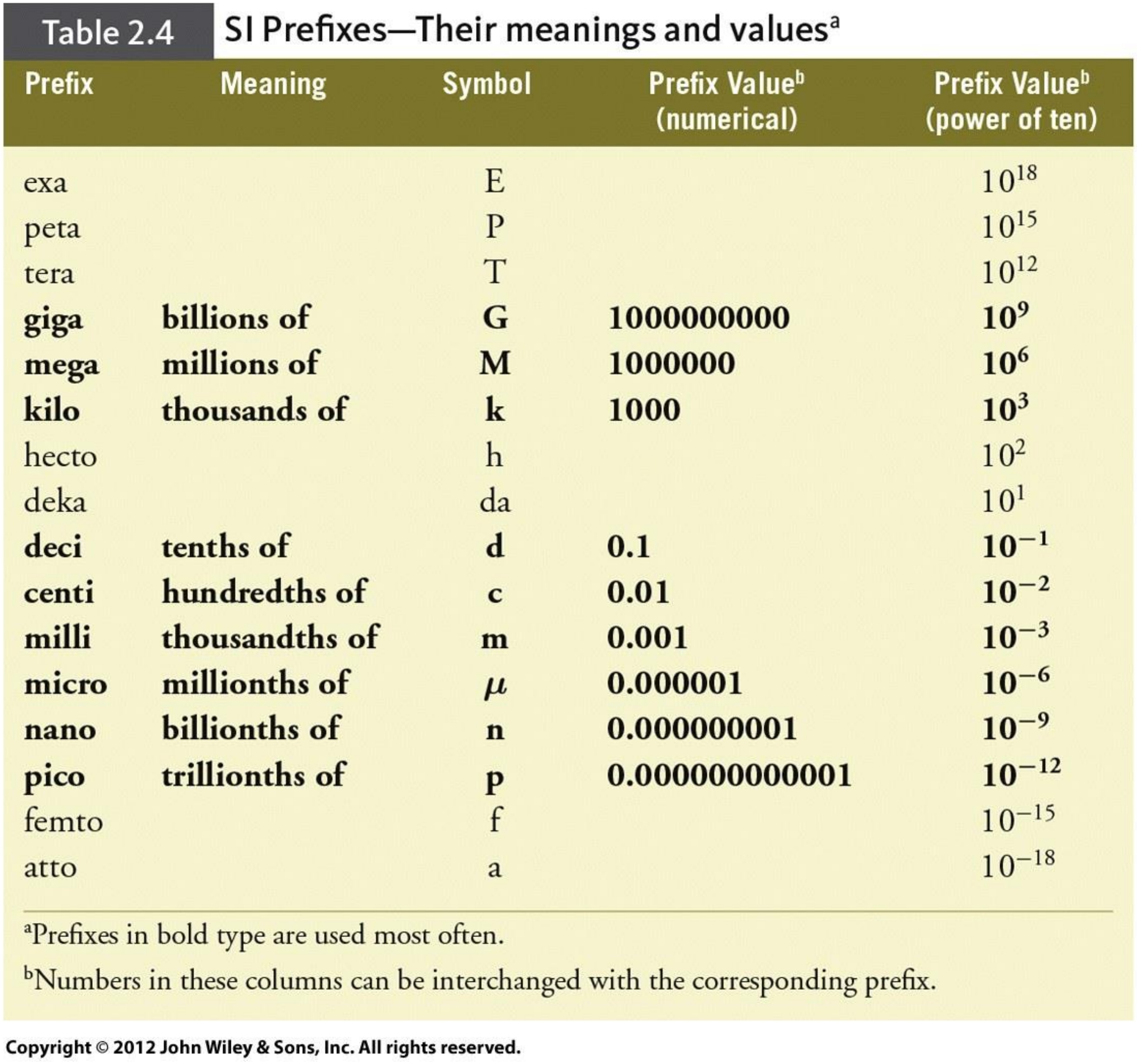

Table 2.4 SI Prefixes—Their meanings and values[a]

Prefix	Meaning	Symbol	Prefix Value[b] (numerical)	Prefix Value[b] (power of ten)
exa		E		10^{18}
peta		P		10^{15}
tera		T		10^{12}
giga	**billions of**	**G**	**1000000000**	$\mathbf{10^{9}}$
mega	**millions of**	**M**	**1000000**	$\mathbf{10^{6}}$
kilo	**thousands of**	**k**	**1000**	$\mathbf{10^{3}}$
hecto		h		10^{2}
deka		da		10^{1}
deci	**tenths of**	**d**	**0.1**	$\mathbf{10^{-1}}$
centi	**hundredths of**	**c**	**0.01**	$\mathbf{10^{-2}}$
milli	**thousandths of**	**m**	**0.001**	$\mathbf{10^{-3}}$
micro	**millionths of**	$\boldsymbol{\mu}$	**0.000001**	$\mathbf{10^{-6}}$
nano	**billionths of**	**n**	**0.000000001**	$\mathbf{10^{-9}}$
pico	**trillionths of**	**p**	**0.000000000001**	$\mathbf{10^{-12}}$
femto		f		10^{-15}
atto		a		10^{-18}

[a] Prefixes in bold type are used most often.

[b] Numbers in these columns can be interchanged with the corresponding prefix.

Using Decimal Multipliers

- Use prefixes on SI base units when number is too large or too small for convenient usage
- Numerical values of multipliers can be interchanged with prefixes

Ex. 1 mL = 10^{-3} L

  - 1 km = 1000 m
  - 1 ng = 10^{-9} g
  - 1,130,000,000 s = 1.13×10^{9} s = 1.13 Gs

Laboratory Measurements

- **Four common**
  1. Distance (*d*)
  2. Volume
  3. Mass
  4. Temperature

Laboratory Measurements

1. Distance (*d*)

- SI Unit is **meter (m)**
- Meter too large for most laboratory measurements
- Commonly use
  - **Centimeter (cm)**
    - 1 cm = 10^{-2} m = 0.01 m
  - **Millimeter (mm)**
    - 1 mm = 10^{-3} m = 0.001 m

2. Volume (V)

- Dimensions of (*dm*)^3
- SI unit for Volume = m^3
- Most laboratory measurements use *V* in liters (L)
  - 1 L = 1 dm^3 (exactly)
- Chemistry glassware marked in L or mL
  - 1 L = 1000 mL
- What is a mL?
  - 1 mL = 1 cm^3

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3. Mass

- SI unit is **kilogram (kg)**
  - Frequently use grams (g) in laboratory as more realistic size
- 1 kg = 1000 g 1 g = 0.1000 kg = $\frac{1}{1000}$ g

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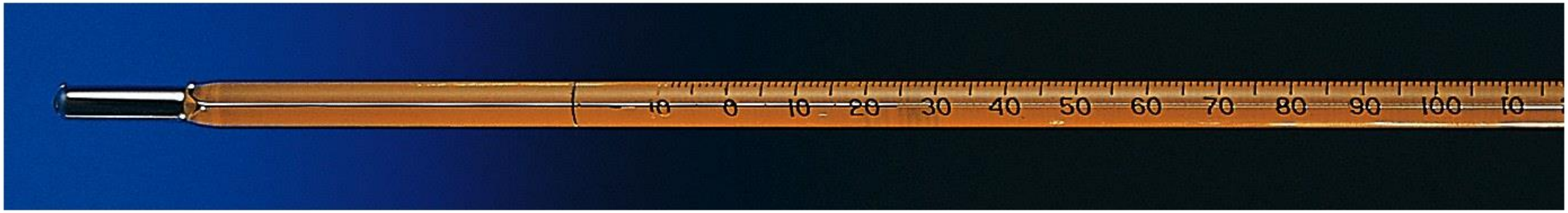
4. Temperature

A. Celsius scale

- Most common for use in science
- Water freezes at 0 °C
- Water boils at 100 °C
- 100 degree units between melting and boiling points of water



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4. Temperature

B. Kelvin scale

- SI unit of temperature is **kelvin (K)**
- Water freezes at 273.15 K and boils at 373.15 K
  - 100 degree units between melting and boiling points

Absolute Zero

  - Zero point on Kelvin scale
  - 0 K= - 273.15 °C

Temperature Conversions

- Must convert to Kelvin scale

$$\boxed{T_{\mathrm{K}} = (t_{\mathrm{C}} + 273.15\,^{\circ}\mathrm{C})\frac{1\,\mathrm{K}}{1\,^{\circ}\mathrm{C}}}$$

- **Ex.** What is the Kelvin temperature of a solution at 25 °C?

$$T_{\mathrm{K}} = (25\,^{\circ}\mathrm{C} + 273.15\,^{\circ}\mathrm{C})\frac{1\,\mathrm{K}}{1\,^{\circ}\mathrm{C}} \quad \mathbf{= 298\ K}$$

Learning Check: T Conversions

Ex. **Convert 77 K to the Celsius scale.**

$$T_K = (t_C + 273.15\,^\circ\text{C})\frac{1\,\text{K}}{1\,^\circ\text{C}} \qquad t_C = (T_K - 273.15\text{K})\frac{1\,^\circ\text{C}}{1\,\text{K}}$$

$$t_C = (77\,\text{K} - 273.15\text{K})\frac{1\,^\circ\text{C}}{1\,\text{K}}$$

= –196 °C

Table 2.2 Some Non-SI Metric Units Commonly Used in Chemistry

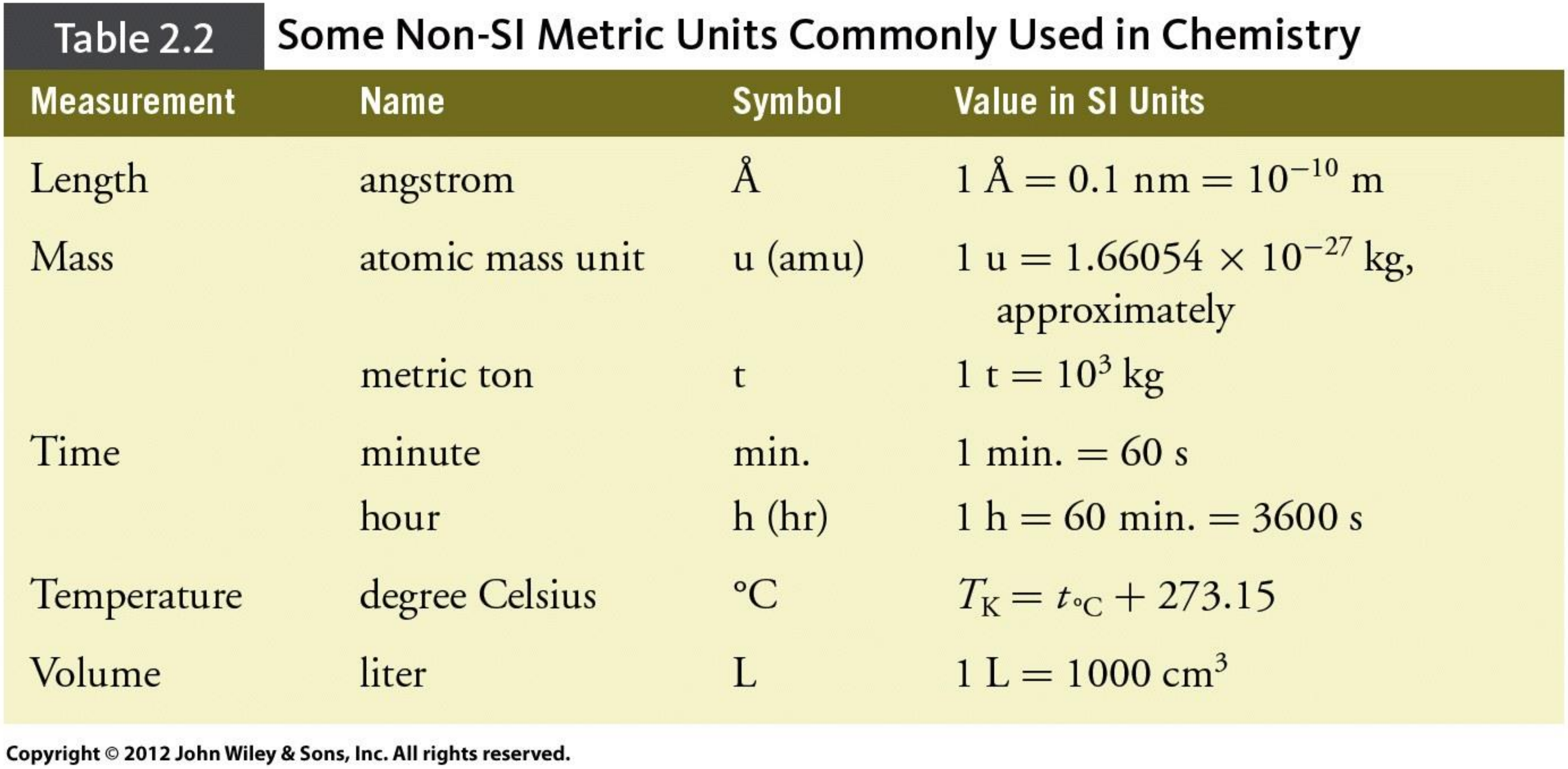

Table 2.2 Some Non-SI Metric Units Commonly Used in Chemistry

Measurement	Name	Symbol	Value in SI Units
Length	angstrom	Å	1 Å = 0.1 nm = 10^{-10} m
Mass	atomic mass unit	u (amu)	1 u = 1.66054×10^{-27} kg, approximately
	metric ton	t	1 t = 10^3 kg
Time	minute	min.	1 min. = 60 s
	hour	h (hr)	1 h = 60 min. = 3600 s
Temperature	degree Celsius	°C	$T_K = t_{°C} + 273.15$
Volume	liter	L	1 L = 1000 cm^3

Derived SI Units

- All physical quantities will have units derived from these seven SI base units

  Ex. Area

  - Derived from SI units based on definition of area
  - length × width = area
  - meter × meter = area

    $m \times m = m^2$
  - SI unit for area = square meters = m^2

Density

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$d = \frac{m}{V}$$

Units

- **g/mL** or **g/cm^3**

Learning Check

- What is the SI unit for velocity?

$$\text{Velocity } (v) = \frac{\text{distance}}{\text{time}}$$

$$\text{Velocity units} = \frac{\text{meters}}{\text{seconds}} = \frac{\text{m}}{\text{s}}$$

- What is the SI unit for volume of a cube?

Volume (V) = length × width × height

V = meter × meter × meter

$\boldsymbol{V = \text{m}^3}$

More Derived Units

Quantity	Definition	Units
Area	Length × width	m^2
Volume	Length × width × height	m^3
Density	Mass / volume	kg/m^3, g/cm^3, g/mL
Speed	Distance / time	m s^{-1}
Acceleration	Change in speed / time	m s^{-2}
Frequency	Event / time	s^{-1}
Force	Mass × acceleration	kg m s^{-2} (newton, N)
Pressure	Force / area	kg m^{-1} s^{-2} (pascal, Pa)
Energy	Force × distance	kg m^2 s^{-2} (joule, J)

Stoichiometry

Stoichiometric Calculations

- Conversions from one set of units to another using Dimensional Analysis

$$m = n \times MM$$

$$N = n \times N_A$$

m: mass, n: amount (mol), MM: molar mass, N: number of particles, N_A: Avogadro's no

The Mole

- Number of atoms in exactly 12 grams of ^{12}C atoms

Ex. How many atoms in 1 mole of ^{12}C ?

  - Based on experimental evidence

1 mole of ^{12}C = 6.022×10^{23} atoms = 12.011 g

Avogadro's number = N_A

- **1 mole of X = 6.022×10^{23} units of X**
- Number of atoms, molecules or particles in one mole
  - 1 mole Xe = 6.022×10^{23} Xe atoms
  - 1 mole NO_2 = 6.022×10^{23} NO_2 molecules

Moles of Compounds

Atoms

- **Atomic Mass**
  - Mass of atom (from periodic table)
- **1 mole of atoms = gram atomic mass**
  = 6.022×10^{23} atoms

Molecules

- **Molecular Mass**
  - Sum of atomic masses of all atoms in compound's formula

1 mole of molecule X = gram molecular mass of X
= 6.022×10^{23} molecules

Moles of Compounds

Ionic compounds

- **Formula Mass**
  - Sum of atomic masses of all atoms in ionic compound's formula

1 mole ionic compound X = gram formula mass of X

= 6.022×10^{23} formula units

General

Molar mass (MM)

- Mass of 1 mole of substance (element, molecule, or ionic compound) under consideration

1 mol of X = gram molar mass of X

= 6.022×10^{23} formula units

SI Unit for Amount = Mole

1 mole of substance X = gram molar mass of X

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  - 1 mole S = 32.06 g S
  - 1 mole NO_2= 46.01 g NO_2
- Molar mass is our conversion factor between g & moles
- **1 mole of X = 6.022 × 10^{23} units of X**
- N_A is our conversion factor between moles & molecules
  - 1 mole H_2O = 6.022 × 10^{23} molecules H_2O
  - 1 mole NaCl = 6.022 × 10^{23} formula units NaCl

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Learning Check: Using Molar Mass

Ex. How many moles of iron (Fe) are in 15.34 g Fe?

- What do we know?

1 mol Fe = 55.85 g Fe

- What do we want to determine?

15.34 g Fe = ? Mol Fe

Start → 15.34 g Fe

End → Mol Fe

- Set up ratio so that what you want is on top & what you start with is on the bottom

$$15.34\,\cancel{\text{g Fe}} \times \left(\frac{1\,\text{mol Fe}}{55.85\,\cancel{\text{g Fe}}}\right) = 0.2747 \text{ mole Fe}$$

Learning Check: Using Molar Mass

Ex. If we need 0.168 mole $Ca_3(PO_4)_2$ for an experiment, how many grams do we need to weigh out?

- Calculate MM of $Ca_3(PO_4)_2$

3 × mass Ca = 3 × 40.08 g = 120.24 g

2 × mass P = 2 × 30.97 g = 61.94 g

8 × mass O = 8 × 16.00 g = 128.00 g

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1 mole $Ca_3(PO_4)_2$ = 310.18 g $Ca_3(PO_4)_2$

- What do we want to determine?

0.168 g $Ca_3(PO_4)_2$ = ? Mol Fe

Start → ← End

Learning Check: Using Molar Mass

$$0.160\ \cancel{\text{mol Ca}_3(\text{PO}_4)_2} \times \left(\frac{310.18\text{g Ca}_3(\text{PO}_4)_2}{1\ \cancel{\text{mol Ca}_3(\text{PO}_4)_2}}\right)$$

= 52.11 g $Ca_3(PO_4)_2$

Your Turn!

Ex. How many moles of CO_2 are there in 10.0 g?

A. 1.00 mol

B. 0.0227 mol

C. 4.401 mol

D. 44.01 mol

E. 0.227 mol

Molar mass of CO_2

1 × 12.01 g = 12.01 g C

2 × 16.00 g = 32.00 g O

1 mol CO_2 = 44.01 g CO_2

n=m/MM

$$10.0\ \cancel{\text{g CO}_2}\left(\frac{1\ \text{mol CO}_2}{44.01\ \cancel{\text{g CO}_2}}\right)$$

= 0.227 mol CO_2

Your Turn!

Ex. How many grams of platinum (Pt) are in 0.475 mole Pt?

A. 195 g

B. 0.0108 g

C. 0.000513 g

D. 0.00243 g

E. 92.7 g

Molar mass of Pt = 195.08 g/mol

$$0.475\,\cancel{\text{mol Pt}} \times \left(\frac{195.08\,\text{g Pt}}{1\,\cancel{\text{mol Pt}}}\right)$$

= 92.7 g Pt

Ex. How many silver atoms are in a 85.0 g silver bracelet?

- What do we know?

107.87 g Ag = 1 mol Ag

1 mol Ag = 6.022×10^{23} Ag atoms

- What do we want to determine?

85.0 g silver = ? atoms silver

g Ag ⟶ mol Ag ⟶ atoms Ag

$$85.0\ \cancel{\text{g Ag}} \times \left(\frac{1\ \cancel{\text{mol Ag}}}{107.87\ \cancel{\text{g Ag}}}\right) \times \left(\frac{6.022\times10^{23}\ \text{atoms Ag}}{1\ \cancel{\text{mol Ag}}}\right)$$

= **4.7×10^{23} Ag atoms**

Using Avogadro's Number

Ex. What is the mass, in grams, of one molecule of octane, C_8H_{18}?

Molecules octane ⟶ mol octane ⟶ g octane

1. Calculate molar mass of octane

Mass C $= 8 \times 12.01 \text{ g} = 96.08 \text{ g}$

Mass H $= 18 \times 1.008 \text{ g} = 18.14 \text{ g}$

1 mol octane = 114.22 g octane

2. Convert 1 molecule of octane to grams

$$\left(\frac{114.22 \text{ g octane}}{1\ \cancel{\text{mol octane}}}\right) \times \left(\frac{1\ \cancel{\text{mol octane}}}{6.022 \times 10^{23} \text{ molecules octane}}\right)$$

$= \mathbf{1.897 \times 10^{-22}}$ **g octane**

Learning Check: Mole Conversions

Ex. Calculate the number of formula units of Na_2CO_3 in 1.29 moles of Na_2CO_3.

$$1.29\,\cancel{\text{mol Na}_2\text{CO}_3}\left(\frac{6.0223\times10^{23}\text{ formula units Na}_2\text{CO}_3}{1\,\cancel{\text{mol Na}_2\text{CO}_3}}\right)$$

$= 7.77\times10^{23}$ particles Na_2CO_3

Ex. How many moles of Na_2CO_3 are there in 1.15 x 10^5 formula units of Na_2CO_3 ?

$$1.15\times10^{5}\,\cancel{\text{formula units Na}_2\text{CO}_3}\left(\frac{1\text{ mol Na}_2\text{CO}_3}{6.0223\times10^{23}\,\cancel{\text{formula units Na}_2\text{CO}_3}}\right)$$

$= 1.91\times10^{-19}$ mol Na_2CO_3

Your Turn!

Ex. How many atoms are in 1.00 x 10^{-9} g of U? Molar mass U = 238.03 g/mole.

A. 6.02 x 10^{14} atoms

B. 4.20 x 10^{11} atoms

C. 2.53 x 10^{12} atoms

D. 3.95 x 10^{-31} atoms

E. 2.54 x 10^{21} atoms

$$\left(1.00\times10^{-9}\ \cancel{\text{g U}}\right)\left(\frac{1\ \cancel{\text{mol U}}}{238.03\ \cancel{\text{g U}}}\right)\left(\frac{6.022\times10^{23}\ \text{atoms U}}{1\ \cancel{\text{mol U}}}\right)$$

= 2.53 x 10^{12} atoms U

Your Turn!

Ex. Calculate the mass in grams of $FeCl_3$ in 1.53 × 10^{23} formula units. (molar mass = 162.204 g/mol)

A. 162.2 g

B. 0.254 g

C. 1.661×10^{-22} g

D. 41.2 g

E. 2.37×10^{-22}

$$1.53\times10^{23}\ \cancel{\text{units FeCl}_3}\left(\frac{1\ \cancel{\text{mol FeCl}_3}}{6.022\times10^{23}\ \cancel{\text{units FeCl}_3}}\right)\times\left(\frac{162.2\text{ g FeCl}_3}{1\ \cancel{\text{mol FeCl}_3}}\right)$$

= 41.2 g $FeCl_3$

Mole-to-Mole Conversion Factors

In H_2O there are:

  - 2 mol H ⇔ 1 mol H_2O
  - 1 mol O ⇔ 1 mol H_2O
  - 2 mol H ⇔ 1 mol O
- on atomic scale
  - 2 atom H ⇔ 1 molecule H_2O
  - 1 atom O ⇔ 1 molecule H_2O
  - 2 atom H ⇔ 1 molecule O

Stoichiometric Equivalencies

Ex. N_2O_5

$2 \text{ mol N} \Leftrightarrow 1 \text{ mol } N_2O_5$

$5 \text{ mol O} \Leftrightarrow 1 \text{ mol } N_2O_5$

$2 \text{ mol N} \Leftrightarrow 5 \text{ mol O}$

Calculating the Amount of a Compound by Analyzing One Element

Ex. sample is found to contain 0.864 moles of phosphorus P. How many moles of $Ca_3(PO_4)_2$ are in that sample?

- What do we want to find?

  $0.864 \text{ mol P} = ? \text{ mol } Ca_3(PO_4)_2$

- What do we know?

  $2 \text{ mol P} \Leftrightarrow 1 \text{ mol } Ca_3(PO_4)_2$

- Solution $0.864 \cancel{\text{mol P}} \left(\frac{1 \text{ mol } Ca_3(PO_4)_2}{2 \cancel{\text{mol P}}} \right)$

  $\boldsymbol{= 0.432 \text{ mol } Ca_3(PO_4)_2}$

Your Turn!

Ex. Calculate the number of **moles** of calcium in 2.53 moles of $Ca_3(PO_4)_2$

A. 2.53 mol Ca

B. 0.432 mol Ca

C. 3.00 mol Ca

D. 7.59 mol Ca

E. 0.843 mol Ca

2.53 moles of $Ca_3(PO_4)_2$ = ? mol Ca

3 mol Ca ⇔ 1 mol $Ca_3(PO_4)_2$

$$2.53\,\cancel{\text{mol } Ca_3(PO_4)_2}\left(\frac{3\text{ mol Ca}}{1\,\cancel{\text{mol } Ca_3(PO_4)_2}}\right)$$

= 7.59 mol Ca

Mass-to-Mass Calculations

Ex. Chlorophyll, the green pigment in leaves, has the formula $C_{55}H_{72}MgN_4O_5$. If 0.0011 g of Mg is available to a plant for chlorophyll synthesis, how many grams of carbon will be required to completely use up the magnesium?

- Analysis

  0.0011 g Mg ⇔ ? g C

  0.0011 g Mg → mol Mg → mol C → g C

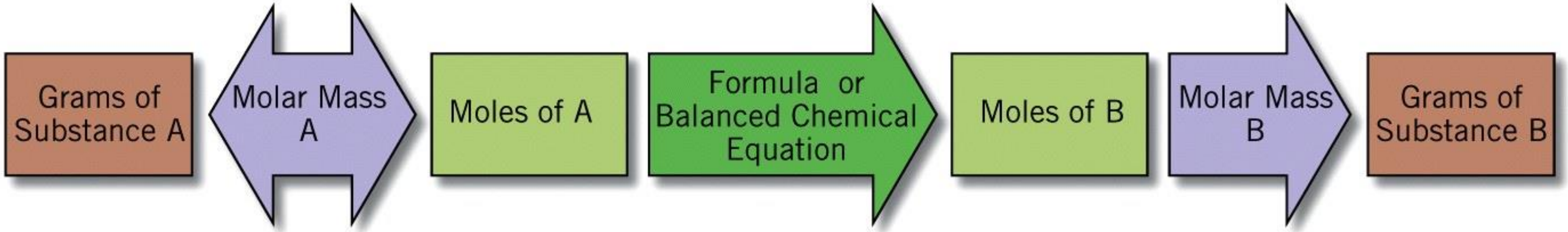
- Assembling the tools

  24.3050 g Mg = 1 mol Mg

  1 mol Mg ⇔ 55 mol C

  1 mol C = 12.011 g C

Ex. Mass-to-Mass Conversion



Grams of Substance A

Molar Mass A

Moles of A

Formula or Balanced Chemical Equation

Moles of B

Molar Mass B

Grams of Substance B

1 mol Mg ⇔ 24.3 g Mg

1 mol C ⇔ 12.0 g C

$$0.0011\ \text{g Mg} \longrightarrow \text{mol Mg} \longrightarrow \text{mol C} \longrightarrow \text{g C}$$

1 mol Mg ⇔ 55 mol C

$$0.0011\,\cancel{\text{g Mg}} \times \left(\frac{1\,\cancel{\text{mol Mg}}}{24.3\,\cancel{\text{g Mg}}}\right) \times \left(\frac{55\,\cancel{\text{mol C}}}{1\,\cancel{\text{mol Mg}}}\right) \times \left(\frac{12.0\,\text{g C}}{1\,\cancel{\text{mol C}}}\right)$$

= 0.030 g C

Your Turn!

Ex. How many g of iron are required to use up all of 25.6 g of oxygen atoms (O) to form Fe_2O_3?

A. 59.6 g

B. 29.8 g

C. 89.4 g

D. 134 g

E. 52.4 g

mass O → mol O → mol Fe → mass Fe

25.6 g O → ? g Fe

3 mol O ⇔ 2 mol Fe

$$25.6\,\cancel{\text{g O}} \times \left(\frac{1\,\cancel{\text{mol O}}}{16.0\,\cancel{\text{g O}}}\right) \times \left(\frac{2\,\cancel{\text{mol Fe}}}{3\,\cancel{\text{mol O}}}\right) \times \left(\frac{55.845\,\text{g Fe}}{1\,\cancel{\text{mol Fe}}}\right)$$

= 59.6 g Fe

Percentage Composition

- Percentage composition tells us mass of each element in 100.00 g of substance

Percentage by Mass: %

$$\%\text{ by mass of element} = \frac{\text{mass of element}}{\text{mass of sample}} \times 100\%$$

Ex. Na_2CO_3 is

  - 43.38% Na
  - 11.33% C
  - 45.29% O

- What is sum of % by mass? **100.00%**

Ex. Percent Composition

Ex. A sample of a liquid with a mass of 8.657 g was decomposed into its elements and gave 5.217 g of carbon, 0.9620 g of hydrogen, and 2.478 g of oxygen. What is the percentage composition of this compound?

Ex. % Composition of Compound

For C: $\left(\frac{g\ \text{C}}{g\ total}\right)\times 100\% = \frac{5.217\ \text{g C}}{8.657\ \text{g}}\times 100\% = 60.26\%\ \text{C}$

For H: $\left(\frac{g\ \text{H}}{g\ total}\right)\times 100\% = \frac{0.9620\ \text{g H}}{8.657\ \text{g}}\times 100\% = 11.11\%\ \text{H}$

For O: $\left(\frac{g\ \text{O}}{g\ total}\right)\times 100\% = \frac{2.478\ \text{g O}}{8.657\ \text{g}}\times 100\% \underline{= 28.62\%\ \text{O}}$

Sum of percentages: 99.99%

Your Turn!

Ex. A sample was analyzed and found to contain 0.1417 g nitrogen and 0.4045 g oxygen. What is the percentage composition of this compound?

1. Calculate total mass of sample

Total sample mass = 0.1417 g + 0.4045 g = 0.5462 g

2. Calculate % Composition of N

$$\left(\frac{\text{g N}}{\text{g total}}\right)\times 100\% = \left(\frac{0.1417\,\text{g N}}{0.5462\,\text{g}}\right)\times 100\% \quad \mathbf{= 25.94\%\ N}$$

3. Calculate % Composition of O

$$\left(\frac{\text{g O}}{\text{g total}}\right)\times 100\% = \left(\frac{0.4045\,\text{g O}}{0.5462\,\text{g}}\right)\times 100\% \quad \mathbf{= 74.06\%\ O}$$

Ex. Using Percent Composition

Are the mass percentages 30.54% N & 69.46% O consistent with the formula N_2O_4?

Procedure:

1. Assume 1 mole of compound
2. Subscripts tell how many moles of each element are present
   - 2 mol N & 4 mol O
3. Use molar masses of elements to determine mass of each element in 1 mole
   - Molar Mass of N_2O_4 = 92.14 g N_2O_4 / 1 mol
4. Calculate % by mass of each element

Ex. Using Percent Composition (cont)

$$2\,\cancel{\text{mol N}} \times \frac{14.07\,\text{g N}}{1\,\cancel{\text{mol N}}} = 28.14\text{ g N}$$

$$4\,\cancel{\text{mol O}} \times \frac{16.00\,\text{g O}}{1\,\cancel{\text{mol O}}} = 64.00\text{ g O}$$

$$\%\text{N} = \frac{28.14\,\text{g N}}{92.14\,\text{g N}_2\text{O}_4} \times 100\% \mathbf{\ = 30.54\%\ N\ in\ N_2O_4}$$

$$\%\text{O} = \frac{64.00\,\text{g O}}{92.14\,\text{g N}_2\text{O}_4} \times 100\% \mathbf{\ = 69.46\%\ N\ in\ N_2O_4}$$

- The experimental values match the theoretical percentages for the formula N_2O_4.

Your Turn

Ex. If a sample containing only phosphorous & oxygen has percent composition 56.34% P & 43.66% O, is this P_4O_{10}?

A. Yes

B. No

4 mol P $\Leftrightarrow$ 1 mol P_4O_{10}

10 mol O $\Leftrightarrow$ 1 mol P_4O_{10}

4 mol P = 4 × 30.97 g/mol P = 123.9 g P

10 mol O = 10 × 16.00 g/mol O = <u>160.0 g O</u>

1 mol P_4O_{10} = **283.9 g** P_4O_{10}

$$\%P = \frac{123.9\,g\,P}{283.9\,g\,P_4O_{10}} \times 100\% \quad = 43.64\ \%\ P$$

$$\%O = \frac{160.0\,g\,O}{283.9\,g\,P_4O_{10}} \times 100\% \quad = 56.36\ \%\ O$$

Determining Empirical & Molecular Formulas

- When making or isolating new compounds one must characterize them to determine structure &

Molecular Formula

  - Exact composition of one molecule
  - Exact whole # ratio of atoms of each element in molecule

Empirical Formula

  - Simplest ratio of atoms of each element in compound
  - Obtained from experimental analysis of compound

glucose	**Empirical formula**	CH_2O
	Molecular formula	$C_6H_{12}O_6$

Strategy for Determining Empirical Formulas

1. Determine mass in **g** of each element
2. Convert mass in **g** to **moles**
3. Divide all quantities by smallest number of moles to get smallest ratio of moles
4. Convert any non-integers into integer numbers.
   - If number ends in decimal equivalent of fraction, multiply all quantities by least common denominator
   - Otherwise, round numbers to nearest integers

1. Empirical Formula from Mass Data

Ex. When a 0.1156 g sample of a compound was analyzed, it was found to contain 0.04470 g of C, 0.01875 g of H, and 0.05215 g of N. Calculate the empirical formula of this compound.

Step 1: Calculate moles of each substance

$$0.04470\,\cancel{\text{g C}} \times \frac{1\text{ mol C}}{12.011\,\cancel{\text{g C}}} = 3.722 \times 10^{-3}\text{ mol C}$$

$$0.01875\,\cancel{\text{g H}} \times \frac{1\text{ mol H}}{1.008\,\cancel{\text{g H}}} = 1.860 \times 10^{-2}\text{ mol H}$$

$$0.05215\,\cancel{\text{g N}} \times \frac{1\text{ mol N}}{14.0067\,\cancel{\text{g N}}} = 3.723 \times 10^{-3}\text{ mol N}$$

1. Empirical Formula from Mass Data

Step 2: Select the smallest # of moles.

- Lowest is 3.722×10^{-3} mole

Mole ratio Integer ratio

- $C = \dfrac{3.722 \times 10^{-3} \text{ mol C}}{3.722 \times 10^{-3} \text{ mol C}} = 1.000 = 1$
- $H = \dfrac{1.860 \times 10^{-2} \text{ mol H}}{3.722 \times 10^{-3} \text{ mol C}} = 4.997 = 5$
- $N = \dfrac{3.723 \times 10^{-3} \text{ mol N}}{3.722 \times 10^{-3} \text{ mol C}} = 1.000 = 1$

Step 3: Divide all # of moles by the smallest one

Empirical formula = CH_5N

Empirical Formula from Mass Composition

Ex. One of the compounds of iron Fe and oxygen O, When a 2.448 g sample was analyzed it was found to have 1.771 g of Fe and 0.677 g of O. Calculate the empirical formula of this compound.

Assembling the tools:

1 mol Fe = 55.845 g Fe   1 mol O = 16.00 g O

1. Calculate moles of each substance

$$1.771\,\cancel{\text{g Fe}} \times \frac{1\,\text{mol Fe}}{55.485\,\cancel{\text{g Fe}}} = 0.03171\text{ mol Fe}$$

$$0.677\,\cancel{\text{g O}} \times \frac{1\,\text{mol O}}{16.00\,\cancel{\text{g O}}} = 0.0423\text{ mol O}$$

1. Empirical Formula from Mass Data

2. Divide both by smallest #mol to get smallest whole # ratio.

$$\frac{0.03171\,\text{mol Fe}}{0.03171\,\text{mol Fe}} = 1.000\text{ Fe} \times 3 = 3.000\text{ Fe}$$

$$\frac{0.0423\,\text{mol O}}{0.03171\,\text{mol Fe}} = 1.33\text{ O} \times 3 = 3.99\text{ O}$$

Or $$\text{Fe}_{\frac{0.03171}{0.03171}}\text{O}_{\frac{0.0423}{0.03171}} = \text{Fe}_{1.00}\text{O}_{1.33}$$

$$\text{Fe}_{(1.00\times 3)}\text{O}_{(1.33\times 3)} = \text{Fe}_3\text{O}_{3.99}$$

Empirical Formula = Fe_3O_4

2. Empirical Formula from % Composition

Ex. Calculate the empirical formula of a compound whose % composition data is 43.64 % P and 56.36 % O. If the molar mass is determined to be 283.9 g/mol, what is the molecular formula?

Step 1: Assume 100 g of compound.

▪ 43.64 g P	1 mol P = 30.97 g
▪ 56.36 g O	1 mol O = 16.00 g

$$43.64\,\cancel{\text{g P}} \times \frac{1\ \text{mol P}}{30.97\,\cancel{\text{g P}}} = 1.409\ \text{mol P}$$

$$56.36\,\cancel{\text{g O}} \times \frac{1\ \text{mol O}}{16.00\,\cancel{\text{g O}}} = 3.523\ \text{mol P}$$

2. Empirical Formula from % Composition

Step 2: Divide by smallest number of moles

$$\frac{1.409\,\text{mol P}}{1.409\,\text{mol P}} = 1.000 \quad \times 2 = 2$$

$$\frac{3.523\,\text{mol O}}{1.409\,\text{mol P}} = 2.500 \quad \times 2 = 5$$

Step 3: Multiple by **n** to get smallest integer ratio

Here **n = 2**

Empirical formula = P_2O_5

Determining Molecular Formula

- Need molecular mass & empirical formula
- Calculate ratio of molecular mass to mass predicted by empirical formula & round to nearest integer

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

Ex. Glucose

Molecular mass is 180.16 g/mol

Empirical formula = CH_2O

Empirical formula mass = 30.03 g/mol

$$n = \frac{180.16\text{ g}}{30.03\text{ g}} = 6$$

Molecular formula = $C_6H_{12}O_6$

Learning Check

The empirical formula of a compound is P_2O_5. If the molar mass is determined to be 283.9 g/mol, what is the molecular formula?

Step 1: Calculate empirical mass

$$\text{empirical mass } P_2O_5 = (2 \times \text{mass P}) + (5 \times \text{mass O})$$

$$= (2 \times 30.97\ \text{g/mol}) + (5 \times 16.00\ \text{g/mol})$$

$$= (61.94 + 80.00)\ \text{g/mol}$$

$$= 141.94\ \text{g/mol}\, P_2O_5$$

Step 2: Calculate ratio of molecular to empirical mass

$$n = \frac{283.9\ \text{g/mol}}{141.94\ \text{g/mol}} = 2$$

Molecular formula = P_4O_{10}

Your Turn!

Ex. The empirical formula of hydrazine is NH_2, and its molecular mass is 32.0. What is its molecular formula?

A. NH_2

B. N_2H_4

C. N_3H_6

D. N_4H_8

E. $N_{1.5}H_3$

Molar mass of NH_2 =

(1×14.01)g + (2×1.008)g = 16.017g

n = (32.0/16.02) = 2

Atomic Mass: N:14.007; H:1.008; O:15.999

Learning Check: Balancing Equations

unbalanced

$AgNO_3(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + NaNO_3(aq)$

- balanced

$3AgNO_3(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + 3NaNO_3(aq)$

unbalanced

$Zn(s) + HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

Balanced

$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$

Balance by Inspection

$\_\_C_3H_8(g) + \_\_O_2(g) \rightarrow \_\_CO_2(g) + \_\_H_2O(\ell)$

Assume 1 in front of C_3H_8

3C $\qquad$ 1C × 3

8H $\qquad$ 2H × 4

$1C_3H_8(g) + \_\_O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$

$2O \times 5 = 10$ $\qquad$ $O = (3 \times 2) + 4 = 10$

8H $\qquad$ $H = 2 \times 4 = 8$

$1C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$

Your Turn!

Ex. Balance each of the following equations. What are the coefficients in front of each compound?

$\underline{\ 1\ }\ Ba(OH)_2(aq) + \underline{\ 1\ }\ Na_2SO_4(aq) \rightarrow \underline{\ 1\ }\ BaSO_4(s) + \underline{\ 2\ }\ NaOH(aq)$

$\underline{\ 2\ }\ KClO_3(s) \rightarrow \underline{\ 2\ }\ KCl(s) + \underline{\ 3\ }\ O_2(g)$

$\underline{\ 2\ }\ H_3PO_4(aq) + \underline{\ 3\ }\ Ba(OH)_2(aq) \rightarrow \underline{\ 1\ }\ Ba_3(PO_4)_2(s) + \underline{\ 6\ }\ H_2O(\ell)$

Stoichiometric Ratios

- Consider the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

- Could be read as:

"When 1 **molecule** of nitrogen reacts with 3 **molecules** of hydrogen, 2 **molecules** of ammonia are formed."

- **Molecular relationships**
- 1 molecule $N_2 \Leftrightarrow$ 2 molecule NH_3
- 3 molecule $H_2 \Leftrightarrow$ 2 molecule NH_3
- 1 molecule $N_2 \Leftrightarrow$ 3 molecule H_2

Stoichiometric Ratios

- Consider the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

- Could also be read as:

“When 1 **mole** of nitrogen reacts with 3 **moles** of hydrogen, 2 **moles** of ammonia are formed.”

- **Molar relationships**
  - 1 mole $N_2 \Leftrightarrow$ 2 mole NH_3
  - 3 mole $H_2 \Leftrightarrow$ 2 mole NH_3
  - 1 mole $N_2 \Leftrightarrow$ 3 mole H_2

Using Stoichiometric Ratios

Ex. For the reaction $N_2 + 3\ H_2 \rightarrow 2NH_3$, how many moles of N_2 are used when 2.3 moles of NH_3 are produced?

- Assembling the tools
  - 2 moles NH_3 = 1 mole N_2
  - 2.3 mole NH_3 = ? moles N_2

$$2.3\ \cancel{\text{mol}\ NH_3}\left(\frac{1\ \text{mol}\ N_2}{2\ \cancel{\text{mol}\ NH_3}}\right) = 1.2\ \text{mol}\ N_2$$

Your Turn!

Ex. If 0.575 mole of CO_2 is produced by the combustion of propane, C_3H_8, how many moles of oxygen are consumed?

$$\mathbf{C_3H_8(\mathit{g}) + 5O_2(\mathit{g}) \rightarrow 3CO_2(\mathit{g}) + 4H_2O(\mathit{g})}$$

A. 0.575 mole

B. 2.88 mole

C. 0.192 mole

D. 0.958 mole

E. 0.345 mole

Assembling the tools

- 0.575 mole CO_2 = ? moles O_2
- 3 moles CO_2 = 5 mole O_2

$$0.575\ \cancel{\text{mol CO}_2}\left(\frac{5\ \text{mol O}_2}{3\ \cancel{\text{mol CO}_2}}\right) = 0.958\ \text{mol O}_2$$

Using Balanced Equation to Determine Stoichiometry

Ex. What mass of O_2 will react with 96.1 g of propane (C_3H_8) gas, to form gaseous carbon dioxide & water?

Strategy

1. Write the balanced equation

$$\mathbf{C_3H_8(\mathit{g}) + 5O_2(\mathit{g}) \rightarrow 3CO_2(\mathit{g}) + 4H_2O(\mathit{g})}$$

2. Assemble the tools

96.1 g C_3H_8 → moles C_3H_8 → moles O_2 → g O_2

1 mol C_3H_8 = 44.1 g C_3H_8

1 mol O_2 = 32.00 g O_2

1 mol C_3H_8 = 5 mol O_2

Using Balanced Equation to Determine Stoichiometry

Ex. What mass of O_2 will react with 96.1 g of propane in a complete combustion?

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

3. Assemble conversions so units cancel correctly

$$96.1\ \text{g}\ \cancel{C_3H_8} \times \frac{1\ \cancel{\text{mol}\ C_3H_8}}{44.1\ \cancel{\text{g}\ C_3H_8}} \times \frac{5\ \cancel{\text{mol}\ O_2}}{1\ \cancel{\text{mol}\ C_3H_8}} \times \frac{32.0\ \text{g}\ O_2}{1\ \cancel{\text{mol}\ O_2}}$$

= **349 g** of O_2 are needed

Your Turn!

Ex. How many grams of Al_2O_3 are produced when 41.5 g Al react?

$$2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(\ell)$$

A. 78.4 g

B. 157 g

C. 314 g

D. 22.0 g

E. 11.0 g

$$41.5\ \cancel{\text{g Al}}\left(\frac{1\ \cancel{\text{mol Al}}}{26.98\ \cancel{\text{g Al}}}\right)\left(\frac{1\ \cancel{\text{mol Al}_2\text{O}_3}}{2\ \cancel{\text{mol Al}}}\right)\left(\frac{101.96\ \text{g Al}_2\text{O}_3}{1\ \cancel{\text{mol Al}_2\text{O}_3}}\right)$$

$$= 78.4\ \text{g Al}_2\text{O}_3$$

Limiting Reactant

- Reactant that is completely used up in the reaction
- Present in lower # of moles
- It determines the amount of product produced
- For this reaction = ethylene

Excess reactant

- Reactant that has some amount left over at end
- Present in higher # of moles
- For this reaction = water

Ex. Limiting Reactant Calculation

How many grams of NO can form when 30.0 g NH_3 and 40.0 g O_2 react according to:

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$$

Solution: Step 1

$$\text{mass } NH_3 \rightarrow \text{mole } NH_3 \rightarrow \text{mole } O_2 \rightarrow \text{mass } O_2$$

Assembling the tools

- 1 mol NH_3 = 17.03 g
- 1 mol O_2 = 32.00 g
- 4 mol $NH_3 \Leftrightarrow$ 5 mol O_2

Only have 40.0 g O_2,
O_2 limiting reactant

$$30.0\,\cancel{g\,NH_3} \times \frac{1\,\cancel{mol\,NH_3}}{17.03\,\cancel{g\,NH_3}} \times \frac{5\,\cancel{mol\,O_2}}{4\,\cancel{mol\,NH_3}} \times \frac{32.00\,g\,O_2}{1\,\cancel{mol\,O_2}}$$

= 70.5 g O_2 needed

Ex. Limiting Reactant Calculation

How many grams of NO can form when 30.0 g NH_3 and 40.0 g O_2 react according to:

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$$

Solution: Step 2

mass O_2 → mole O_2 → mole NO → mass NO

Assembling the tools

$\boxed{\text{Can only form 30.0 g NO.}}$

- 1 mol O_2 = 32.00 g
- 1 mol NO = 30.01 g
- 5 mol $O_2 \Leftrightarrow$ 4 mol NO

$$40.0\ \cancel{g\ O_2} \times \frac{1\ \cancel{mol\ O_2}}{32.00\ \cancel{g\ O_2}} \times \frac{4\ \cancel{mol\ NO}}{5\ \cancel{mol\ O_2}} \times \frac{30.01\ g\ NO}{1\ \cancel{mol\ NO}}$$

= 30.0 g NO formed

Your Turn!

Ex. If 18.1 g NH_3 is reacted with 90.4 g CuO, what is the maximum amount of Cu metal that can be formed?

$$2NH_3(g) + 3CuO(s) \rightarrow N_2(g) + 3Cu(s) + 3H_2O(g)$$

(MM) (17.03) (79.55) (28.01) (64.55) (18.02)

(g/mol)

$$18.1\,g\,NH_3 \times \frac{1\,mol\,NH_3}{17.03\,g\,NH_3} \times \frac{3\,mol\,CuO}{2\,mol\,NH_3} \times \frac{79.55\,g\,CuO}{1\,mol\,CuO}$$

A. 127 g

B. 103 g

C. 72.2 g

D. 108 g

E. 56.5 g

127 g CuO needed.
Only have 90.4g so CuO limiting

$$90.4\,g\,CuO \times \frac{1\,mol\,CuO}{79.55\,g\,CuO} \times \frac{3\,mol\,Cu}{3\,mol\,CuO} \times \frac{63.546\,g\,Cu}{1\,mol\,Cu}$$

72.2 g Cu can be formed

Theoretical vs. Actual Yield

- **Theoretical Yield**
  - Maximum amount of product that must be obtained if no losses occur.
  - Amount of product formed if all of limiting reagent is consumed.
- **Actual Yield**
  - Amount of product that is actually isolated at end of reaction.
  - Amount obtained experimentally
  - How much is obtained in mass units or in moles.

Percentage Yield

Useful to calculate % yield.

Percent yield

- Relates the actual yield to the theoretical yield

- It is calculated as:

$$\boxed{\text{percentage yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100}$$

Ex. If a cookie recipe predicts a yield of 36 cookies and yet only 24 are obtained, what is the % yield?

$$\text{percentage yield} = \left(\frac{24}{36}\right) \times 100 = 67\%$$

Ex. Percentage Yield Calculation

When 18.1 g NH_3 and 90.4 g CuO are reacted, the theoretical yield is 72.2 g Cu. The actual yield is 58.3 g Cu. What is the percent yield?

$$2NH_3(g) + 3CuO(s) \rightarrow N_2(g) + 3Cu(s) + 3H_2O(g)$$

$$\%\text{ yield} = \frac{58.3\,\text{g Cu}}{72.2\,\text{g Cu}} \times 100\% \mathbf{= 80.7\%}$$

Learning Check: Percentage Yield

Ex. A chemist set up a synthesis of solid phosphorus trichloride PCl_3 by mixing 12.0 g of solid phosphorus with 35.0 g chlorine gas and obtained 42.4 g of solid phosphorus trichloride. Calculate the percentage yield of this compound.

Analysis:

Write balanced equation

$$P(s) + Cl_2(g) \longrightarrow PCl_3(s)$$

Determine Limiting Reagent → Determine Theoretical Yield → Calculate Percentage Yield

Learning Check: Percentage Yield

Assembling the Tools:

- 1 mol P = 30.97 g P
- 1 mol Cl_2 = 70.90 g Cl_2
- 3 mol Cl_2 ⇔ 2 mol P

Solution

1. Determine Limiting Reactant

$$12.0\ \cancel{\text{g P}} \times \frac{1\ \cancel{\text{mol P}}}{30.97\ \cancel{\text{g P}}} \times \frac{3\ \cancel{\text{mol Cl}_2}}{2\ \cancel{\text{mol P}}} \times \frac{70.90\ \text{g Cl}_2}{1\ \cancel{\text{mol Cl}_2}} = 41.2\ \text{g Cl}_2$$

- But you only have 35.0 g Cl_2, so Cl_2 is limiting reactant

Learning Check: Percentage Yield

Solution

2. Determine Theoretical Yield

$$35.0\,\cancel{\text{g}\,\text{Cl}_2} \times \frac{1\,\cancel{\text{mol}\,\text{Cl}_2}}{70.90\,\cancel{\text{g}\,\text{Cl}_2}} \times \frac{2\,\cancel{\text{mol}\,\text{PCl}_3}}{3\,\cancel{\text{mol}\,\text{Cl}_2}} \times \frac{137.32\,\text{g}\,\text{PCl}_3}{1\,\cancel{\text{mol}\,\text{PCl}_3}}$$

$= 45.2\ \text{g}\ \text{PCl}_3$

3. Determine Percentage Yield

- Actual yield = 42.4 g

$$\text{percentage yield} = \left(\frac{42.2\,\text{g}\,\text{PCl}_3}{45.2\,\text{g}\,\text{PCl}_3}\right) \times 100 \quad \mathbf{= 93.8\ \%}$$

Your Turn!

Ex. When 6.40 g of CH_3OH was mixed with 10.2 g of O_2 and ignited, 6.12 g of CO_2 was obtained. What was the percentage yield of CO_2?

$$2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O$$

MM(g/mol) (32.04) (32.00) (44.01) (18.02)

A. 6.12%
B. 8.79%
C. 100%
D. 142%
E. 69.6%

$$6.40\text{ g }CH_3OH \times \frac{1\text{ mol }CH_3OH}{32.04\text{ g }CH_3OH} \times \frac{3\text{ mol }CO_2}{2\text{ mol }CH_3OH} \times \frac{32.00\text{ g }O_2}{1\text{ mol }O_2}$$

=9.59 g O_2 needed; CH_3OH limiting

$$6.40\text{ g }CH_3OH \times \frac{1\text{ mol }CH_3OH}{32.04\text{ g }CH_3OH} \times \frac{2\text{ mol }CO_2}{2\text{ mol }CH_3OH} \times \frac{44.01\text{ g }CO_2}{1\text{ mol }CO_2}$$

= 8.79 g CO_2 in theory

$$\frac{6.12\text{ g }CH_3OH\text{ actual}}{8.79\text{ g }CH_3OH\text{ theory}} \times 100\% = 69.6\%$$

Molarity Concentration

- Number of moles of solute per liter of solution.
- Allows us to express relationship between moles of solute and volume of solution
- Hence, 0.100 *M* solution of NaCl contains 0.100 mole NaCl in 1.00 liter of solution
- Same concentration results if you dissolve 0.0100 mol of NaCl in 0.100 liter of solution

$$\boxed{\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mole}}{\text{Volume}}}$$

$$\frac{0.100\,\text{mol NaCl}}{1.00\,\text{L NaCl soln}} = \frac{0.0100\,\text{mol NaCl}}{0.100\,\text{L NaCl soln}} = 0.100\,M\ \text{NaCl}$$

Learning Check: Calculating Molarity (from grams and volume)

Ex. Calculate the molarity (*M*) of a solution prepared by dissolving 11.5 g NaOH (40.00 g/mol) solid in enough water to make 1.50 L of solution.

g NaOH ⟶ mol NaOH ⟶ *M* NaOH

$$11.5\ \cancel{\mathrm{g\ NaOH}} \times \frac{1\ \mathrm{mol\ NaOH}}{40.00\ \cancel{\mathrm{g\ NaOH}}} = 0.288\ \mathrm{mol\ NaOH}$$

$$M = \frac{\mathrm{moles\ NaOH}}{\mathrm{L\ soln}} = \frac{0.288\ \mathrm{mol\ NaOH}}{1.50\ \mathrm{L\ soln}}$$

$$\boxed{= 0.192\,M\ \mathrm{NaOH}}$$

Learning Check: Calculating Volume (from Molarity and moles)

Ex. How many mL of 0.250 *M* NaCl solution are needed to obtain 0.100 mol of NaCl?

- Use *M* definition

$$0.250\,M\ \text{NaCl} = \frac{0.250\ \text{mol NaCl}}{1.00\ \text{L NaCl soln}}$$

- Given molarity and moles, need volume

$$0.100\ \cancel{\text{mol NaCl}} \times \frac{1.00\ \cancel{\text{L NaCl soln}}}{0.250\ \cancel{\text{mol NaCl}}} \times \frac{1000\ \text{mL NaCl soln}}{1\ \cancel{\text{L NaCl soln}}}$$

= 400 mL of 0.250 *M* NaCl solution

Temperature Insensitive Concentration

1. Percent Concentrations

- Also called percent by mass or percent by weight

$$\textbf{percent by mass} = \frac{\textbf{mass of solute}}{\textbf{mass of solution}} \times \textbf{100\%}$$

- This is sometimes indicated %(w/w) where "w" stands for weight
- The "(w/w)" is often omitted

Ex. Percent by Mass

What is the percent by mass of NaCl in a solution consisting of 12.5 g of NaCl and 75.0 g water?

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

$$wt\%_{NaCl} = \frac{12.5\,\text{g}}{(12.5 + 75.0)\,\text{g}} \times 100$$

$$wt\%_{NaCl} = 14.3\%\ \text{NaCl}$$

Learning Check

Ex. How many grams of sea salt would be needed to prepare 62.5 L of 3.5% w/w solution with density of 1.03 g/mL. ?

- What do we need to find?
  - 62.5 L ⇔ ? g sea salt
- What do we know?
  - 3.5 g sea salt ⇔ 100 g solution
  - 1.03 g soln ⇔ 1.00 mL solution
  - 1000 mL ⇔ 1.00 L

$$62.5\,\cancel{\text{L}} \times \frac{1000\,\cancel{\text{mL}}}{1\,\cancel{\text{L}}} \times \frac{1.03\,\cancel{\text{g soln}}}{1.00\,\cancel{\text{mL soln}}} \times \frac{3.5\text{ g sea salt}}{100\,\cancel{\text{g soln}}}$$

= 2.2×10^3 g sea salt

More Temperature Insensitive Concentration Units

Molality (*m*)

- Number of moles of solute per kilogram solvent

$$\boxed{\text{molality} = m = \frac{mol\text{ of solute}}{kg\text{ of }solvent}}$$

- Also ***Molal concentration***
- Independent of temperature

Ex. Concentration Calculation

A. If you prepare a solution by dissolving 25.38 g of I_2 in 500.0 g of water, what is the molality (***m***) of the solution?

- What do we need to find?
  - 25.38 g ⇔ ? *m*
- What do we know?
  - 253.8 g I_2 ⇔ 1 mol I_2
  - *m* = mol solute/kg solvent
  - 500.0 g ⇔ 0.5000 kg
- Solve it

$$25.38\,\cancel{g}\,I_2 \times \frac{1\,\text{mol}\,I_2}{253.8\,\cancel{g}\,I_2} \times \frac{1}{0.5000\,\text{kg water}}$$

$$= 0.2000\ \text{mol}\ I_2/\text{kg water} = \mathbf{0.2000}\ \boldsymbol{m}$$

Ex. Calculating *M* from *m* (cont.)

B. What is the molarity (*M*) of this solution? The density of this solution is 1.59 g/mL.

- What do we need to find?
  - 25.38 g ⇔ ? *M*
- What do we know?
  - 253.8 g I_2 ⇔ 1 mol I_2
  - *M* = mol solute/L soln
  - 1.59 g soln ⇔ 1 mL soln
  - g of soln = g I_2 + g H_2O = 500.0 g + 25.38 g
- Solve it

$$25.38\,\cancel{\mathrm{g\,I_2}} \times \frac{1\,\mathrm{mol\,I_2}}{253.8\,\cancel{\mathrm{g\,I_2}}} \times \frac{1}{525.38\,\cancel{\mathrm{g\,soln}}} \times \frac{1.59\,\cancel{\mathrm{g}}}{1.00\,\cancel{\mathrm{mL}}} \times \frac{1000\,\cancel{\mathrm{mL}}}{1\,\mathrm{L}}$$

$$= 0.3030\ \mathrm{mol\ I_2/L\ soln} = \mathbf{0.3030}\ \boldsymbol{M}$$

Converting between Concentrations

Ex. Calculate the molarity and the molality of a 40.0% HBr solution. The density of this solution is 1.38 g/mL.

$$40.0\%\ \text{HBr} = wt\% = \frac{40.0\,g\ \text{HBr}}{100\ g\ \text{solution}} * 100$$

If we assume 100.0 g of solution, then 40.0 g of HBr.

$$m = \frac{mol\ \text{HBr}}{kg\ \text{of}\ \text{H}_2O} \qquad mol\ \text{HBr} = \frac{40.0\,g\ \text{HBr}}{80.91\,g\ \text{HBr}/mol} = 0.494\,mol\ \text{HBr}$$

If 100 g solution, then

mass $\mathbf{H_2O}$ = $100.0\ g\ \text{soln} - 40.0\ g\ \text{HBr} = 60.0\ g\ \text{H}_2\text{O}$

$$m = \frac{mol\ \text{HBr}}{kg\ \text{H}_2\text{O}} = \frac{0.494\ mol\ \text{HBr}}{0.0600\ kg\ \text{H}_2O} = 8.24\,m$$

Converting between Concentrations (cont.)

Now Calculate Molarity of 40% HBr

$$M = \frac{mol\ \text{HBr}}{L\ \text{solution}}$$

$$Vol\ \text{Soln} = \frac{\text{mass}}{\text{density}} = \frac{100g}{1.38g\ /\ mL} \mathbf{= 72.\underline{4}6\ mL}$$

$$\boldsymbol{mol}\ \textbf{HBr} = 0.494\ \boldsymbol{mol}$$

$$M = \frac{0.494 mol\ \text{HBr}}{72.46 mL\ \text{solution}} \times \frac{1000 mL}{1L} \mathbf{= 6.82}\ \boldsymbol{M}$$

Your Turn!

Ex. What is the molality of 50.0% (w/w) NaOH solution?

A. 0.500 *m*

B. 1.25 *m*

C. 0.025 *m*

D. 25 *m*

E. 50 *m*

100.0 g soln = 50.0 g NaOH + 50.0 g water

$$50.0\,\text{g NaOH} \times \frac{1\,\text{mol NaOH}}{40.00\,\text{g NaOH}} \times \frac{1\,m}{\text{mol/kg}} \times \frac{1000\,\text{g}}{1\,\text{kg}} \times \frac{1}{50.0\,\text{g water}}$$

= 25 *m*

MM(g/mol) H_2O: 18.02; NaOH: 40.00

Your Turn!

Ex. What is the molarity of the 50%(w/w) solution if its density is 1.529 g/mL?

A. 19 *M*

B. 1.25 *M*

C. 1.9 *M*

D. 0.76 *M*

$$50\text{ g NaOH} \times \frac{1\text{ mol NaOH}}{40.0\text{ g}} \times 1.529\,\frac{\text{g soln}}{\text{mL}}$$

$$\times \frac{1}{100\text{ g soln}} \times \frac{1000\text{ mL}}{\text{L}} = 19M$$

or

$$25\ \frac{\text{mmol}}{\text{g soln}} \times \frac{50\text{ g H}_2\text{O}}{100\text{ g soln}} \times \frac{1.529\text{ g}}{\text{mL}} = 19M$$

Other Temperature Insensitive Concentration Units

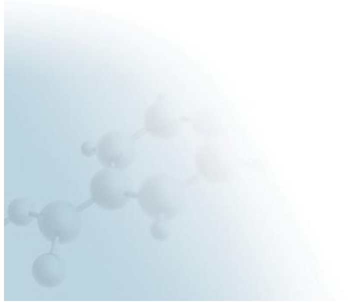
- **Mole Fraction**

$$\chi_A = \frac{\text{\# mol A}}{\text{Totalmoles of all components}}$$

Chapter 2
Properties of Gases

Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop



Properties of Common Gases

- Despite wide differences in chemical properties, ALL gases more or less obey the same set of **physical properties**.

Four Physical Properties of Gases

1. Pressure (**P**)
2. Volume (**V**)
3. Temperature (**T**)
4. Amount = moles (**n**)

Units of Pressure

Pascal = ***Pa***

- SI unit for **Pressure**
- Very small
- $1 atm \equiv 101{,}325\ Pa = 101\ kPa$

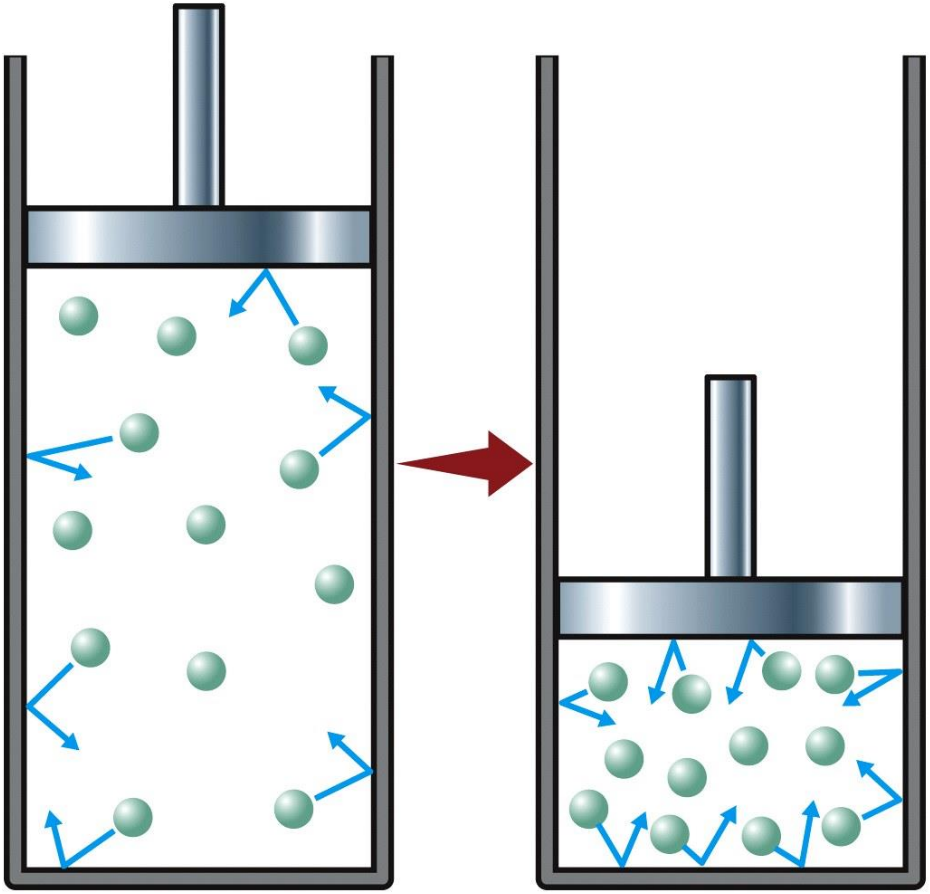
- $1\ atm$ too big for most lab work

$$1 torr = \frac{1}{760} atm \qquad 1\ atm \equiv 760\ mm\ Hg$$

At sea level $1\ torr = 1\ mm\ Hg$

Boyle's Law

- Studied relationship between *P* and *V*
- Work done at constant *T* as well as constant number of moles (*n*)
- $T_1 = T_2$
- As *V*↓, *P*↑



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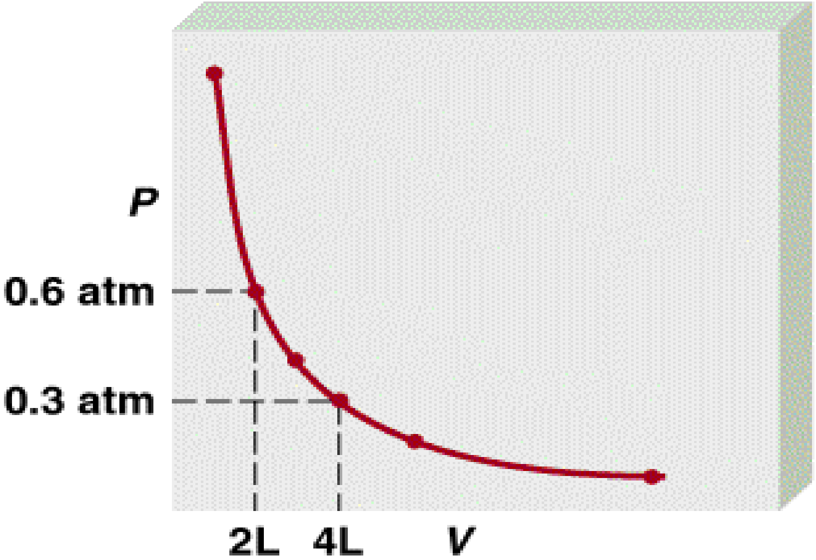
The volume of a fixed quantity of gas at constant temperature is **inversely proportional** to the pressure.

A plot of V versus P results in a curve

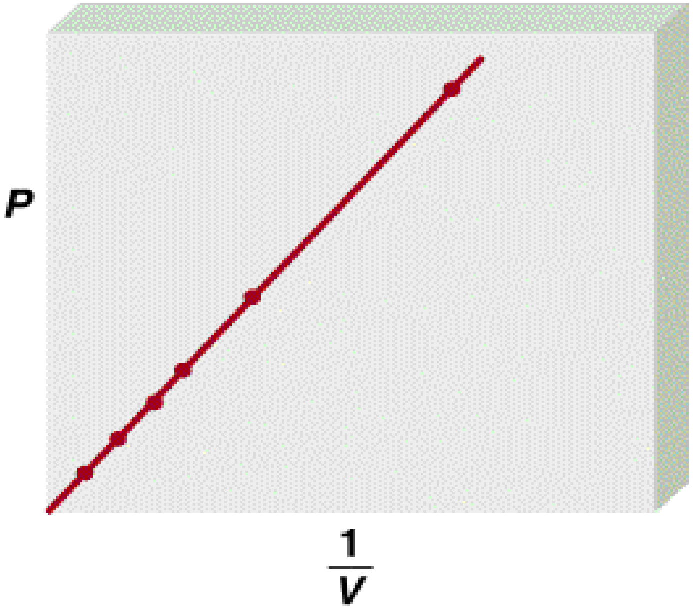


$P \alpha 1/V$

$P \times V = \text{constant}$

$P_1 \times V_1 = P_2 \times V_2$

A plot of V versus $1/P$ will be a straight line



$P = k(1/V)$

This means a plot of P versus $1/V$ will be a straight line.

Ex: A sample of chlorine gas occupies a volume of 946 mL at a pressure of 726 mmHg. What is the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL?

$$P_1 \times V_1 = P_2 \times V_2$$

P_1 = 726 mmHg

P_2 = ?

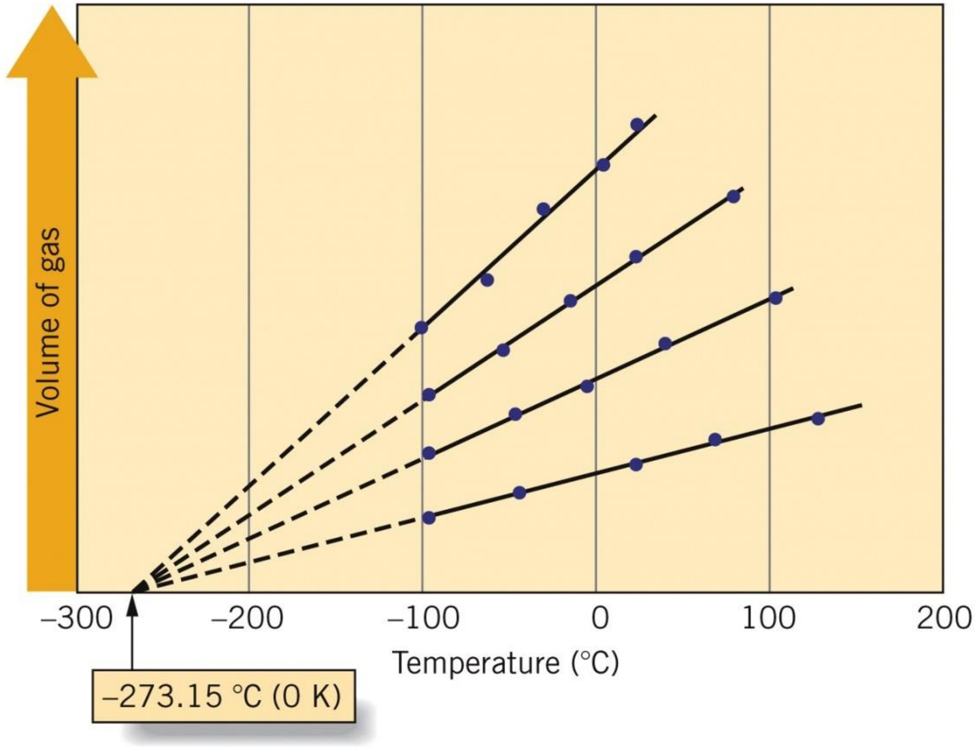
V_1 = 946 mL

V_2 = 154 mL

$$P_2 = \frac{P_1 \times V_1}{V_2} = \frac{726 \text{ mmHg} \times 946 \cancel{\text{mL}}}{154 \cancel{\text{mL}}} = 4460 \text{ mmHg}$$

Charles's Law

- Charles worked on relationship of how ***V*** changes with ***T***
- Kept ***P*** and ***n*** constant
- Showed ***V***↑ as ***T***↑
  - i.e., $\frac{V}{T} = k$



- The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature. $V_1/T_1 = V_2/T_2$

- Ex. Anesthetic gas is normally given to a patient when the room temperature is 20.0 °C and the patient's body temperature is 37.0°C. What would this temperature change do to 1.60 L of gas if the pressure and mass stay the same?

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{1.60\,L \times 310.15\,K}{293.15\,K}$$

$V_2 = 1.69\ L$

Ex: A sample of carbon monoxide gas occupies 3.20 L at 125 ^{0}C. At what temperature will the gas occupy a volume of 1.54 L if the pressure remains constant?

$$V_1/T_1 = V_2/T_2$$

$V_1 = 3.20\ \mathrm{L}$

$V_2 = 1.54\ \mathrm{L}$

$T_1 = 398.15\ \mathrm{K}$

$T_2 = ?$

$$T_2 = \frac{V_2 \times T_1}{V_1} = \frac{1.54\ \cancel{\mathrm{L}} \times 398.15\ \mathrm{K}}{3.20\ \cancel{\mathrm{L}}} = 192\ \mathrm{K}$$

Gay-Lussac's Law

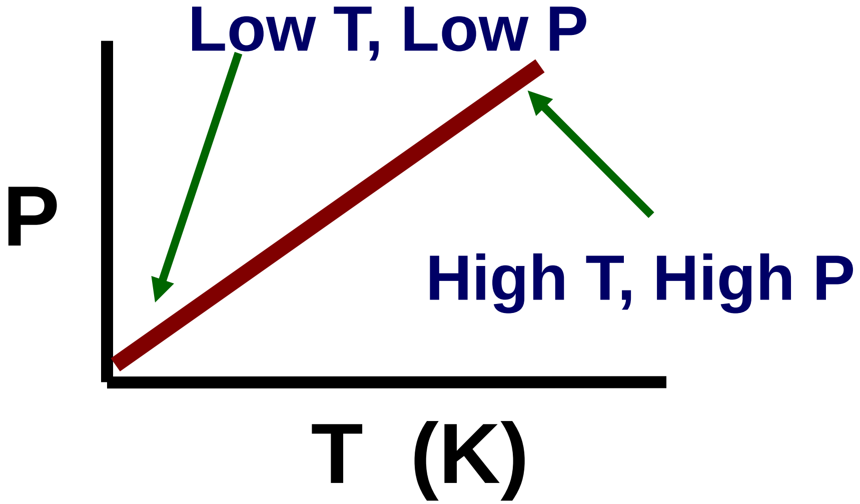
- Volume (***V***) and number of moles (***n***) are constant
- ***P*** ↑ as ***T*** ↑

V= constant, n= Constant

The pressure of a fixed amount of gas at constant volume is directly proportional to its absolute temperature.

$$\boldsymbol{P \propto T}$$

$$P_1T_2 = P_2\,T_1$$



Combined Gas Law

- Ratio $\dfrac{PV}{T}$
- Constant for fixed amount of gas (***n***)
- $\dfrac{PV}{T} = C$ for fixed amount (moles)

$$\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$$

How Other Laws Fit into Combined Gas Law

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Boyle's Law	$T_1 = T_2$	$P_1V_1 = P_2V_2$
Charles' Law	$P_1 = P_2$	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay-Lussac's Law	$V_1 = V_2$	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$

Combined Gas Law

- Ex. If a sample of air occupies 500. mL at STP*, what is the volume at 85 °C and 560 torr?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\boxed{\frac{760\ \text{torr} \times 500.\ \text{mL}}{273.15\ \text{K}} = \frac{560\ \text{torr} \times V_2}{358.15\ \text{K}}}$$

= 890 mL

***Standard Temperature (273.15K)**

Standard Pressure (1 atm)

Ex. Using Combined Gas Law

- What will be the final pressure of a sample of nitrogen gas with a volume of 950 m^3 at 745 torr and 25.0 °C if it is heated to 60.0 °C and given a final volume of 1150 m^3?

P_1 = 745 torr

P_2 = ?

V_1 = 950 m^3

V_2 = 1150 m^3

T_1 = 25.0 °C + 273.15
= 298.15 K

T_2 = 60.0 °C + 273.15
= 333.15 K

$$P_2 = \frac{P_1 V_1 T_2}{T_1 V_2} = \frac{745\,torr \times 950\,m^3 \times 333.15\,K}{298.15\,K \times 1150\,m^3}$$

P_2 = 688 torr

Your Turn!

Ex. Which units must be used in all gas law calculations?

A. K

B. atm

C. L

D. no specific units as long as they cancel

Relationships between Gas Volumes

- In reactions in which products and reactants are gases:
  - If T and P are constant
  - Simple relationship among volumes
- hydrogen + chlorine → hydrogen chloride

1 vol 1 vol 2 vol

- hydrogen + oxygen → water (gas)

2 vol 1 vol 2 vol

- ratios of simple, whole numbers

Avogadro's Principle

- When measured at same ***T*** and ***P***, equal ***V***'s of gas contain equal number of moles
- Volume of a gas is directly proportional to its number of moles, ***n***
- $\mathbf{V} \propto \mathbf{n}$ (at constant P and T)

	$H_2\ (g)$	+ $Cl_2\ (g)$	$\longrightarrow$ $2\ HCl\ (g)$
Coefficients	1	1	2
Volumes	1	1	2
Molecules	1	1	2 (Avogadro's Principle)
Moles	1	1	2

Learning Check:

Ex. Calculate the volume of ammonia formed by the reaction of 25L of hydrogen with excess nitrogen.

$$\mathbf{N_2\,(\mathit{g}) + 3H_2\,(\mathit{g}) \rightarrow 2NH_3\,(\mathit{g})}$$

$$\boxed{\frac{25\text{ L H}_2}{1} \times \frac{2\text{ L NH}_3}{3\text{ L H}_2} = 17\text{ L NH}_3}$$

Learning Check:

If 125 L H_2 react with 50L N_2, what volume of NH_3 can be expected?

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

$$\frac{125\,L\,H_2}{1} \times \frac{2\,L\,NH_3}{3\,L\,H_2} = 83.3\,L\,NH_3$$

$$\frac{50\,L\,N_2}{1} \times \frac{2\,L\,NH_3}{1\,L\,N_2} = 100\,L\,NH_3$$

H_2 is limiting reagent 83.3 L

Learning Check:

Ex. How many liters of N_2 (*g*) at 1.00 atm and 25.0 °C are produced by the decomposition of 150. g of NaN_3? $2NaN_3\ (s) \rightarrow 2Na\ (s) + 3N_2\ (g)$

$$\frac{150.\text{g NaN}_3}{1} \times \frac{1\text{ mol NaN}_3}{65.0099\text{ g}} \times \frac{3\text{ mol N}_2}{2\text{ mol NaN}_3} = 3.461\text{ mol N}_2$$

$$\frac{3.461\text{ mol N}_2}{1} \times \frac{22.4\text{ L}}{1\text{ mol at STP}} = 77.53\text{ L}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2};\ V_2 = \frac{V_1 T_2}{T_1}$$

$$V_2 = \frac{177.53\text{ L} \times 298.15\text{ K}}{273.15\text{K}} = 84.62\text{ L}$$

Your Turn!

Ex. How many liters of SO_3 will be produced when 25 L of sulfur dioxide reacts with 75 L of oxygen ? All gases are at STP.

A. 25 L
B. 50 L
C. 100 L
D. 150 L
E. 75 L

$$25\text{ L }SO_2 \times \frac{2\text{ L }SO_3}{2\text{ L }SO_2} = 25\text{ L }SO_3$$

$$75\text{ L }O_2 \times \frac{2\text{ L }SO_3}{1\text{ L }O_2} = 150\text{ L }SO_3$$

Ideal Gas Law

- With Combined Gas Law we saw that

$$\frac{PV}{T} = C$$

- With Avogadro's results we see that this is modified to

$$\frac{PV}{T} = n \times R$$

- Where R = a new constant = Universal Gas constant

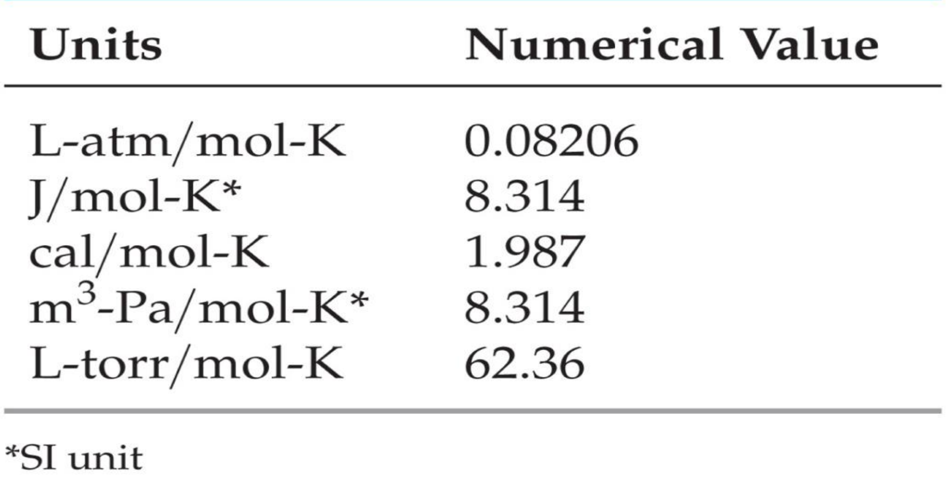
$$\boxed{PV = nRT}$$

Standard Molar Volume

- Volume of 1 mole gas must be identical for all gases under same P and T
- Standard Conditions of Temperature and Pressure — STP
  - **STP = 1 atm and 273.15 K (0.0°C)**
  - Under these conditions
  - 1 mole gas occupies V = 22.4 L
  - 22.4 L ≡ standard molar volume

What is the value of *R*?

- Plug in values of ***T***, ***V***, ***n*** and ***P*** for 1 mole of gas at STP (1 atm and 0.0°C)
  - ***T*** = 0.0°C = 273.15 K
  - ***P*** = 1 atm
  - ***V*** = 22.4 L
  - ***n*** = 1 mol



Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m^3-Pa/mol-K*	8.314
L-torr/mol-K	62.36

*SI unit

$$R = \frac{PV}{nT} = \frac{1\,atm \times 22.4\,L}{1\,mol \times 273.15\,K}$$

$$R = 0.082057\ L\cdot atm\cdot mol^{-1}\cdot K^{-1}$$

Learning Check:

Ex. How many liters of $N_2(g)$ at 1.00 atm and 25.0 °C are produced by the decomposition of 150. g of NaN_3? $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

V = ?

V = nRT/P

P = 1 atm

T = 25C + 273.15 = 298.15 K

$$n = \text{mol } N_2 = \frac{150.\text{g } NaN_3}{1} \times \frac{1 \text{ mol } NaN_3}{65.0099 \text{ g}} \times \frac{3 \text{ mol } N_2}{2 \text{ mol } NaN_3}$$

n = 3.461 mol N_2

$$V = \frac{(3.461 \text{mol } N_2)\left(0.082057 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(298.15\text{K})}{1\text{atm}}$$

V=84.62L

Your Turn!

Ex. Solid $CaCO_2$ decomposes to solid CaO and CO_2 when heated. What is the pressure, in atm, of CO_2 in a 50.0 L container at 35 ºC when 75.0 g of calcium carbonate decomposes?

A. 0.043 atm

B. 0.010 atm

C. 0.38 atm

D. 0.08 atm

E. 38 atm

$$PV = nRT$$

$$P = m \times R \times T / MM \times V$$

$$\frac{75.0 \text{ g } CaO_2 \times \dfrac{1 \text{ mol } CaCO_3}{100.1 \text{ g}} \times \dfrac{1 \text{ mol } CO_2}{1 \text{ mol } CaCO_3} \times 0.0821 \dfrac{\text{L atm}}{\text{K mol}} \times 308 \text{ K}}{50.0 \text{ L}}$$

$= 0.38$ atm

- Ex. A gas allowed to flow into a 300 mL gas bulb until the pressure was 685 torr. The sample now weighed 1.45 g; its temperature was 27.0°C. What is the molecular mass of this gas?

$$T = 27.0\,°C + 273.15\ K = 300.2\ K$$

$$V = 300 mL \times \frac{1 L}{1000 mL} = 0.300 L$$

$$P = 685 torr \times \frac{1 atm}{760 torr} = 0.901 atm$$

$$n = \frac{PV}{RT} = \frac{0.901 atm \times 0.300 L}{0.082057 (atm \cdot L / mol \cdot K) \cdot 300.2 K} =$$

$$= 0.01098\ mole$$

$$MM = \frac{mass}{n} = \frac{1.45 g}{0.01098 mol} = 132\ g/mol$$

Gas = Xe

Ex. A gaseous compound with an empirical formula of PF_2 was found to have a density of 5.60 g/L at 23.0 °C and 750 torr. Calculate its molecular mass and its molecular formula.

$$T = 23.0\,°C + 273.15\ K = 296.2\ K$$

$$P = 750\,torr \times \frac{1\,atm}{760\,torr} = 0.9868\,atm$$

$$n = \frac{PV}{RT} = \frac{0.9868\,atm \times 1.000\,L}{0.082057\,(atm \cdot L / mol \cdot K) \cdot 296.2\,K} =$$

$$0.04058\ mole$$

$$MM = \frac{mass}{n} = \frac{5.60\,g}{0.04058\,mol} = \mathbf{138\ g/mol}$$

Ex. Solution (cont)

- Now to find molecular formula given ***empirical formula*** and ***MM***
- First find mass of empirical formula unit
- 1 **P** $= 1 \times 31 g/mol = 31 g/mol$
- 2 **F** $= 2 \times 19\ g/mol = 38\ g/mol$

- Mass of PF_2 $= 69$ g/mol

$$MM = \frac{molecular\ \ mass}{empirical\ \ mass} = \frac{138 g / mol}{69 g / mol} = 2$$

$\therefore$ the correct molecular formula is P_2F_4

Your Turn!

Ex. 7.52 g of a gas with an empirical formula of NO_2 occupies 2.0 L at a pressure of 1.0 atm and 25 ^{o}C. Determine the molar mass and molecular formula of the compound.

A. 45.0 g/mol, NO_2

B. 90.0 g/mol, N_2O_4

C. 7.72 g/mol, NO

D. 0.0109 g/mol, N_2O

E. Not enough data to determine molar mass

Your Turn! - Solution

$$\text{MW} = \frac{7.52\ \text{g x } 0.0821\ \frac{\text{L atm}}{\text{K mol}}\ \text{x } 298\ \text{K}}{1.0\ \text{atm x } 2.0\ \text{L}} \quad 90.0\ \text{g/mol}$$

$$90\ \frac{\text{g}}{\text{mol}}\ \text{x}\ \frac{1\ \text{mol}\ NO_2}{45.0\ \text{g}} = \frac{2\ \text{mol}\ NO_2}{\text{mol}}$$

Molecular formula is N_2O_4

Stoichiometry of Reactions Between Gases

- Can use stoichiometric coefficients in equations to relate volumes of gases
  - Provided ***T*** and ***P*** are constant
  - Volume ∝ moles **$V \propto n$**

Ex. Methane burns according to the following equation.

$$CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

1 vol 2 vol 1 vol 2 vol

Ex.

- The combustion of 4.50 *L* of CH_4 consumes how many liters of O_2? (Both volumes measured at STP.)

- ***P*** and ***T*** are all constant so just look at ratio of stoichiometric coefficients

$$\text{Volume of } O_2 = 4.50L * \frac{2L\ O_2}{1L\ CH_4}$$

$$= 9.00\ L\ O_2$$

Ex. Gas bulb with a volume of 250 mL. How many grams of Na_2CO_3 (*s*) would be needed to prepare enough CO_2 (*g*) to fill this bulb when the pressure is at 738 torr and the temperature is 23 °C? The equation is:

$$Na_2CO_3(s) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + CO_2(g) + H_2O(\ell)$$

$$V = 250mL \times \frac{1L}{1000mL} = 0.250L$$

$$P = 738torr \times \frac{1atm}{760torr} = 0.971atm$$

$$T = 23.0\,°C + 273.15\ K = 296.2\ K$$

$$n = \frac{PV}{RT} = \frac{0.971atm \times 0.250L}{0.082057(atm \cdot L / mol \cdot K) \cdot 296.2K}$$

Ex. Solution (cont)

$= 9.989 \text{ x } 10^{-3} \textit{ mole } \mathrm{CO_2}$

$$9.989 \times 10^{-3} \, mol \;\; CO_2 \times \frac{1 mol \;\; Na_2CO_3}{1 mol \;\; CO_2}$$

$= 9.989 \text{ x } 10^{-3} \textit{ mol } \mathrm{Na_2CO_3}$

$$9.989 \times 10^{-3} \, mol \;\; Na_2CO_3 \times \frac{106 g \;\; Na_2CO_3}{1 mol \;\; Na_2CO_3}$$

$= 1.06 \; g \; \mathrm{Na_2CO_3}$

Your Turn!

Ex. How many grams of sodium are required to produce 20.0 L of hydrogen gas at 25.0 C, and 750 torr ?

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

A. 18.6 g

B. 57.0 g

C. 61.3 g

D. 9.62 g

E. 37.1 g

Your Turn! - Solution

- Moles of H_2 produced:

$$n = \frac{750\ \text{torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} \times 20.0\ \text{L}}{0.0821\ \frac{\text{L atm}}{\text{K mol}} \times 298\ \text{K}} = 0.807\ \text{mol}\ H_2$$

- Grams of sodium required:

$$\text{g Na} = 0.807\ \text{mol}\ H_2 \times \frac{2\ \text{mol Na}}{\text{mol}\ H_2} \times \frac{23.0\ \text{g}}{\text{mol Na}} = 37.1\ \text{g}$$

Dalton's Law of Partial Pressure

- For mixture of non-reacting gases in container
- Total pressure exerted is sum of the individual partial pressures that each gas would exert alone
- $P_{total} = P_a + P_b + P_c + \cdots$
- Where P_a, P_b, **and** P_c = **partial pressures**
- **Partial pressure**
  - Pressure that particular gas would exert if it were alone in container

Dalton's Law of Partial Pressures

- Assuming each gas behaves ideally
- Partial pressure of each gas can be calculated from Ideal Gas Law

$$P_a = \frac{n_a RT}{V} \qquad P_b = \frac{n_b RT}{V} \qquad P_c = \frac{n_c RT}{V}$$

- So Total Pressure is

$$P_{total} = P_a + P_b + P_c + \cdots$$
$$= \frac{n_a RT}{V} + \frac{n_b RT}{V} + \frac{n_c RT}{V} + \cdots$$

Dalton's Law of Partial Pressures

- Rearranging

$$P_{total} = (n_a + n_b + n_c + \cdots)\left(\frac{RT}{V}\right)$$

- Or

$$\boxed{P_{total} = n_{total}\left(\frac{RT}{V}\right)}$$

- Where $n_{total} = n_a + n_b + n_c + \cdots$

n_{total} = sum of # moles of various gases in mixture

- Ex. Mixtures of 46 *L* He at 25 °C and 1.0 *atm* and 12 *L* O_2 at 25 °C and 1.0 *atm* were pumped into a tank with a volume of 5.0 *L*. Calculate the partial pressure of each gas and the total pressure in the tank at 25 °C.

He			O_2	
P_i = 1.0 atm	$P_f = P_{He}$		P_i = 1.0 atm	$P_f = P_{O2}$
V_i = 46 L	V_f = 5.0 L		V_i = 12 L	V_f = 5.0 L

Ex. Solution (cont)

- First calculate pressure of each gas in 5 L tank (P_f) using combined gas law

$$P_{He} = \frac{P_i V_i}{V_f} = \frac{1 atm \times 46 L}{5 L} = 9.2 atm$$

$$P_{O_2} = \frac{P_i V_i}{V_f} = \frac{1 atm \times 12 L}{5 L} = 2.4 atm$$

- Then use these partial pressures to calculate total pressure

$$P_{total} = P_{He} + P_{O_2} = 9.2 atm + 2.4 atm = 11.6 atm$$

Your Turn!

Ex. 250 mL of methane, CH_4, at 35 °C and 0.55 atm and 750 mL of propane, C_3H_8, at 35 °C and 1.5 atm, were introduced into a 10.0 L container. What is the final pressure, in torr, of the mixture?

A. 95.6 torr

B. 6.20×10^4 torr

C. 3.4×10^3 torr

D. 760 torr

E. 59.8 torr

Your Turn! - Solution

$$P(CH_4) = \frac{0.55 \text{ atm x } 0.250 \text{ L}}{10.0 \text{ L}} = 0.0138 \text{ atm}$$

$$P(C_3H_8) = \frac{1.5 \text{ atm x } 0.750 \text{ L}}{10.0 \text{ L}} = 0.112 \text{ atm}$$

$$P_T = \left(0.0138 + 0.112\right) \text{ atm x } \frac{760 \text{ torr}}{\text{atm}} = 95.6 \text{ torr}$$

Mole Fractions and Mole Percents

Mole Fraction

- Ratio of number moles of given component in mixture to total number moles in mixture

$$\boxed{X_A = \frac{n_A}{n_A + n_B + n_C + \cdots + n_Z} = \frac{n_A}{n_{total}}}$$

$$n_A = P_A\left(\frac{V}{RT}\right)$$

$$\boxed{X_A = \frac{P_A}{P_{total}} = \frac{n_A}{n_{total}}}$$

$$\boxed{P_A = X_A \times P_{total}}$$

- Ex. The partial pressure of oxygen was observed to be 156 *torr* in air with a total atmospheric pressure of 743 *torr*. Calculate the mole fraction of O_2 present

$$X_A = \frac{P_A}{P_{total}}$$

$$X_{O2} = \frac{156 torr}{743 torr} = 0.210$$

- Ex. The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N_2 in air when the atmospheric pressure is 760. *torr*.

$$P_{N_2} = X_{N_2} \times P_{total}$$

$$P_{N_2} = 0.7808 \times 760 torr = 593 torr$$

Your Turn!

Ex. 250 mL of methane, CH_4, at 35 °C and 0.55 atm and 750 mL of propane, C_3H_8, at 35 °C and 1.5 atm were introduced into a 10.0 L container. What is the mole fraction of methane in the mixture?

A. 0.50

B. 0.11

C. 0.89

D. 0.25

E. 0.33

Your Turn! - Solution

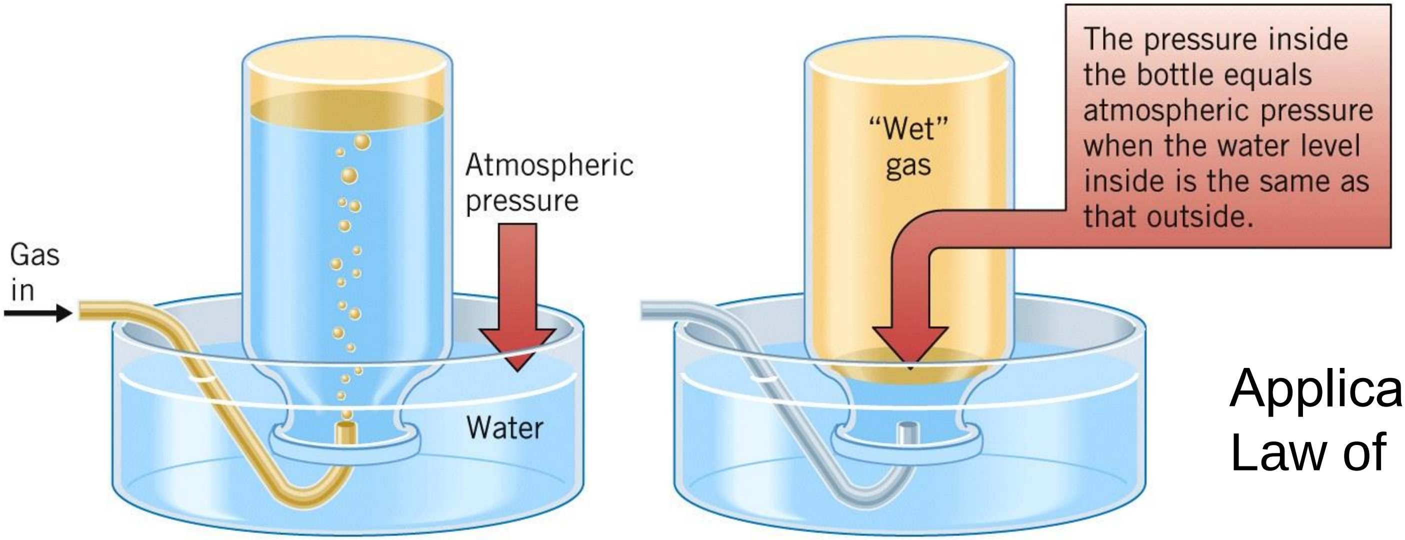
$$P(CH_4) = \frac{0.55\text{ atm x }0.250\text{ L}}{10.0\text{ L}} = 0.0138\text{ atm}$$

$$P(C_3H_8) = \frac{1.5\text{ atm x }0.750\text{ L}}{10.0\text{ L}} = 0.112\text{ atm}$$

$$X_{CH_4} = \frac{0.0138\text{ atm}}{(0.0138 + 0.112)\text{ atm}} = 0.110$$

Collecting Gases over Water

- Water vapor is present because molecules of water escape from surface of liquid and collect in space above liquid
- Molecules of water return to liquid
- rate of escape = rate of return
  - Number of water molecules in vapor state remains constant
- Gas saturated with water vapor = "Wet" gas



The pressure inside the bottle equals atmospheric pressure when the water level inside is the same as that outside.

Application of Dalton's Law of Partial Pressures

Vapor Pressure

- Pressure exerted by vapor present in space above any liquid
  - Constant at constant T
- When wet gas collected over water, we usually want to know how much "dry" gas this corresponds to
- $P_{total} = P_{gas} + P_{water}$
- Rearranging
- $P_{gas} = P_{total} - P_{water}$

Ex. A sample of oxygen is collected over water at 20.0 °C and a pressure of 738 torr. Its volume is 310 *mL*. The vapor pressure of water at 20°C is 17.54 torr.

a. What is the partial pressure of O_2?

b. What would the volume be when dry at STP?

a. $P_{O_2} = P_{total} - P_{water}$

$= 738 \text{ torr} - 17.5 \text{ torr} = $ **720 torr**

Ex. Solution

b. calculate P_{O2} at STP

P_1 = 720 torr P_2 = 760 torr

V_1 = 310 mL V_2 = ?

T_1 = 20.0 + 273.12 = 293 K

T_2 = 0.0 + 273 K = 273 K

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$V_2 = \frac{720 torr \times 310 mL \times 273 K}{293 K \times 760 torr}$$

V_2 = **274 *mL***

Your Turn!

Ex. An unknown gas was collected by water displacement. The following data was recorded: T = 27.0 °C; P = 750 torr; V = 37.5 mL; Gas mass = 0.0873 g; $P^{vap}(H_2O)$ = 26.98 torr

Determine the molecular weight of the gas.

A. 5.42 g/mol

B. 30.2 g/mol

C. 60.3 g/mol

D. 58.1 g/mol

E. 5.81 g/mol

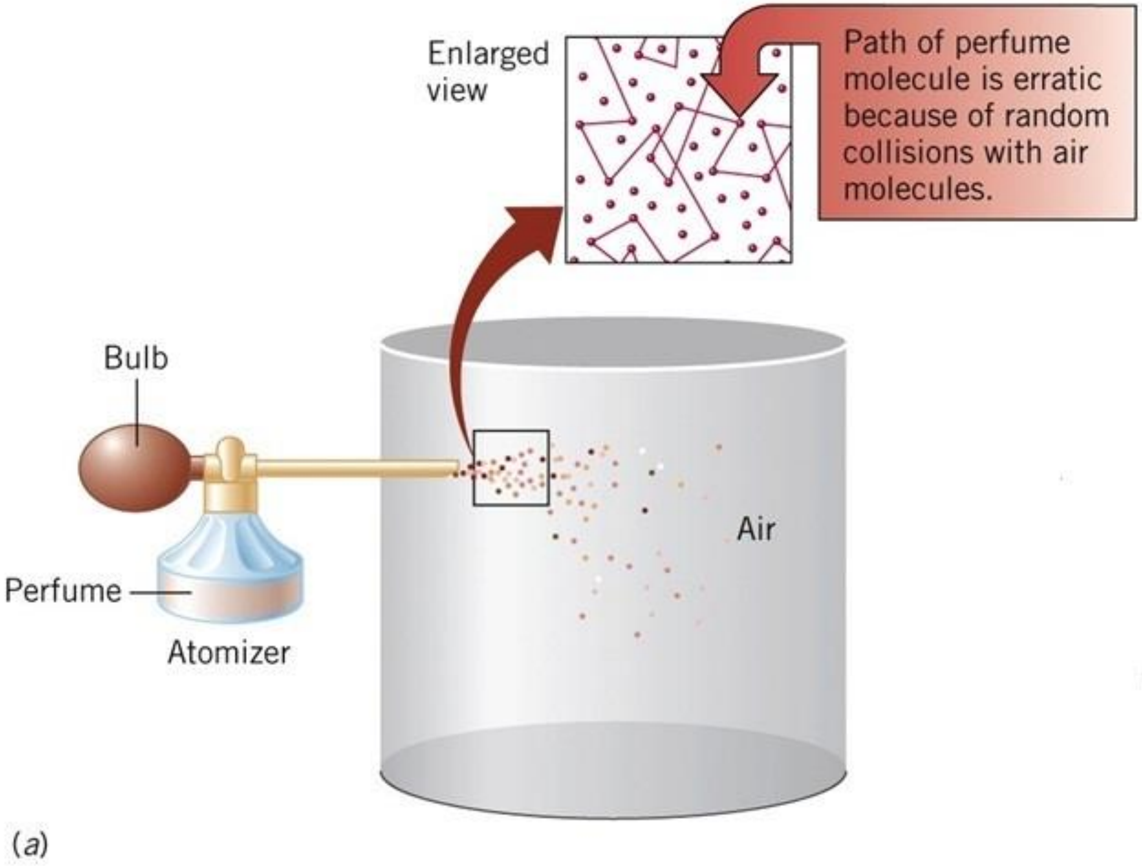
Your Turn! - Solution

$$MW = \frac{\text{gRT}}{\text{PV}} = \frac{0.0873\ \text{g x } 0.0821\ \dfrac{\text{L atm}}{\text{K mol}}\ \text{x } 300\ \text{K}}{(750 - 26.98)\text{torr x } 0.0375\ \text{L}}$$

$$MW = 60.3\ \text{g/mol}$$

Diffusion

- Complete spreading out and intermingling of molecules of one gas into and among those of another gas
  - **Ex.** Perfume in room

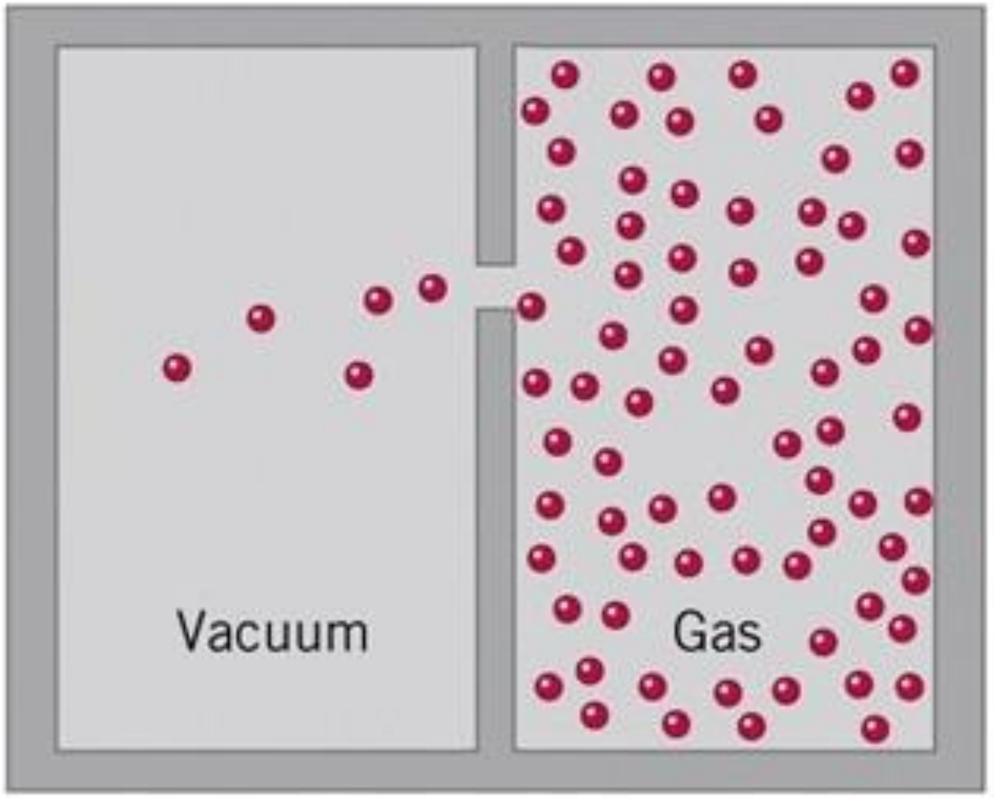


Effusion

- Movement of gas molecules
- Through extremely small opening into vacuum

Vacuum

  - No other gases present in other half



Graham's Law of Effusion

- Rates of effusion of gases are inversely proportional to square roots of their densities, ***d***, when compared at identical pressures and temperatures

$$\text{Effusion Rate} \propto \frac{1}{\sqrt{d}} \qquad (\text{constant } P \text{ and } T)$$

$$\frac{\text{Effusion Rate }(A)}{\text{Effusion Rate }(B)} = \frac{\sqrt{d_B}}{\sqrt{d_A}} = \sqrt{\frac{d_B}{d_A}}$$

$$\boxed{\frac{\text{Effusion Rate }(A)}{\text{Effusion Rate }(B)} = \sqrt{\frac{d_B}{d_A}} = \sqrt{\frac{M_B}{M_A}}}$$

Graham's Law of Effusion

Ex. Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6) - a gas used in the enrichment process to produce fuel for nuclear reactors.

- First must compute MM's
  - MM (H_2) = 2.016 g/mol
  - MM (UF_6) = 352.02 g/mol

$$\frac{\text{Effusion Rate}(H_2)}{\text{Effusion Rate}(UF_6)} = \sqrt{\frac{M_{UF_6}}{M_{H_2}}} = \sqrt{\frac{352.02}{2.016}} = 13.2$$

- Thus the very light H_2 molecules effuse ~13 times as fast as the massive UF_6 molecules.

- Ex. For the series of gases He, Ne, Ar, H_2, and O_2 what is the order of increasing rate of effusion?

substance	He	Ne	Ar	H_2	O_2
MM	4	20	40	2	32

- Lightest are fastest
- So H_2 > He > Ne > O_2 >Ar

Heavier gases effuse more slowly
Lighter gases effuse more rapidly

Postulates of Kinetic Theory of Gases

1. Particles are so small compared with distances between them, so volume of individual particles can be assumed to be negligible.
    - $V_{gas} \sim 0$

2. Particles are in constant motion
    - Collisions of particles with walls of container are cause of pressure exerted by gas
    - number collisions $\propto P_{gas}$

Postulates of Kinetic Theory of Gases

3. Particles are assumed to exert no force on each other
   - Assumed neither to attract nor to repel each other
4. Average kinetic energy of collection of gas particles is assumed to be directly proportional to Kelvin Temperature
   - $KE_{avg} \propto T_K$

Root-mean-square speed $v_{\mathrm{rms}} = \sqrt{\frac{3RT}{M_m}}$

Ex: What are the rms speeds of helium atoms, and nitrogen, hydrogen, and oxygen molecules at 25 °C?

T = 25 °C + 273 = 298 K.   R = 8.314 J/mol K

$$v_{\mathrm{rms}} = \sqrt{\frac{3RT}{M_m}}$$

Element	Mass (kg)	rms speed (m/s)
He	6.64×10^{-27}	1360
H_2	3.32×10^{-27}	1930
N_2	4.64×10^{-26}	515
O_2	5.32×10^{-26}	482

Kinetic Theory of Gases

- This means **T** $\propto$ **KE$_{ave}$**
- Specifically

- As increase T, ↑ KE$_{ave}$,
  - ↑ number collisions with walls, thereby increasing P
  - Kinetic energy For 1 mole of gas is:

$$\boxed{KE_{ave} = \frac{3}{2}RT}$$

Real Gases

- Have ***finite*** volumes
- ***Do*** exert forces on each other

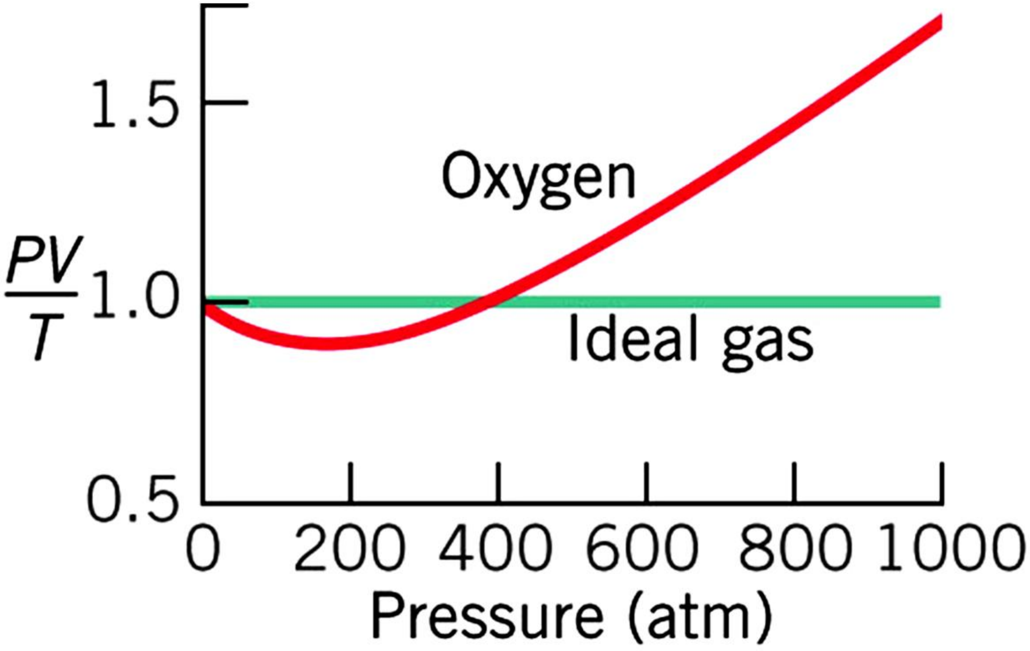
- Real Gases deviate ***Why?***

$$\frac{PV}{T} = \text{constant}$$

$$\frac{PV}{nT} = R$$

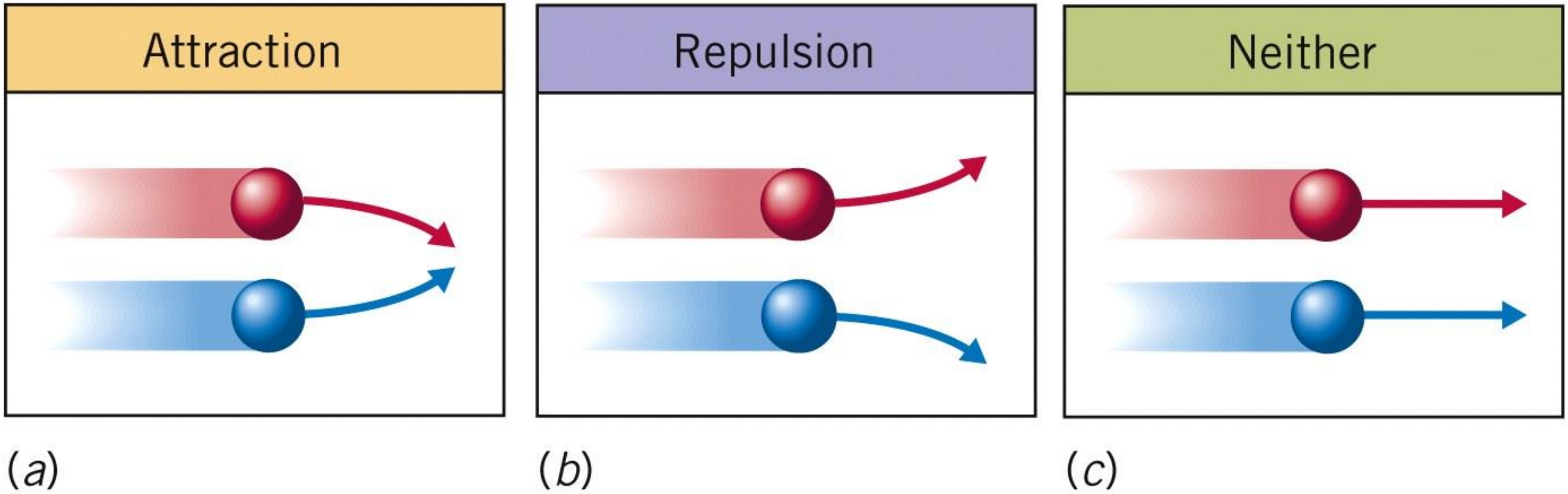
Real Gases Deviate from Ideal Gas Law

1. Gas molecules have finite V's
   - ∴ Take up space
   - Less space of kinetic motions
   - $V_{motions} < V_{container}$
   - ∴ particles hit walls of container more often
   - ↑ P over ideal



Real Gases

2. Particles DO attract each other
   - Even weak attractions means they hit walls of container less often
   - ∴ ↓ P over ideal gas



van der Waal's equation for Real Gases

$$\underbrace{\left(P+\frac{n^{2}a}{V^{2}}\right)}_{\text{corrected P}} * \underbrace{\left(V-nb\right)}_{\text{corrected V}} = nRT$$

- **a** and **b** are **van der Waal's** constants
- Obtained by measuring **P, V, and T** for real gases over wide range of conditions

van der Waal's equation for Real Gases

$$\underbrace{\left(P + \frac{n^2 a}{V^2}\right)}_{\text{corrected P}} * \left(V - nb\right) = nRT$$

- ***a*** — Pressure correction
  - Indicates some ***attractions*** between molecules
  - Large ***a***
    - Means strong attractive forces between molecules
  - Small ***a***
    - Means weak attractive forces between molecules

van der Waal's equation for Real Gases

$$\left(P+\frac{n^2a}{V^2}\right)*\underbrace{(V-nb)}_{\text{corrected V}}=nRT$$

- ***b*** — Volume correction
  - Deals with ***sizes*** of molecules
  - Large ***b***
    - Means large molecules
  - Small ***b***
    - Means small molecules
  - Gases that are most easily liquefied have largest van der Waal's constants

Ex: When will a real gas behave most like an ideal gas?

A) at high temperatures and high pressures

B) at low temperatures and high pressures

C) at low temperatures and low pressures

D) at high temperatures and low pressures

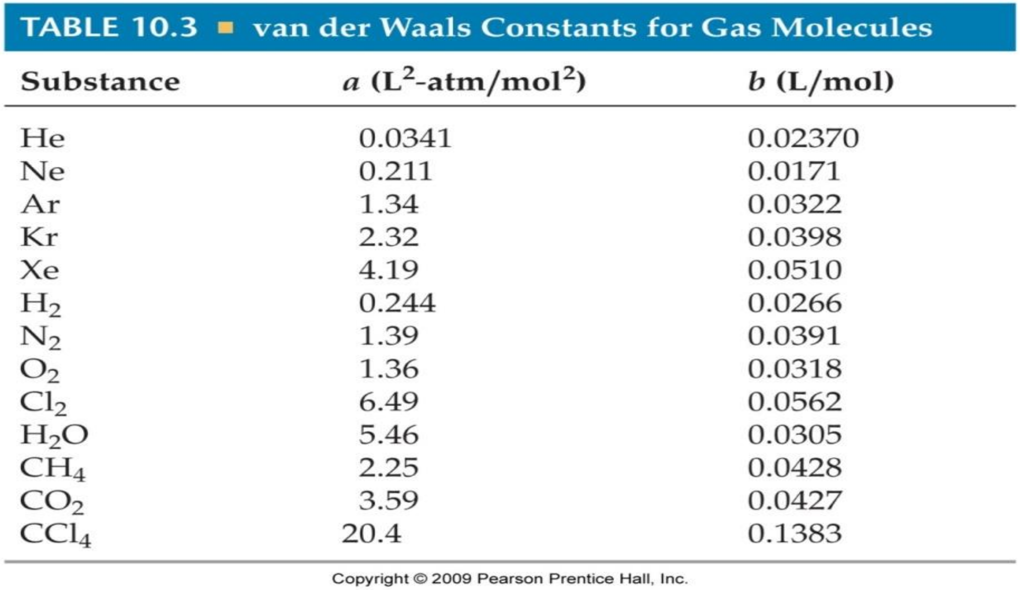
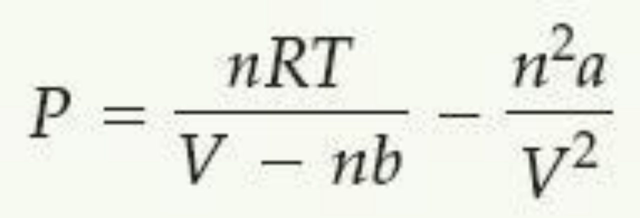


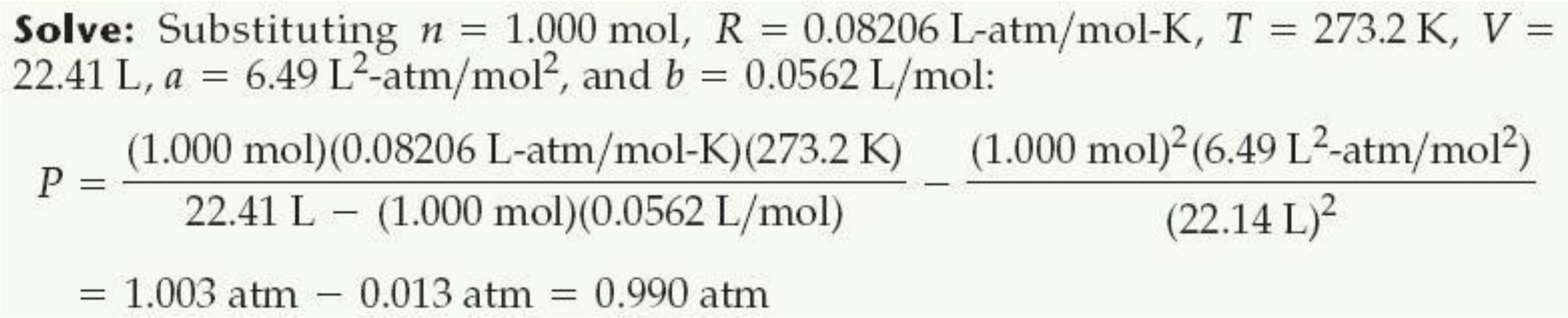
TABLE 10.3 ■ van der Waals Constants for Gas Molecules

Substance	a (L^2-atm/mol^2)	b (L/mol)
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

Ex: If 1.000 mol of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 1.000 atm. Use the van der Waals equation and the constants in Table 10.3 to estimate the pressure exerted by 1.000 mol of $Cl_2(g)$ in 22.41 L at 0.0 °C.



$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$



Solve: Substituting $n = 1.000$ mol, $R = 0.08206$ L-atm/mol-K, $T = 273.2$ K, $V = 22.41$ L, $a = 6.49$ L^2-atm/mol^2, and $b = 0.0562$ L/mol:

$$P = \frac{(1.000\ \text{mol})(0.08206\ \text{L-atm/mol-K})(273.2\ \text{K})}{22.41\ \text{L} - (1.000\ \text{mol})(0.0562\ \text{L/mol})} - \frac{(1.000\ \text{mol})^2(6.49\ \text{L}^2\text{-atm/mol}^2)}{(22.14\ \text{L})^2}$$

$$= 1.003\ \text{atm} - 0.013\ \text{atm} = 0.990\ \text{atm}$$

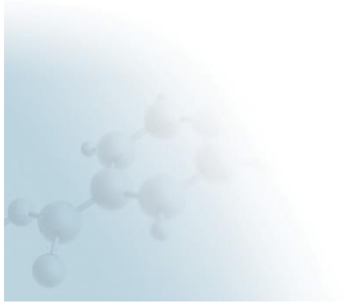
Ex.2. Use Van de Waal's equation to calculate the pressure exerted by 1.00 molCl_2 confined to a volume of 2.00 L at 273K. The value of a=6.49L^2 atm/mol^2 and b=0.0562 L/mol

Chapter 3

Energy and Chemical Change Thermodynamics

Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop



Thermochemistry

- Study of energies given off by or absorbed by reactions.

Thermodynamics

- Study of energy transfer (flow)

Energy (E)

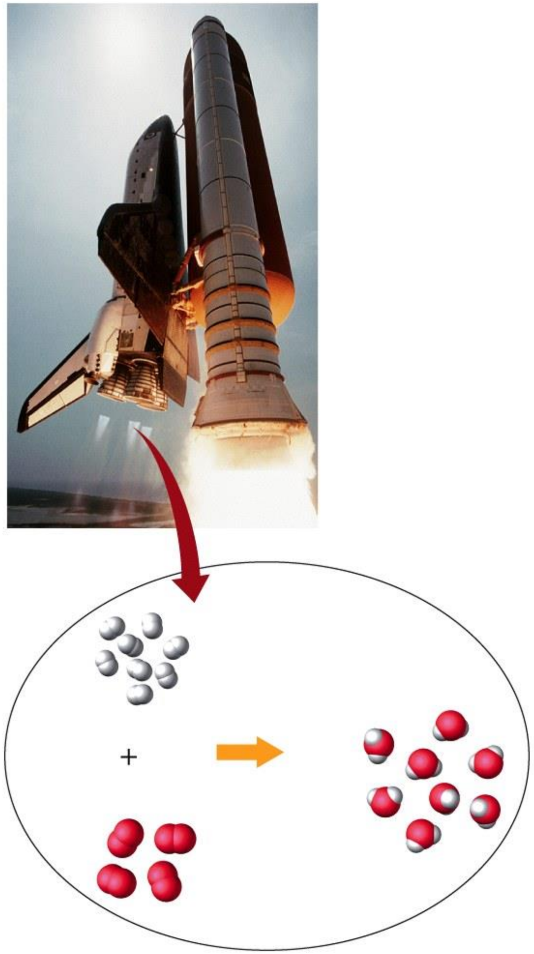
  - Ability to do work or to transfer heat.

Kinetic Energy (KE)

  - Energy of motion
  - **KE = $\frac{1}{2}mv^2$**

Potential Energy (PE)

- Stored energy
- Exists in natural attractions and repulsions
  - Gravity
  - Positive and negative charges
  - Springs

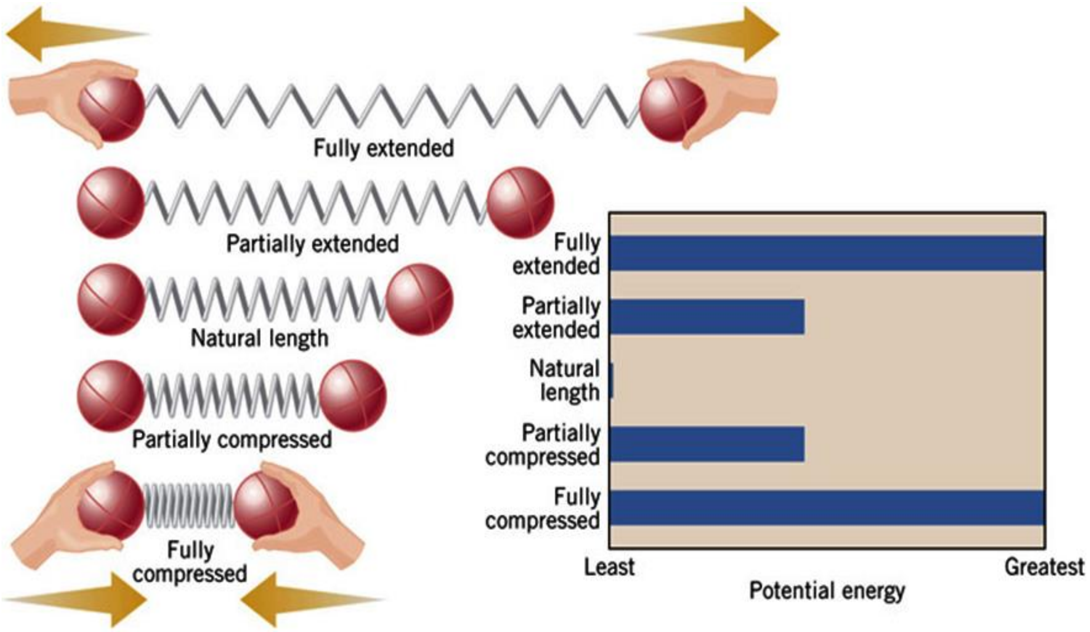


Chemical Energy

- PE possessed by chemicals
- Stored in chemical bonds
- Breaking bonds requires energy
- Forming bonds releases energy

Law of Conservation of Energy

- Energy can neither be created nor destroyed
- Can only be converted from one form to another
- Total Energy of universe is constant



Total Energy = Potential Energy + Kinetic Energy

Temperature vs. Heat

Temperature

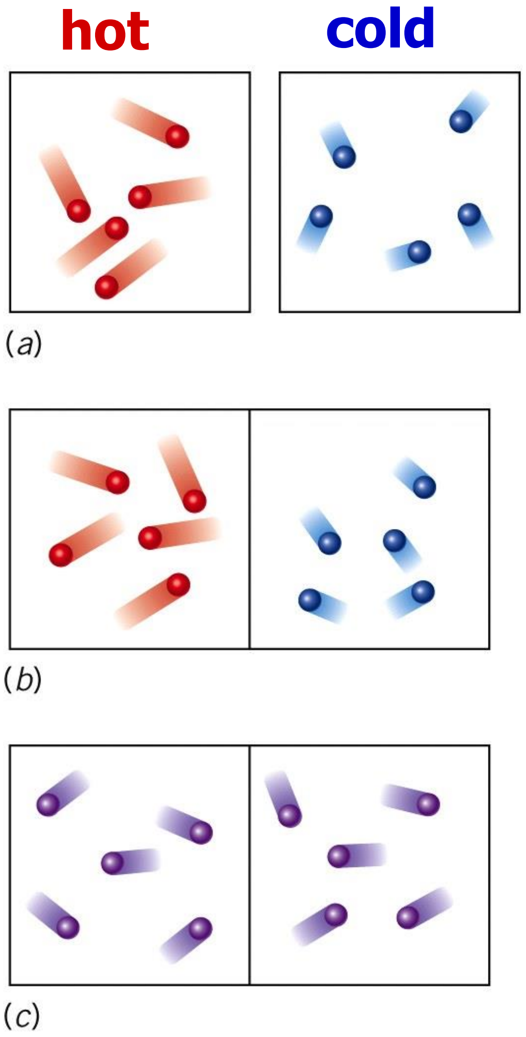
  - Proportional to **average** kinetic energy of object’s particles
- Higher average kinetic energy means
  - Higher temperature
  - Faster moving molecules

Heat

  - Energy transferred between objects
  - Caused by temperature difference
  - Always passes spontaneously from warmer objects to colder objects
  - Transfers until both are the same temperature

Heat Transfer

- Hot and cold objects placed in contact
    - Molecules in hot object moving faster
- KE transfers from hotter to colder object
    - ↓ average KE of hotter object
    - ↑ average KE of colder object
- Over time
    - Average KEs of both objects becomes the same
    - Temperature of both becomes the same



Units of Energy

Joule (J)

$$1J = \frac{1 kg \cdot m^2}{s^2}$$

- value is greater than 1000 J, use kJ

- 1 kJ = 1000 J

calorie (cal)

Energy needed to raise T of 1 g H_2O by 1 °C

1 cal = 4.184 J (exactly)

Internal Energy (*E*)

- Sum of energies of all particles in system

  E = Total energy of system

  E = Potential + Kinetic **=** $PE + KE$

Change in Internal Energy

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

  - Δ means change
  - final – initial
  - What we can actually measure

- Want to know change in E associated with given process

ΔE, Change in Internal Energy

- For reaction: **reactants $\longrightarrow$ products**
- $\Delta E = E_{\text{products}} - E_{\text{reactants}}$
  - Can use to do something useful
    - Work
    - Heat
- If system absorbs energy during reaction
  - Energy coming into system is positive (+)
  - Final energy > initial energy

  Ex. Photosynthesis *or* charging battery
  - As system absorbs energy
    - Increase potential energy
    - Available for later use

ΔE, Change in Internal Energy

- $\Delta E = E_{\text{products}} - E_{\text{reactants}}$
  - Energy change can appear entirely as heat
  - Can measure heat
  - Can't measure E_{product} or E_{reactant}
  - Fortunately, we are more interested in ΔE
  - Energy of system depends only on its current condition
    - DOES NOT depend on:
    - How system got it
    - What E for system might be sometime in future

State Functions

- Any property that **only** depends on object's current state or condition
- Independence from method, path or mechanism by which change occurs is important feature of all state functions
- Some State functions:
  - Internal energy $\Delta E = E_f - E_i$
  - Pressure $\Delta P = P_f - P_i$
  - Temperature $\Delta t = t_f - t_i$
  - Volume $\Delta V = V_f - V_i$

Defining the System

System

- What we are interested in studying
    - Reaction in beaker

Surroundings

- Everything else
    - Room in which reaction is run

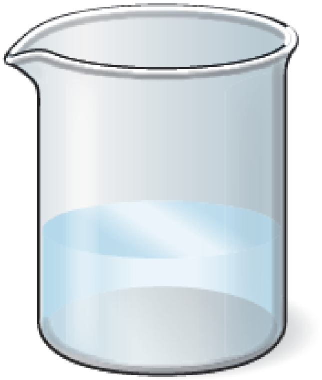
Boundary

- Separation between system and surroundings
    - Visible **Ex.** Walls of beaker
    - Invisible **Ex.** Line separating warm and cold fronts

Three Types of Systems

Open System

- Open to atmosphere
- Gain or lose mass and energy across boundary
- Most reactions done in open systems



Open system

Closed System

- Not open to atmosphere
- Energy can cross boundary, but mass **cannot**

Closed system

Three Types of Systems

Isolated System

- No energy or matter can cross boundary
- Energy and mass are constant

Ex. Thermos bottle

Isolated system

Your Turn!

Ex. A closed system can __________

A. include the surroundings.

B. absorb energy and mass.

C. not change its temperature.

D. not absorb or lose energy and mass.

E. absorb or lose energy, but not mass.

Heat (q)

- Can't measure heat directly
- Heat (q) gained or lost by an object
  - Directly proportional to temperature change (Δt) it undergoes. $\Delta t = t_f - t_i$
  - Adding heat, increases temperature $\Delta t > 0, q > 0$
  - Removing heat, decreases temperature $\Delta t < 0, q < 0$
- Measure changes in temperature to quantify amount of heat transferred

$$q = C \times \Delta t$$

- C = heat capacity

Heat Capacity (*C*)

- Amount of heat (***q***) required to raise temperature of object by 1 °C

  Heat Exchanged = Heat Capacity × Δ*t*

  $$q = C \times \Delta t$$

  - **Units** = ***J/°C*** or ***J·°C^{-1}***

Depends on two factors

1. Sample size or amount (mass)
   - Doubling amount doubles heat capacity
2. Identity of substance
   - Water vs. iron

Learning Check: Heat Capacity

Ex. A cup of water is used in an experiment. Its heat capacity is known to be 720 J/ °C. How much heat will it absorb if the experimental temperature changed from 19.2 °C to 23.5 °C?

$$q = C \times \Delta t$$

$$q = 720\,\frac{J}{°C} \times (23.5 - 19.2°C)$$

$$q = 720\,\frac{J}{°C} \times (4.3°C)$$

$$\boldsymbol{q = 3.1 \times 10^3\ \mathrm{J}}$$

Learning Check: Heat Capacity

Ex. If it requires 4.184 J to raise the temperature of 1.00 g of water by 1.00 °C, calculate the heat capacity of 1.00 g of water.

$$C = \frac{q}{\Delta t}$$

$$C_{1.00\text{ g}} = \frac{4.184\text{ J}}{1.00\ ^\circ\text{C}} = \mathbf{4.18\ J/^\circ C}$$

Your Turn!

Ex. What is the heat capacity of 300 g of water if it requires 2510 J to raise the temperature of the water by 2.00 °C?

A. 4.18 J/°C

B. 418 J/°C

C. 837 J/°C

D. 1.26×10^3 J/°C

E. 2.51×10^3 J/°C

$$C_{300\text{ g}} = \frac{2510\text{ J}}{2.00\ ^\circ\text{C}} =$$

Specific Heat (*s*)

- Amount of Heat Energy needed to raise T of 1 g substance by 1 °C

$$C = s \times m \qquad \text{or} \qquad s = \frac{C}{m}$$

- **Units**
  - **J/(g·°C)** or **J g^{-1}°C^{-1}**
- Unique to each substance
- Large specific heat means substance releases large amount of heat as it cools

Learning Check

Ex. Calculate the specific heat of water if it the heat capacity of 100 g of water is 418 J/°C.

$$s = \frac{C}{m} \qquad s = \frac{418\ \text{J}/^\circ\text{C}}{100.\ \text{g}} = \mathbf{4.18\ J/(g{\cdot}{}^\circ C)}$$

- What is the specific heat of water if heat capacity of 1.00 g of water is 4.18 J/°C?

$$s = \frac{4.18\ \text{J}/^\circ\text{C}}{1.00\ \text{g}} = \mathbf{4.18\ J/(g{\cdot}{}^\circ C)}$$

- Thus, heat capacity is independent of amount

Your Turn!

Ex. The specific heat of silver 0.235 J g^{-1} $°C^{-1}$. What is the heat capacity of a 100. g sample of silver?

$$C = s \times m$$

A. 0.235 J/°C

B. 2.35 J/°C

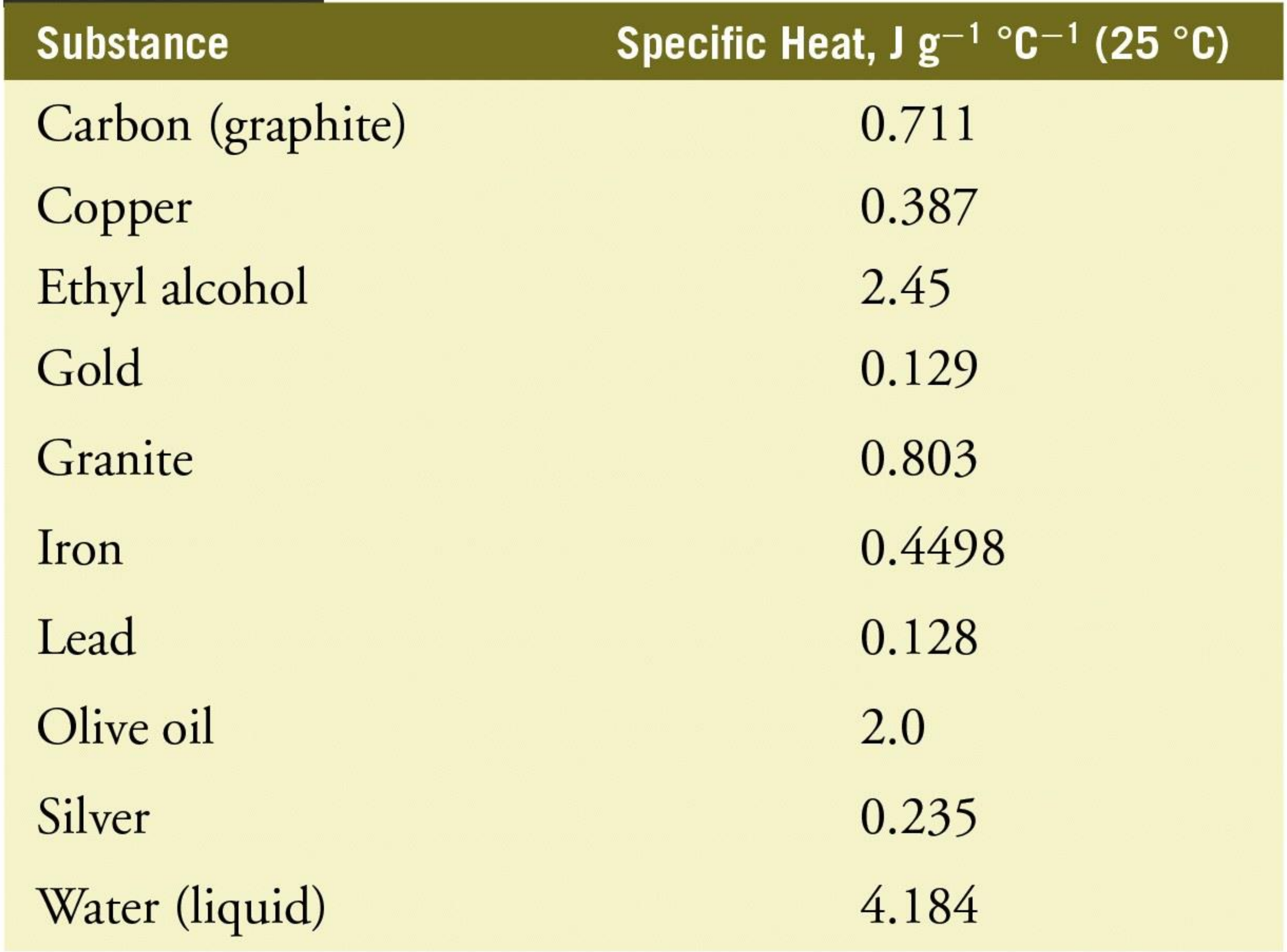
C. 23.5 J/°C

D. 235 J/°C

E. 2.35×10^3 J/°C

$$C = 0.235 \frac{J}{g \cdot {}^\circ C} \times 100.\ g$$

Table 7.1 Specific Heats



Substance	Specific Heat, J g^{-1} °C^{-1} (25 °C)
Carbon (graphite)	0.711
Copper	0.387
Ethyl alcohol	2.45
Gold	0.129
Granite	0.803
Iron	0.4498
Lead	0.128
Olive oil	2.0
Silver	0.235
Water (liquid)	4.184

Using Specific Heat

Heat Exchanged = (Specific Heat × mass) × Δ*t*

$$q = s \times m \times \Delta t$$

Units = J/(g × °C) × g × °C = **J**

- Substances with high specific heats resist ΔT changes
- Makes it difficult to change temperature widely
- Water has unusually high specific heat

Learning Check: Specific Heat

Ex. Calculate the specific heat of a metal if it takes 235 J to raise the temperature of a 32.91 g sample by 2.53°C.

$$q = m \times s \times \Delta t$$

$$s = \frac{q}{m \times \Delta t} = \frac{235\text{J}}{32.91\text{g} \times 2.53^{\circ}\text{C}}$$

$$\boxed{s = 2.82 \frac{\text{J}}{\text{g}^{\circ}\text{C}}}$$

Ex. 1 Using Specific Heat

Ex. If a 38.6 g of gold absorbs 297 J of heat, what will the final temperature if the initial temperature is 24.5 °C? The specific heat of gold is 0.129 J g^{-1} $°C^{-1}$.

Need to find t_{final} $\Delta t = t_f - t_i$

First use $q = s \times m \times \Delta t$ to calculate Δt

$$\Delta t = \frac{q}{s \cdot m} = \frac{297\,\text{J}}{0.129\,\text{J} \cdot \text{g}^{-1} \cdot {}^{\circ}\text{C}^{-1} \times 38.6\,\text{g}} = \mathbf{59.6\ {}^{\circ}C}$$

$59.6\ °C = t_f - 24.5\ °C$

$t_f = 59.6\ °C + 24.5\ °C$

$= \mathbf{84.1\ °C}$

Exothermic Reaction

- Reaction where products have less chemical energy than reactants
  - Some chemical energy converted to kinetic energy
  - Reaction releases heat to surroundings
  - Heat leaves the system; q negative (–)
  - Reaction gets warmer (↑T)

Ex.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \text{heat}$$

Endothermic Reaction

- Reaction where products have more chemical energy than reactants
  - Some kinetic energy converted to chemical energy
  - Reaction absorbs heat from surroundings
  - Heat added to system; q positive (+)
  - Reaction becomes colder (T ↓)

Ex. Photosynthesis

$$6CO_2(g) + 6H_2O(g) + \text{solar energy} \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

Work Convention

Work = $-P \times \Delta V$

- **P** = opposing pressure against which piston pushes
- **ΔV** = change in volume of gas during expansion
- **ΔV** = $V_{final} - V_{initial}$
- For Expansion
  - Since $V_{final} > V_{initial}$
  - **ΔV** must be positive
  - So expansion work is negative **$\Delta V > 0$**
  - Work done **by** system on surrounding, **$W < 0$**

Your Turn!

Ex. Calculate the work associated with the expansion of a gas from 152.0 L to 189.0 L at a constant pressure of 17.0 atm.

A. 629 L atm

B. –629 L atm

C. –315 L atm

D. 171 L atm

E. 315 L atm

Work = –P×ΔV

$\Delta V = 189.0\ \text{L} - 152.0\ \text{L}$

$w = -17.0\ \text{atm} \times 37.0\ \text{L}$

First Law of Thermodynamics

- "Energy of system may be transferred as heat or work, but not lost or gained."
- If we monitor heat transfers (***q***) of all materials involved and all work processes, can predict that their sum will be zero
  - Some materials gain (have +) energy
  - Others lose (have –) energy
- By monitoring surroundings, we can predict what is happening to system

Two Methods of *Energy* Exchange Between System and Surroundings

Heat ***q*** Work ***w***

$$\Delta E = q + w$$

- **Conventions of heat and work**

q	+	Heat **absorbed** by system	E_{system} ↑
q	–	Heat **released** by system	E_{system} ↓
w	+	Work done **on** system	E_{system} ↑
w	–	Work done **by** system	E_{system} ↓

Heat and Work

Two ways system can exchange internal energy with surroundings

1. Heat

- Heat absorbed, System’s q ↑
- Heat lost, System’s q ↓

2. Work

- Is exchanged when pushing force moves something through distance

Ex. Compression of system’s gas $W>0$

expansion of system’s gas $W<0$

Your Turn!

Ex. A gas releases 3.0 J of heat and then performs 12.2 J of work. What is the change in internal energy of the gas?

A. –15.2 J

B. 15.2 J

C. –9.2 J

D. 9.2 J

E. 3.0 J

$$\Delta E = q + w$$

$$\Delta E = -3.0\ \text{J} + (-12.2\ \text{J})$$

Heat at Constant Pressure (q_P)

- Chemists usually do NOT run reactions at constant ***V***
- Usually do reactions in open containers
  - Open to atmosphere; constant ***P***
  - Heat of reaction at constant Pressure (q_P)
- $\Delta E = q_P + w = q_P - P\Delta V$
- $q_P = \Delta E + P\Delta V$

  H = state function
- At constant Pressure: $\Delta H = q_P$

  $\Delta H = \Delta E + P\Delta V$

Enthalpy Change (ΔH)

ΔH = state function

- **$\Delta H = H_{\text{final}} - H_{\text{initial}}$**
- **$\Delta H = H_{\text{products}} - H_{\text{reactants}}$**

- Significance of sign of ΔH

Endothermic reaction

- System absorbs energy from surroundings
- **$\Delta H > 0$ positive**

Exothermic reaction

- System loses energy to surroundings
- **$\Delta H < 0$ negative**

Enthalpy vs. Internal Energy

- $\Delta H = \Delta E + P\Delta V$

Rearranging gives

- $\Delta H - \Delta E = P\Delta V$
- Difference between ΔH and ΔE is $P\Delta V$
- Reactions where form or consume gases
  - $P\Delta V$ can be large
- Reactions involving only liquids and solids
  - ΔV negligible $\Delta V \approx 0$
  - So $\Delta H \approx \Delta E$

Enthalpy Changes in Chemical Reactions

- Focus on systems

- Endothermic
  - Reactants + ***heat*** $\longrightarrow$ products

- Exothermic
  - Reactants $\longrightarrow$ products + ***heat***

ΔH in Chemical Reactions

Standard Conditions for $\Delta H°$

- 25 °C and 1 atm

Standard Heat of Reaction ($\Delta H°$)

- Enthalpy change for reaction at 1 atm and 25 °C

Ex.

$$N_2(g) \; + \; 3H_2(g) \longrightarrow 2\,NH_3(g)$$

1.000 mol 3.000 mol 2.000 mol

- When N_2 and H_2 react to form NH_3 at 25 °C and 1 atm
- 92.38 kJ released
- $\Delta H° = -92.38$ kJ

Thermochemical Equation

- Write $\Delta H°$ immediately after equation

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H° = -92.38\ \text{kJ}$

- **Must give physical states of products and reactants**
  - ΔH_{rxn} different for different states

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) \quad \Delta H = -890.5\ \text{kJ}$

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H = -802.3\ \text{kJ}$

  - Difference = energy to vaporize water

Thermochemical Equation

- Write ΔH° immediately after equation

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H^\circ = -92.38$ kJ

- **coefficients = # moles**
  - 92.38 kJ released ⇔ 2 moles of NH_3 formed
  - If 10 mole of NH_3 formed

    $5N_2(g) + 15H_2(g) \rightarrow 10NH_3(g) \quad \Delta H^\circ = -461.9$ kJ

    - $\Delta H^\circ_{\mathbf{rxn}} = (5 \times -92.38 \text{ kJ}) = -461.9$ kJ
  - Can have fractional coefficients

    $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g) \quad \Delta H^\circ = -46.19$ kJ

State Matters!

$$C_3H_8(g) + 5O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(\mathbf{g})$$

$$\Delta H = -\ 2043\ \text{kJ}$$

$$C_3H_8(g) + 5O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(\boldsymbol{\ell})$$

$$\Delta H = -\ 2219\ \text{kJ}$$

Note: there is difference in energy because states do not match

If $H_2O(\ell) \rightarrow H_2O(g)$ $\Delta H = 44\ \text{kJ/mol}$

$4H_2O(\ell) \rightarrow 4H_2O(g)$ $\Delta H = 176\ \text{kJ/mol}$

$4H_2O(\boldsymbol{\ell}) \rightarrow 4\ H_2O(\boldsymbol{\ell})$ $\Delta H = -2219\ \text{kJ} + 176\ \text{kJ} = -2043\ \text{kJ}$

Learning Check:

Ex. Consider the following reaction:

$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$

$\Delta H = -2511\ \text{kJ}$

How many kJ are released for 1 mol C_2H_2?

$2\ \text{mol}\ C_2H_2 \rightarrow -2511\ \text{kJ}$

$1\ \text{mol}\ C_2H_2 \rightarrow \quad ? \quad \text{kJ}$

$$\frac{-2511\,\text{kJ}}{2\,\text{mol}\ C_2H_2} \times 1\,\text{mol}\ C_2H_2 = \quad \textbf{−1,256 kJ}$$

Learning Check:

EX. Consider the reaction

$6CO_2(g) + 6H_2O \rightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H = 2816\text{ kJ}$

A) how many kJ are required for 44 g CO_2 (MM = 44.01 g/mol)?

$$44\text{ g }CO_2 \times \frac{1\text{ mol }CO_2}{44.01\text{g }CO_2} \times \frac{2816\text{ kJ}}{6\text{ mol }CO_2} = \mathbf{470\ kJ}$$

B) If 100. kJ are provided, what mass of CO_2 can be converted to glucose?

$$100\text{kJ} \times \frac{6\text{mol }CO_2}{2816\text{kJ}} \times \frac{44.0\text{g}CO_2}{1\text{mol }CO_2} = \mathbf{9.38\ g}$$

Your Turn!

Ex. Based on the reaction

$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(g) + 4HCl(g)$

$\Delta H = -434\ \text{kJ/mol}\ CH_4$

What energy change occurs when 1.2 moles of methane reacts?

A. -3.6×10^2 kJ

B. $+5.2 \times 10^2$ kJ

C. -4.3×10^2 kJ

D. $+3.6 \times 10^2$ kJ

E. -5.2×10^2 kJ

$\Delta H = -434\ \text{kJ/mol} \times 1.2\ \text{mol}$

$\Delta H = -5\underline{2}0.8\ \text{kJ}$

Running Thermochemical Equations in Reverse

Consider the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

$$\Delta H^\circ = -\ 802.3\ \text{kJ}$$

- Reverse thermochemical equation
- Must change sign of ΔH

$$CO_2(g)\ +\ 2H_2O(g)\ \rightarrow\ CH_4(g)\ +\ 2O_2(g)$$

$$\Delta H^\circ = +\ 802.3\ \text{kJ}$$

Hess's Law
Multiple Paths; Same ΔH°

Path a: Single step

$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = -393.5\ \text{kJ}$

Path b: Two step

~~Step 1: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H^\circ = -110.5\ \text{kJ}$~~

Step 2: $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = -283.0\ \text{kJ}$

Net Rxn: $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = -393.5\ \text{kJ}$

- Chemically and thermochemically, identical results

Ex. Multiple Paths; Same ΔH°

Path a: $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ $\Delta H° = 68\ kJ$

Path b:

Step 1: $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H° = 180.\ kJ$

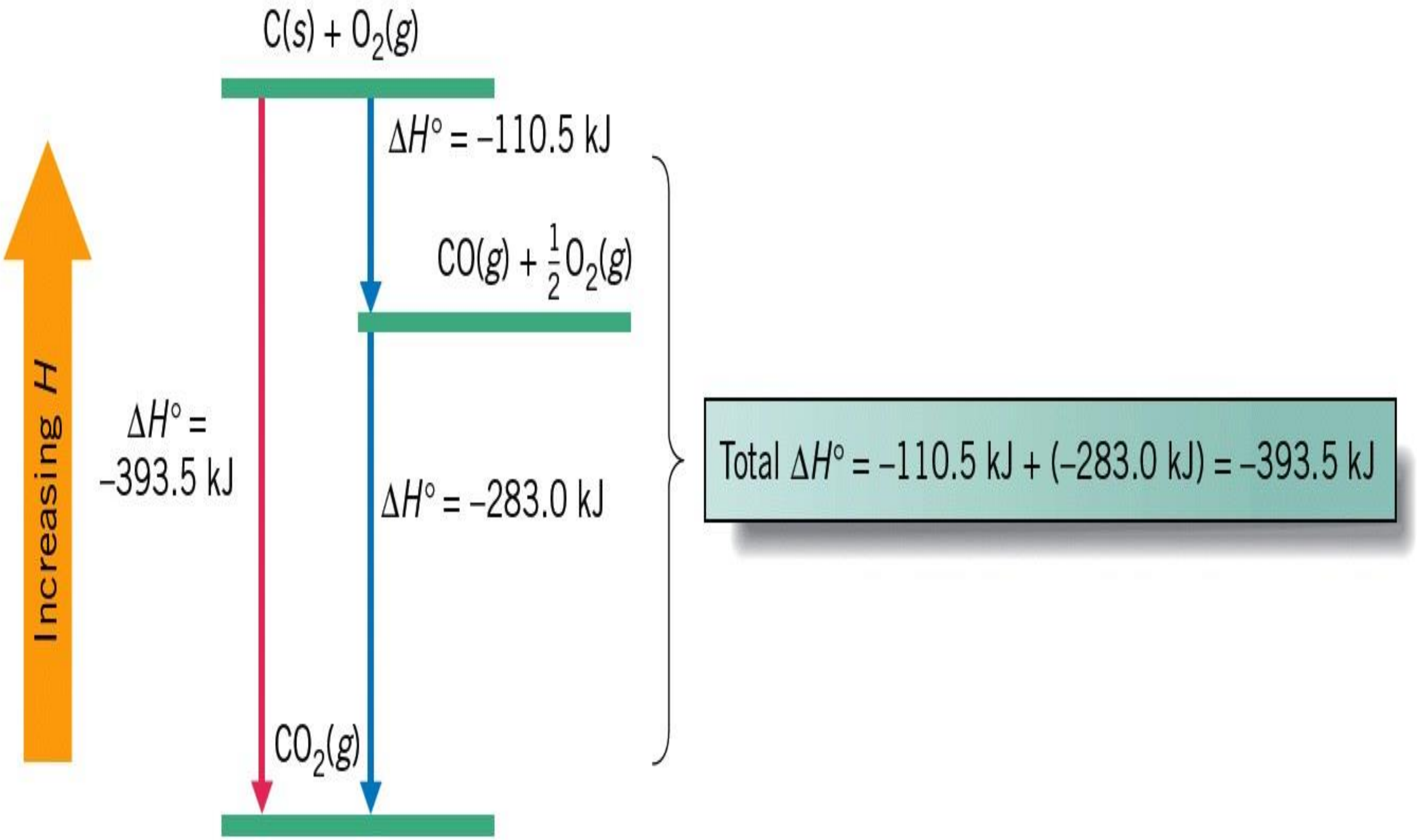
Step 2: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H° = -112\ kJ$

Net rxn: $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ $\Delta H° = 68\ kJ$

Hess's Law of Heat Summation

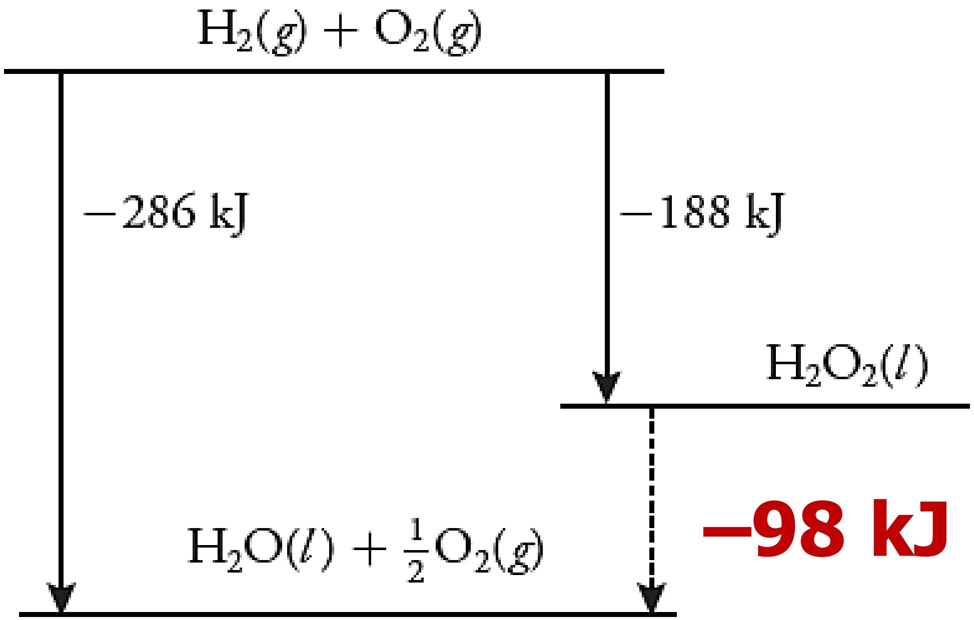
For any reaction that can be written into steps, value of ΔH° for reactions = sum of ΔH° values of each individual step

Enthalpy Diagrams



Total $\Delta H° = -110.5 \text{ kJ} + (-283.0 \text{ kJ}) = -393.5 \text{ kJ}$

Enthalpy Diagrams



Ex. $H_2O_2(\ell) \rightarrow H_2O(\ell) + \frac{1}{2}O_2(g)$

$-286\text{kJ} = -188\text{kJ} + \Delta H_{rxn}$

$\Delta H_{rxn} = -286\text{ kJ} - (-188\text{ kJ})$

$\mathbf{\Delta H_{rxn} = -98\text{ kJ}}$

Rules for Manipulating Thermochemical Equations

1. When equation is reversed, sign of $\Delta H°$ must also be reversed (- $\Delta H°$) .
2. If all coefficients of equation are multiplied or divided by same factor, value of $\Delta H°$ must likewise be multiplied or divided by that factor
3. Formulas canceled from both sides of equation must be for substance in ***same*** physical states

Ex. Calculate ΔH° for

$$\mathrm{C}_{\text{graphite}}(s) \longrightarrow \mathrm{C}_{\text{diamond}}(s)$$

Given $\mathrm{C}_{gr}(s) + \mathrm{O}_2(g) \rightarrow \mathrm{CO}_2(g) \qquad \Delta H^\circ = -394\text{ kJ}$

$-1\times[\ \mathrm{C}_{dia}(s) + \mathrm{O}_2(g) \rightarrow \mathrm{CO}_2(g) \qquad \Delta H^\circ = -396\text{ kJ}\ ]$

- To get desired equation, must reverse 2nd equation and add resulting equations

$$\begin{array}{ll} \mathrm{C}_{gr}(s) + \mathrm{O}_2(g) \rightarrow \mathrm{CO}_2(g) & \Delta H^\circ = -394\text{ kJ} \\ \mathrm{CO}_2(g) \rightarrow \mathrm{C}_{dia}(s) + \mathrm{O}_2(g) & \Delta H^\circ = -(-396\text{ kJ}) \\ \hline \end{array}$$

$$\mathrm{C}_{gr}(s) + \cancel{\mathrm{O}_2(g)} + \cancel{\mathrm{CO}_2(g)} \rightarrow \mathrm{C}_{dia}(s) + \cancel{\mathrm{O}_2(g)} + \cancel{\mathrm{CO}_2(g)}$$

$$\Delta H^\circ = -394\text{ kJ} + 396\text{ kJ} = +\boxed{2\text{ kJ}}$$

Learning Check

Ex. Calculate $\Delta H°$ for

$$2\ C_{gr}(s) + H_2(g) \longrightarrow C_2H_2(g)$$

Given the following:

a. $C_2H_2(g) + {}^5/_2O_2(g) \rightarrow 2CO_2(g) + H_2O(\ell)$
$\Delta H° = -\ 1299.6\ \text{kJ}$

b. $C_{gr}(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -393.5\ \text{kJ}$

c. $H_2(g) + ½O_2(g) \rightarrow H_2O(\ell)$ $\Delta H° = -\ 285.8\ \text{kJ}$

Ex. Calculate for

$$2C_{gr}(s) + H_2(g) \longrightarrow C_2H_2(g)$$

$-a$ $2CO_2(g) + H_2O(\ell) \rightarrow C_2H_2(g) + {}^5/_2O_2(g)$

$\Delta H^\circ = -(-1299.6\ \text{kJ}) = +1299.6\ \text{kJ}$

$+2b$ $2C_{gr}(s) + 2O_2(g) \rightarrow 2CO_2(g)$

$\Delta H^\circ = (2 \times -393.5\ \text{kJ}) = -787.0\ \text{kJ}$

$+c$ $H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ $\Delta H^\circ = -285.8\ \text{kJ}$

$\cancel{2CO_2(g)} + \cancel{H_2O(\ell)} + 2C_{gr}(s) + \cancel{2O_2(g)} + H_2(g) + \cancel{\tfrac{1}{2}O_2(g)}$

$\rightarrow C_2H_2(g) + \cancel{{}^5/_2O_2(g)} + \cancel{2CO_2(g)} + \cancel{H_2O(\ell)}$

$2C_{gr}(s) + H_2(g) \rightarrow C_2H_2(g)$ $\Delta H^\circ = \mathbf{+226.8\ kJ}$

Your Turn!

Ex. Given the following data:

$C_2H_2(g) + O_2(g) \rightarrow 2CO_2(g) + H_2O(\ell)$ $\Delta H = -1300.$ kJ

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -394$ kJ

$H_2(g) + O_2(g) \rightarrow H_2O(\ell)$ $\Delta H = -286$ kJ

Calculate for the reaction

$2C(s) + H_2(g) \rightarrow C_2H_2(g)$

A. 226 kJ

B. –1980 kJ

C. –620 kJ

D. –226 kJ

E. 620 kJ

$\Delta H = +1300.$ kJ $+ 2(-394$ kJ$) + (-286$ kJ$)$

Tabulating $\Delta H°$ values

Standard Enthalpy of Formation, $\Delta H_f°$

- Amount of heat absorbed or evolved when one mole of substance is formed
- at 1 atm and 25 °C (298 K) from elements in their standard states
- Standard Heat of Formation $\Delta H_f°$

Standard State

- Most stable form and physical state of element at 1 atm and 25 °C (298 K)

element	**Standard state**
O	$O_2(g)$
C	$C_{gr}(s)$
H	$H_2(g)$
Al	$Al(s)$
Ne	$Ne(g)$

Note: **All ΔH_f° of elements in their standard states = 0**

Forming element from itself.

Uses of Standard Enthalpy (Heat) of Formation, ΔH_f°

1. From definition of ΔH_f°, can write balanced equations directly

$\Delta H_f^\circ\{C_2H_5OH(\ell)\}$

$$2C(s, gr) + 3H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_5OH(\ell)$$
$$\Delta H_f^\circ = -277.03 \text{ kJ/mol}$$

$\Delta H_f^\circ\{Fe_2O_3(s)\}$

$$2Fe(s) + {}^{3}/{}_{2}O_2(g) \rightarrow Fe_2O_3(s) \quad \Delta H_f^\circ = -822.2 \text{ kJ/mol}$$

Your Turn!

Ex. What is the reaction that corresponds to the standard enthalpy of formation of $NaHCO_3(s)$, $\Delta H_f^\circ = -947.7$ kJ/mol?

a. $Na(s) + \frac{1}{2}H_2(g) + {}^{3}/{}_{2}O_2(g) + C(s, gr) \rightarrow NaHCO_3(s)$

b. $Na^+(g) + H^+(g) + 3O^{2-}(g) + C^{4+}(g) \rightarrow NaHCO_3(s)$

c. $Na^+(aq) + H^+(aq) + 3O^{2-}(aq) + C^{4+}(aq) \rightarrow NaHCO_3(s)$

d. $NaHCO_3(s) \rightarrow Na(s) + \frac{1}{2}H_2(g) + {}^{3}/{}_{2}O_2(g) + C(s, gr)$

e. $Na^+(aq) + HCO_3^-(aq) \rightarrow NaHCO_3(s)$

Using ΔH_f°

2. Way to apply Hess's Law without needing to manipulate thermochemical equations

$$\Delta H^\circ_{\text{reaction}} = \left(\begin{array}{l}\text{Sum of all} \\ \Delta H^\circ_{\text{f}}\text{ of all of} \\ \text{the products}\end{array}\right) - \left(\begin{array}{l}\text{Sum of all} \\ \Delta H^\circ_{\text{f}}\text{ of all of} \\ \text{the reactants}\end{array}\right)$$

Consider the reaction:

$$\mathbf{aA + bB \rightarrow cC + dD}$$

$$\Delta H^\circ_{\text{reaction}} = c \times \Delta H^\circ_{\text{f}}(\text{C}) + d \times \Delta H^\circ_{\text{f}}(\text{D}) - \{a \times \Delta H^\circ_{\text{f}}(\text{A}) + b \times \Delta H^\circ_{\text{f}}(\text{B})\}$$

Ex. Calculate ΔH°_{rxn} Using ΔH_f°

Ex. Calculate ΔH°_{rxn} using ΔH_f° data for the reaction

$$SO_3(g) \longrightarrow SO_2(g) + \tfrac{1}{2}O_2(g)$$

1. Add ΔH_f° for each product times its coefficient
2. Subtract ΔH_f° for each reactant times its coefficient.

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f(SO_2(g)) + \tfrac{1}{2}\Delta H^\circ_f(O_2(g)) - \Delta H^\circ_f(SO_3(g))$$

$$\Delta H^\circ_{rxn} = -297\,\text{kJ/mol} + \tfrac{1}{2}(0\,\text{kJ/mol}) - (-396\,\text{kJ/mol})$$

$$\Delta H^\circ_{rxn} = 99\ \text{kJ/mol}$$

Learning Check

Ex. Calculate $\Delta H^\circ_{\text{rxn}}$ using ΔH_f° for the reaction

$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(\ell)$

$$\Delta H^\circ_{\text{rxn}} = 4\Delta H_f^\circ(NO_2(g)) + 6\Delta H_f^\circ(H_2O(\ell))$$

$$- 4\Delta H_f^\circ(NH_3(g)) - 7\Delta H_f^\circ(O_2(g))$$

$$\Delta H^\circ_{\text{rxn}} = 4\text{ mol}(34\text{ kJ/mol}) + 6\text{ mol}(-285.9\text{kJ/mol})$$

$$- 4\text{ mol}(-46.0\text{ kJ/mol}) - 7\text{ mol}(0\text{ kJ/mol})$$

$$\Delta H^\circ_{\text{rxn}} = [136 - 1715.4 + 184]\text{ kJ}$$

$$\boldsymbol{\Delta H^\circ_{\text{rxn}} = -1395\text{ kJ}}$$

Check Using Hess's Law

$4*[NH_3(g) \rightarrow \frac{1}{2} N_2(g) + {}^3/_2\, H_2(g)]$ $-\ 4*\Delta H_f^\circ(NH_3, g)$

$7*[\ O_2(g) \rightarrow \ O_2(g)\ ]$ $-\ 7*\Delta H_f^\circ(O_2, g)$

$4*[\ O_2(g) + \frac{1}{2} N_2(g) \rightarrow NO_2(g)]$ $4*\Delta H_f^\circ(NO_2, g)$

$6*[\ H_2(g) + \frac{1}{2} O_2(g) \rightarrow \ H_2O(\ell)\ ]$ $6*\ \Delta H_f^\circ(H_2O, \ell)$

$$4NH_3(g) + \ 7O_2(g) \longrightarrow \ 4NO_2(g) + \ 6H_2O(\ell)$$

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= 4\Delta H^\circ_{\text{f}}(NO_2(g)) + 6\Delta H^\circ_{\text{f}}(H_2O(\ell)) \\ &\quad - 4\Delta H^\circ_{\text{f}}(NH_3(g)) - 7\Delta H^\circ_{\text{f}}(O_2(g)) \end{aligned}$$

Same as before

Other Calculations

Ex. Given the following data, what is the value of $\Delta H_f^\circ(\mathrm{C_2H_3O_2^-}, aq)$?

$\mathrm{Na^+}(aq) + \mathrm{C_2H_3O_2^-}(aq) + \mathrm{3H_2O}(\ell) \rightarrow \mathrm{NaC_2H_3O_2{\cdot}3H_2O}(s)$

$\Delta H^\circ_{rxn} = -19.7\ \mathrm{kJ/mol}$

$\boldsymbol{\Delta H_f^\circ}(\mathrm{Na^+}, aq)$	-239.7 *kJ/mol*
$\boldsymbol{\Delta H_f^\circ}(\mathrm{NaC_2H_3O_2{\cdot}3H_2O}, s)$	-710.4 *kJ/mol*
$\boldsymbol{\Delta H_f^\circ}(\mathrm{H_2O}, \ell)$	-285.9 *kJ/mol*

Ex. cont.

$\Delta H^\circ_{rxn} = \Delta H_f^\circ(NaC_2H_3O_2 \cdot 3H_2O, s) - \Delta H_f^\circ(Na^+, aq) - \Delta H_f^\circ(C_2H_3O_2^-, aq) - 3\Delta H_f^\circ(H_2O, \ell)$

Rearranging

$\Delta H_f^\circ(C_2H_3O_2^-, aq) = \Delta H_f^\circ(NaC_2H_3O_2 \cdot 3H_2O, s) - \Delta H_f^\circ(Na^+, aq) - \Delta H^\circ_{rxn} - 3\Delta H_f^\circ(H_2O, \ell)$

$\Delta H_f^\circ(C_2H_3O_2^-, aq) = -710.4\text{kJ/mol} - (-239.7\text{kJ/mol}) - (-19.7\text{kJ/mol}) - 3(-285.9\text{kJ/mol})$

$= +\ 406.7\ kJ/mol$

Learning Check

Ex. Calculate ΔH for this reaction using ΔH_f° data.

$$2Fe(s) + 6H_2O(\ell) \rightarrow 2Fe(OH)_3(s) + 3H_2(g)$$

ΔH_f° 0 –285.8 –696.5 0

$$\Delta H^\circ_{rxn} = 2*\Delta H_f^\circ(Fe(OH)_3, s) + 3*\Delta H_f^\circ(H_2, g) - 2*\Delta H_f^\circ(Fe, s) - 6*\Delta H_f^\circ(H_2O, \ell)$$

$$\Delta H^\circ_{rxn} = 2\text{ mol}*(-696.5\text{ kJ/mol}) + 3*0 - 2*0 - 6\text{ mol}*(-285.8\text{ kJ/mol})$$

$$\Delta H^\circ_{rxn} = -1393\text{ kJ} + 1714.8\text{ kJ}$$

$$\mathbf{\Delta H^\circ_{rxn} = 321.8\text{ kJ}}$$

Learning Check

Ex. Calculate ΔH for this reaction using ΔH_f° data.

$$CO_2(g) \;+\; 2H_2O(\ell) \;\rightarrow\; 2O_2(g) \;+\; CH_4(g)$$

ΔH_f° -393.5 -285.8 0 -74.8

$$\Delta H^o_{\text{rxn}} = 2^*\Delta H_f^\circ(O_2, g) + \Delta H_f^\circ(CH_4, g) \\ -\Delta H_f^\circ(CO_2, g) - 2^*\,\Delta H_f^\circ(H_2O, \ell)$$

$$\Delta H^o_{\text{rxn}} = 2\times 0 + 1\text{ mol}\times(-74.8\text{ kJ/mol}) - 1\text{ mol} \\ \times(-393.5\text{ kJ/mol}) - 2\text{ mol}\times(-285.8\text{ kJ/mol})$$

$$\Delta H^o_{\text{rxn}} = -74.8\text{ kJ} + 393.5\text{ kJ} + 571.6\text{ kJ}$$

$$\boldsymbol{\Delta H^o_{\text{rxn}} = 890.3\text{ kJ}}$$

Converting Between ΔE and ΔH For Chemical Reactions

- When reaction occurs
  - ΔV caused by Δn of gas
- Not all reactants and products are gases
  - So redefine as Δn_{gas}

Where $\Delta n_{gas} = (n_{gas})_{products} - (n_{gas})_{reactants}$

- Substituting into

$$\Delta H = \Delta E + P\Delta V$$

  - or

$$\boxed{\Delta H = \Delta E + \Delta n_{gas}RT}$$

Ex. Find ΔE for the following reaction at 25 °C using data in Table 7.2?

$$2\ N_2O_5\ (g) \longrightarrow 4\ NO_2\ (g) + O_2\ (g)$$

Step 1: Calculate ΔH using ΔH_f° data (Table 7.2)

Recall

$$\Delta H^\circ = (\Delta H_f^\circ)_{products} - (\Delta H_f^\circ)_{reactants}$$

$$\Delta H^\circ = 4\Delta H_f^\circ(NO_2) + \Delta H_f^\circ(O_2) - 2\Delta H_f^\circ(N_2O_5)$$

ΔH° = (4 mol)(33.8 kJ/mol) + (1 mol)(0.0 kJ/mol) – (2 mol)(11 kJ/mol)

ΔH° = 113 kJ

Ex. (cont.)

Step 2: Calculate

$$\Delta n_{gas} = (n_{gas})_{products} - (n_{gas})_{reactants}$$

$$\Delta n_{gas} = (4 + 1 - 2)\ mol = 3\ mol$$

Step 3: Calculate ΔE using

R = 8.31451 J/K·mol T = 298 K

$$\Delta E = \Delta H - \Delta n_{gas}RT$$

$$\Delta E = 113\ kJ -$$
$$(3\ mol)(8.31451\ J/K\cdot mol)(298\ K)(1\ kJ/1000\ J)$$

$$\Delta E = 113\ kJ - 7.43\ kJ = \mathbf{106\ kJ}$$

Learning Check

Ex. Consider the following reaction for picric acid:

$$8O_2(g) + 2C_6H_2(NO_2)_3OH(\ell) \rightarrow 3\,N_2(g) + 12CO_2(g) + 6H_2O(\ell)$$

- What type of reaction is it?
- Calculate ΔH°, ΔE°

	$8O_2(g)$	$+\ 2C_6H_2(NO_2)_3OH(\ell) \rightarrow$	$3N_2(g)$	$+\ 12CO_2(g)$	$+\ 6H_2O(\ell)$
ΔH°_f (kJ/mol)	**0.00**	**3862.94**	**0.00**	**-393.5**	**-241.83**

$$\Delta H^0 = 12\text{mol}(-393.5\text{ kJ/mol}) + 6\text{mol}(-241.83\text{kJ/mol}) + 6\text{mol}(0.00\text{kJ/mol}) - 8\text{mol}(0.00\text{kJ/mol}) - 2\text{mol}(3862.94\text{kJ/mol})$$

$\Delta H^0 = -\ 13{,}898.9$ kJ (Exothermic reaction)

$$\Delta E^\circ = \Delta H^\circ - \Delta n_{gas}RT = \Delta H^\circ - (15 - 8)\text{mol}*298*\ 8.314\times10^{-3}$$

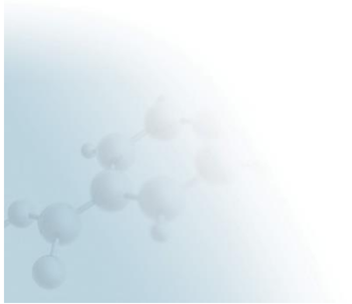
$$\Delta E^\circ = -13{,}898.9\text{ kJ} - 29.0\text{ kJ} = \mathbf{-\ 13{,}927.9\text{ kJ}}$$

Chapter 4

Chemical Kinetics

Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop



Speeds at Which Reactions Occur

Kinetics:

- Study of factors that govern
  - How ***rapidly*** reactions occur **and**
  - How reactants ***change*** into products

Rate of Reaction:

- ***Speed*** with which reaction occurs
- How quickly reactants disappear and products form

Factors that Affect Reaction Rates

1. **Chemical nature of reactants**

- ***What*** elements, compounds, salts are ***involved***?
- What ***bonds*** must be ***formed***, ***broken***?
- What are ***fundamental differences*** in chemical reactivity?

Factors that Affect Reaction Rates

2. Ability of reactants to come in contact

- If two or more reactants **must meet** in order to react
- **Gas** or **solution** phase facilitates this
    - **Reactants** mix and collide with each other easily
    - **Homogeneous reaction**
        - All reactants in ***same*** phase
        - Occurs rapidly
    - **Heterogeneous reaction**
        - Reactants in **different** phases
        - Reactants meet only at ***interface*** between phases
        - Surface area determines reaction **rate**
        - ↑ area, ↑ rate ↓ area, ↓ rate

Factors that Affect Reaction Rates

3. Concentrations of reactants

- Rates of both homogeneous and heterogeneous reactions affected by [X]
- Collision rate between A and B ↑ if we ↑ [A] or ↑ [B].
    - ∴ Often (but not always)
    - Reaction rate ↑ as [X]↑

Factors that Affect Reaction Rates

4. Temperature

- Rates are often very sensitive to T
  - Cooking sugar
- Raising **T** usually makes reaction faster for two reasons:

a. Faster molecules collide more often and collisions have more **Energy**

b. Most reactions, even exothermic reactions, require **Energy** to get going

Factors that Affect Reaction Rates

5. Presence of Catalysts

- **Catalysts**
  - Substances that ↑ rates of chemical and biochemical reactions without being used up
  - Rate-accelerating agents
  - Speed up rate dramatically

Measuring Rate of Reaction

- **Rate of Chemical Reaction**
  - ↓ in [X] of particular species per unit time.

$$\textbf{reaction rate} = \frac{\Delta[\textit{reactant}]}{\Delta \textit{time}}$$

  - Always **with respect to** (**WRT**) given reactant or product
  - [reactants] ↓ w/ time
  - [products] ↑ w/ time

Rate of Reaction with Respect to Given Species X

$$\text{Rate WRT X} = \frac{[X]_{t_2} - [X]_{t_1}}{t_2 - t_1} = \frac{\Delta[X]}{\Delta t}$$

- Concentration in ***M***
- Time in ***s***
- Units on rate: $\frac{\text{mol/L}}{\text{s}} = \frac{\text{mol}}{\text{L} \cdot \text{s}} = \frac{\text{M}}{\text{s}}$
- **Ex.**
  - [product] ↑ by 0.50 *mol/L* per ***second*** ⇒

    rate = 0.50 *M/s*
  - [reactant] ↓ by 0.20 *mol/L* per ***second*** ⇒

    rate = 0.20 *M/s*

WRT: with respect to

Rate of Reaction

- Always +
  - Whether something is ↑ or ↓ in [X].
- **Reactants**
  - Need – sign to make ***rate*** +
  - Reactant consumed
  - So Δ[X] = –

$$\text{Rate} = -\frac{\Delta[\text{reactant}]}{\Delta t}$$

- **Products**
  - Produced as reaction goes along
  - So Δ[X] = +
  - Thus Rate = +

$$\text{Rate} = \frac{\Delta[\text{product}]}{\Delta t}$$

Rates and Coefficients

- Relative rates at which reactants are consumed and products are formed
  - Related by coefficients in balanced chemical equation.
  - Know rate with respect to one product or reactant
  - Can use equation to determine rates WRT all other products and reactants.

Ex. $C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$

Rate of Reaction

$$= -\frac{\Delta[C_3H_8]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[CO_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[H_2O]}{\Delta t}$$

Rates and Coefficients

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$$

- O_2 ***reacts*** **5** times as fast as C_3H_8

$$\text{Rate} = -\frac{\Delta[O_2]}{\Delta t} = -5\frac{\Delta[C_3H_8]}{\Delta t}$$

- CO_2 ***forms*** **3** times faster than C_3H_8 ***consumed***

$$\text{Rate} = \frac{\Delta[CO_2]}{\Delta t} = -3\frac{\Delta[C_3H_8]}{\Delta t}$$

- H_2O ***forms*** **4/5** as fast as O_2 ***consumed***

$$\frac{\Delta[H_2O]}{\Delta t} = -\frac{4}{5}\frac{\Delta[O_2]}{\Delta t}$$

Rates and Coefficients

In general

$$\alpha \mathbf{A} + \beta \mathbf{B} \longrightarrow \gamma \mathbf{C} + \delta \mathbf{D}$$

$$\text{Rate} = -\frac{1}{\alpha}\frac{\Delta A}{\Delta t} = -\frac{1}{\beta}\frac{\Delta B}{\Delta t} = \frac{1}{\gamma}\frac{\Delta C}{\Delta t} = \frac{1}{\delta}\frac{\Delta D}{\Delta t}$$

Your Turn!

Ex. In the reaction $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$, the rate of the reaction of CO is measured to be 2.0 M/s. What would be the rate of the reaction of O_2?

A. the same = 2.0 M/s

B. twice as great = 4.0 M/s

C. half as large = 1.0 M/s

D. you cannot tell from the given information

Change of Reaction Rate with Time

- Generally reaction rate changes during reaction
  - i.e. Not constant
- Often initially fast when lots of reactant present
- Slower at end when reactant used up

Why?

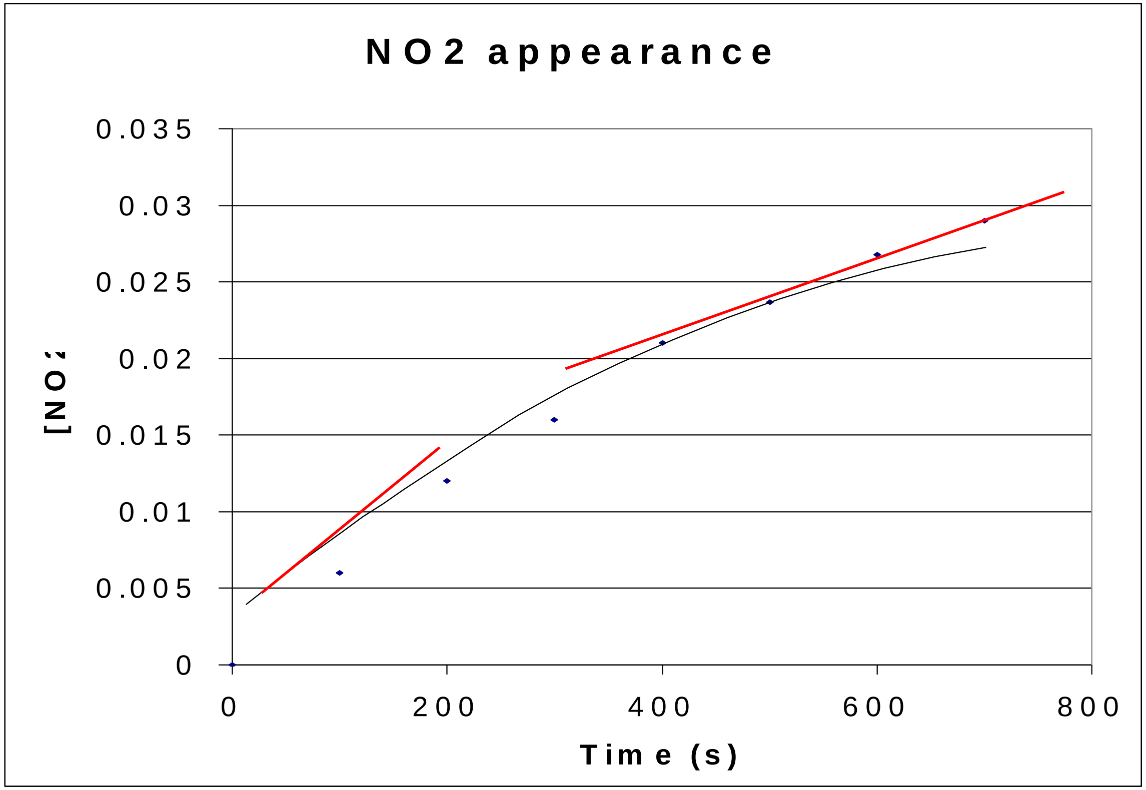
- Rate depends on [reactants]
- Reactants being used up, so [reactant] is ↓
- **[A]** vs. **time** is curve
- **A** is reactant ∴ [A] is ↓ w/ time

Measuring Rates

- Measured in three ways:
  - Instantaneous rate
  - Average rate
  - Initial rate

Instantaneous Reaction Rates

- **Instantaneous rate**
  - Slope of tangent to curve at any specific time
- **Initial rate**
  - Determined at initial time



Average Rate of Reaction

- Slope of line connecting starting and ending coordinates for specified time frame

$$\frac{\Delta[\text{Product}]}{\Delta \text{time}} = \text{rate}$$

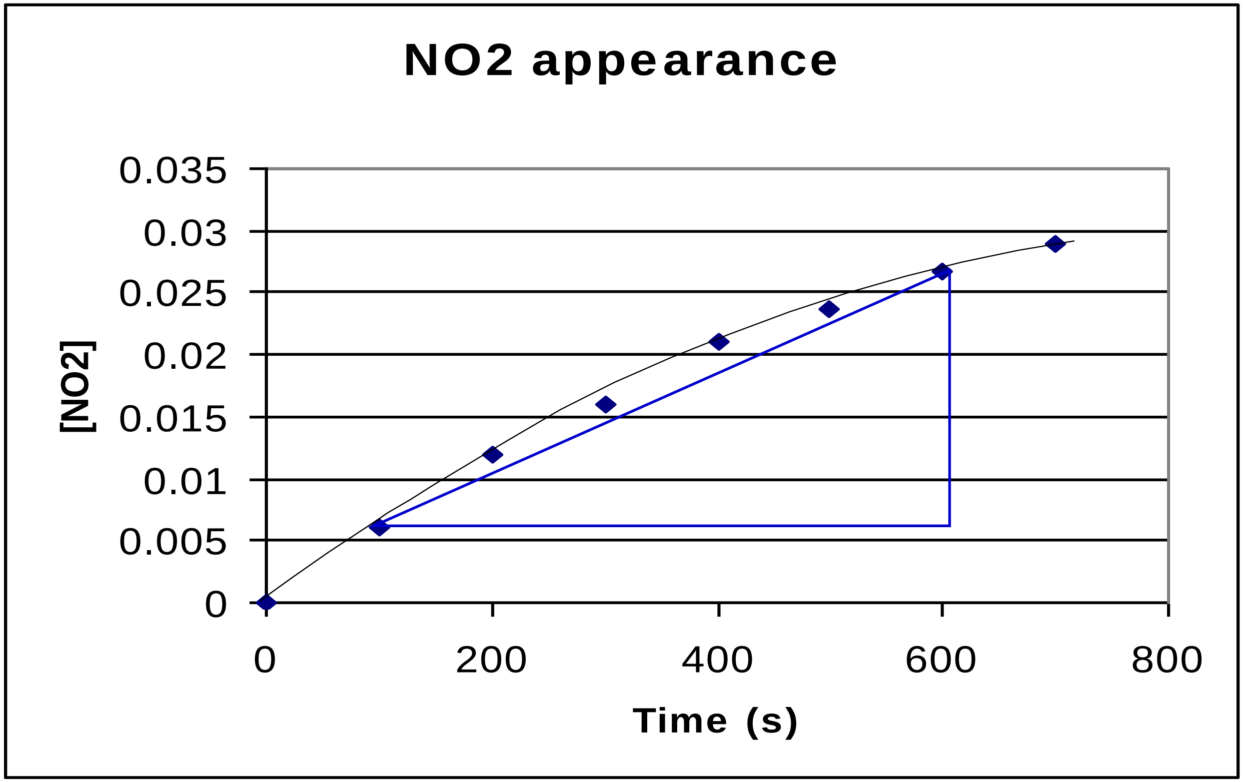


Table 14.1 Data at 508 °C

Ex. $2\ HI(g) \rightarrow H_2(g) + I_2(g)$

[HI] (mol/L)	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300
0.0265	350

Initial rate

rate between first two data points

$$\text{rate} = -\frac{(0.0716 - 0.100)\text{M}}{(50 - 0)\text{s}}$$

$$= \frac{-(-0.0284\text{M})}{50\text{s}}$$

$$= 5.68 \times 10^{-4}\ \text{M/s}$$

Rate at 300 *s*

[HI] (mol/L)	**Time (s)**
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300
0.0265	350

$$2\,HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$$

Rate = tangent of curve at **300 s**

$$\text{Rate} = -\frac{(0.0265 - 0.0296)\text{M}}{(350 - 300)\text{s}}$$

$$= \frac{0.0031\text{M}}{50\text{s}}$$

$$= 6.20 \times 10^{-5}\ \text{M/s}$$

Your Turn!

Ex. The concentration of NO_2 was found to be 0.0258*M* at 5 minutes and at 10 minutes the concentration was 0.0097*M*. What is the average rate of the reaction between 5 min and 10 min?

A. 310 *M*/min

B. 3.2×10^{-3} *M*/min

C. 2.7×10^{-3} *M*/min

D. 7.1×10^{-3} M/min

$$\frac{(0.0258M - 0.0097M)}{10\,\text{min} - 5\,\text{min}} = 3.2 \text{ x } 10^{-3} M / \text{min}$$

Concentration and Rate

Rate Laws

$$\alpha \boldsymbol{A} + \beta \boldsymbol{B} \longrightarrow \gamma \mathbf{C} + \delta \mathbf{D}$$

- Homogeneous reaction
- **Rate = $k[\mathrm{A}]^{m}[\mathrm{B}]^{n}$**
  - *Rate Law* or *Rate expression*
  - ***m*** and ***n*** = exponents found experimentally
  - No necessary connection between stoichiometric coefficients (α, β) and rate exponents (***m, n***)
  - Usually small integers 1, 2 ……
  - Sometimes simple fractions (½, ¾) or zero

Rate Laws

Rate = $k[A]^m[B]^n$

- **Exponents** tell ***Order of Reaction* with respect to** (**WRT**) each reactant
- **Order of Reaction**
  - ***m*** = 1 $[A]^1$ 1^{st} order
  - ***m*** = 2 $[A]^2$ 2^{nd} order
  - ***m*** = 3 $[A]^3$ 3^{rd} order
  - ***m*** = 0 $[A]^0$ 0^{th} order
    - $[A]^0 = 1 \Rightarrow$ means A doesn't affect rate
- **Overall order of reaction**
- sum of orders (***m*** and ***n***) of each reactant in rate law

Learning Check

Ex. The rate law for the reaction $2A + B \rightarrow 3C$ is rate= k[A][B]

If the concentration of A is 0.2M and that of B is 0.3M, and rate constant is 0.045 $M^{-1}s^{-1}$ what will be the reaction rate?

rate=0.045 M^{-1} s^{-1} [0.2][0.3]

rate=0.0027 M/s $\Rightarrow$ 0.003 M/s

Ex.

$$5\ Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

$$-\frac{\Delta[BrO_3^-]}{\Delta t} = k[BrO_3^-]^x[Br^-]^y[H^+]^z$$

- $x = 1$ $y = 1$ $z = 2$
- 1st order WRT BrO_3^-
- 1st order WRT Br^-
- 2nd order WRT H^+
- Overall order = 1 + 1 + 2 = 4

$$rate = k[BrO_3^-]^1[Br^-]^1[H^+]^2$$

Ex.

- Sometimes ***n*** and ***m*** are coincidentally the same as stoichiometric coefficients

$$2\ \mathrm{HI}\ (g) \longrightarrow \mathrm{H_2}\ (g) + \mathrm{I_2}\ (g)$$

$$\text{rate} = -\frac{\Delta[\mathrm{HI}]}{\Delta t} = k[\mathrm{HI}]^2$$

- 2nd order WRT HI
- 2nd order overall

Your Turn!

Ex. The following rate law has been observed: Rate = $k[H_2SeO][I^-]^3[H^+]^2$. The rate with respect to I^- and the overall reaction rate is:

A. 6, 2
B. 2, 3
C. 1, 6
D. 3, 6

Calculating *k* from Rate Law

- If we know rate and concentrations, can use rate law to calculate ***k***

Ex. at 508 °C

- Rate= 2.5 x 10^{-4} *M/s*
- [HI] = 0.0558 *M*

$$\text{rate} = -\frac{\Delta[\text{HI}]}{\Delta t} = k[\text{HI}]^2$$

$$\boldsymbol{k} = \frac{\text{rate}}{[\text{HI}]^2} = \frac{2.5 \times 10^{-4}\,\text{M}/\text{s}}{(0.0558\,\text{M})^2} = 0.08029\,\text{M}^{-1}\text{s}^{-1}$$

How To Determine Exponents in Rate Law

Experiments

- Method of Initial Rates
- If reaction is sufficiently slow
  - or have very fast technique
- Can measure [A] vs. time at very beginning of reaction
  - before it curves up very much, then

$$\text{initial rate} = -\left(\frac{[A]_1 - [A]_0}{t_1 - t_0}\right)$$

  - Set up series of experiments, where initial concentrations vary

Ex. Method of Initial Rates

$$3A + 2B \longrightarrow \text{products}$$

$$\text{Rate} = k[A]^m[B]^n$$

Expt. #	$[A]_0$, *M*	$[B]_0$, *M*	Initial Rate, *M/s*
1	0.10	0.10	1.2×10^{-4}
2	0.20	0.10	4.8×10^{-4}
3	0.20	0.20	4.8×10^{-4}

- Convenient to set up experiments so
  - [X] of one species is doubled or tripled
  - while [X] of all other species are held constant
- Tells us effect of [varied species] on initial rate

Reaction Order and Rate

- If reaction is **1st** order WRT given species **X**,
  - Doubling $[X]^1 \rightarrow 2^1$
  - Rate doubles
- If reaction is **2nd** order WRT **X**,
  - Doubling $[X]^2 \rightarrow 2^2$
  - Rate quadruples
- If reaction is **0th** order WRT **X**,
  - Doubling $[X]^0 \rightarrow 2^0$
  - Rate doesn't change
- If reaction is **nth** order WRT **X**
  - Doubling $[X]^n \rightarrow 2^n$

Back to our Example

Expt. #	$[A]_0$, *M*	$[B]_0$, *M*	Initial Rate, *M/s*
1	0.10	0.10	1.2×10^{-4}
2	0.20	0.10	4.8×10^{-4}
3	0.20	0.20	4.8×10^{-4}

- **Comparing 1 and 2**
  - Doubling [A]
  - Quadruples rate
  - Reaction **2nd** order in A
  - $[A]^2$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{4.8 \times 10^{-4}}{1.2 \times 10^{-4}} = 4$$

$$4 = \frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[A_2]^m[B_2]^n}{k[A_1]^m[B_1]^n} = \frac{\cancel{k}[0.20]^m\cancel{[0.10]^n}}{\cancel{k}[0.10]^m\cancel{[0.10]^n}} = \frac{[0.20]^m}{[0.10]^m} = 2^m$$

$2^m = 4$ **or** $m = 2$

Back to our Example

Expt. #	**$[A]_0$, *M***	**$[B]_0$, *M***	**Initial Rate, *M/s***
1	0.10	0.10	1.2×10^{-4}
2	0.20	0.10	4.8×10^{-4}
3	0.20	0.20	4.8×10^{-4}

- **Comparing 2 and 3**
  - Doubling [B]
  - Rate does not change
  - Reaction **0**^th^ order in B
  - $[B]^0$

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{4.8 \times 10^{-4}}{4.8 \times 10^{-4}} = 1$$

$$1 = \frac{\text{Rate 3}}{\text{Rate 2}} = \frac{k[A_3]^m[B_3]^n}{k[A_2]^m[B_2]^n} = \frac{\cancel{k}\cancel{[0.20]^m}[0.20]^n}{\cancel{k}\cancel{[0.20]^m}[0.10]^n} = \frac{[0.20]^n}{[0.10]^n} = 2^n$$

$$2^n = 1 \quad \text{or} \quad n = 0$$

Ex. Method of Initial Rates

Expt. #	$[A]_0$, *M*	$[B]_0$, *M*	Initial Rate, *M/s*
1	0.10	0.10	1.2×10^{-4}
2	0.20	0.10	4.8×10^{-4}
3	0.20	0.20	4.8×10^{-4}

- **Conclusion: rate = $k[A]^2$**
- Can use data from any experiment to determine ***k***
- Let's choose experiment 1

$$k = \frac{\text{rate}}{[A]^2} = \frac{1.2 \times 10^{-4}\,M/s}{(0.10M)^2} = 1.2 \times 10^{-2}\,M^{-1}s^{-1}$$

Ex. Method of Initial Rates

$$2\,SO_2 \;+\; O_2 \longrightarrow 2\,SO_3$$

$$\text{Rate} = k[SO_2]^m[O_2]^n$$

Expt #	**$[SO_2]$, *M***	**$[O_2]$, *M***	**Initial Rate of SO_3 formation, $M{\cdot}s^{-1}$**
1	0.25	0.30	2.5×10^{-3}
2	0.50	0.30	1.0×10^{-2}
3	0.75	0.60	4.5×10^{-2}
4	0.50	0.90	3.0×10^{-2}

Ex. Compare 1 and 2

- $[SO_2]$ doubles, $[O_2]$ constant,
- Rate quadruples, 2^2

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{1.0 \times 10^{-2}}{2.5 \times 10^{-3}} = 4$$

$$4 = \frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[SO_2]_2^m[O_2]_2^n}{k[SO_2]_1^m[O_2]_1^n} = \frac{\cancel{k}[0.50]^m\cancel{[0.30]^n}}{\cancel{k}[0.25]^m\cancel{[0.30]^n}}$$

$$= \frac{[0.50]^m}{[0.25]^m} = 2^m$$

$2^m = 4$ or $m = 2$

Ex. Compare 2 and 4

- $[O_2]$ triples, $[SO_2]$ constant
- Rate triples, 3^1

$$\frac{\text{Rate 4}}{\text{Rate 2}} = \frac{3.0\times10^{-2}}{1.0\times10^{-2}} = 3$$

$$3 = \frac{\text{Rate 4}}{\text{Rate 2}} = \frac{k[SO_2]_4^m[O_2]_4^n}{k[SO_2]_2^m[O_2]_2^n} = \frac{\cancel{k}\cancel{[0.50]^m}[0.90]^n}{\cancel{k}\cancel{[0.50]^m}[0.30]^n}$$

$$= \frac{[0.90]^n}{[0.30]^n} = 3^n$$

$3^n = 3$ or $n = 1$

Ex.

Rate = $k[SO_2]^2[O_2]^1$

- 1^{st} order WRT O_2
- 2^{nd} order WRT SO_2
- 3^{rd} order overall
- Can use any experiment to find ***k***

$$k = \frac{rate}{[SO_2]^2[O_2]^1} = \frac{3.0 \times 10^{-2} M/s}{(0.50M)^2(0.90M)} = 0.13M^{-2}s^{-1}$$

Ex. Method of Initial Rates

$$BrO_3^- + 5\,Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

$$\text{Rate} = -\frac{\Delta[BrO_3^-]}{\Delta t} = k[BrO_3^-]^m[Br^-]^n[H^+]^p$$

Expt #	**$[BrO_3^-]$, *mol/L***	**$[Br^-]$, *mol/L***	**$[H^+]$, *mol/L***	**Initial Rate, *mol/(L·s)***
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Ex. Compare 1 and 2

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{1.6\times10^{-3}\,M/s}{8.0\times10^{-4}\,M/s} = \frac{\cancel{k}(0.20M)^m\cancel{(0.10M)^n}\cancel{(0.10M)^p}}{\cancel{k}(0.10M)^m\cancel{(0.10M)^n}\cancel{(0.10M)^p}}$$

$$2.0 = \left(\frac{0.20M}{0.10M}\right)^m = (2.0)^m \qquad \therefore m = 1$$

Compare 2 and 3

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{3.2\times10^{-3}\,M/s}{1.6\times10^{-3}\,M/s} = \frac{\cancel{k}\cancel{(0.20M)^m}(0.20M)^n\cancel{(0.10M)^p}}{\cancel{k}\cancel{(0.20M)^m}(0.10M)^n\cancel{(0.10M)^p}}$$

$$2.0 = \left(\frac{0.20M}{0.10M}\right)^n = (2.0)^n \qquad \therefore n = 1$$

Ex. Compare 1 and 4

$$\frac{\text{Rate }4}{\text{Rate }1} = \frac{3.2\times10^{-3}\,M/s}{8.0\times10^{-4}\,M/s} = \frac{\cancel{k}\cancel{(0.10M)^m}\cancel{(0.10M)^n}(0.20M)^p}{\cancel{k}\cancel{(0.10M)^m}\cancel{(0.10M)^n}(0.10M)^p}$$

$$4.0 = \left(\frac{0.20M}{0.10M}\right)^p = (2.0)^p \qquad \therefore p = 2$$

- First order in $[BrO_3^-]$ and $[Br^-]$
- Second order in $[H^+]$
- Overall order = $\boldsymbol{m} + \boldsymbol{n} + \boldsymbol{p} = 1 + 1 + 2 = 4$
- Rate Law is: **Rate =** $\boldsymbol{k[BrO_3^-][Br^-][H^+]^2}$

Your Turn!

Ex. Using the following experimental data, determine the order with respect to NO and O_2 .

Expt #	**[NO], *M***	**[O_2], *M***	**Initial Rate of NO_2 formation, $M\cdot s^{-1}$**
1	0.12	0.25	1.5×10^{-3}
2	0.24	0.25	6.0×10^{-3}
3	0.50	0.50	5.2×10^{-2}

A. 2, 0

B. 3,1

C. 2, 1

D. 1, 1

Your Turn! - Solution

$$\frac{R_2}{R_1} = \frac{6.0 \text{ x } 10^{-3} M\ s^{-1}}{1.5 \text{ x } 10^{-3} M\ s^{-1}} = \frac{[0.24M]^x}{[0.12M]^x} \frac{[0.25M]^y}{[0.25M]^y}$$

$$x = 2$$

$$\frac{R_3}{R_1} = \frac{5.2 \text{ x } 10^{-2} M\ s^{-1}}{1.5 \text{ x } 10^{-3} M\ s^{-1}} = \frac{[0.50M]^2}{[0.12M]^2} \frac{[0.50M]^y}{[0.25M]^y}$$

$$y = 1$$

Concentration and Time

- Rate law tells us how speed of reaction varies with [X]'s.
- Sometimes want to know
  - [reactants] and [products] at given time during reaction
  - How long for [reactants] to drop below some minimum optimal value
- Need dependence of Rate on Time

Concentration vs. Time for 1st Order Reactions

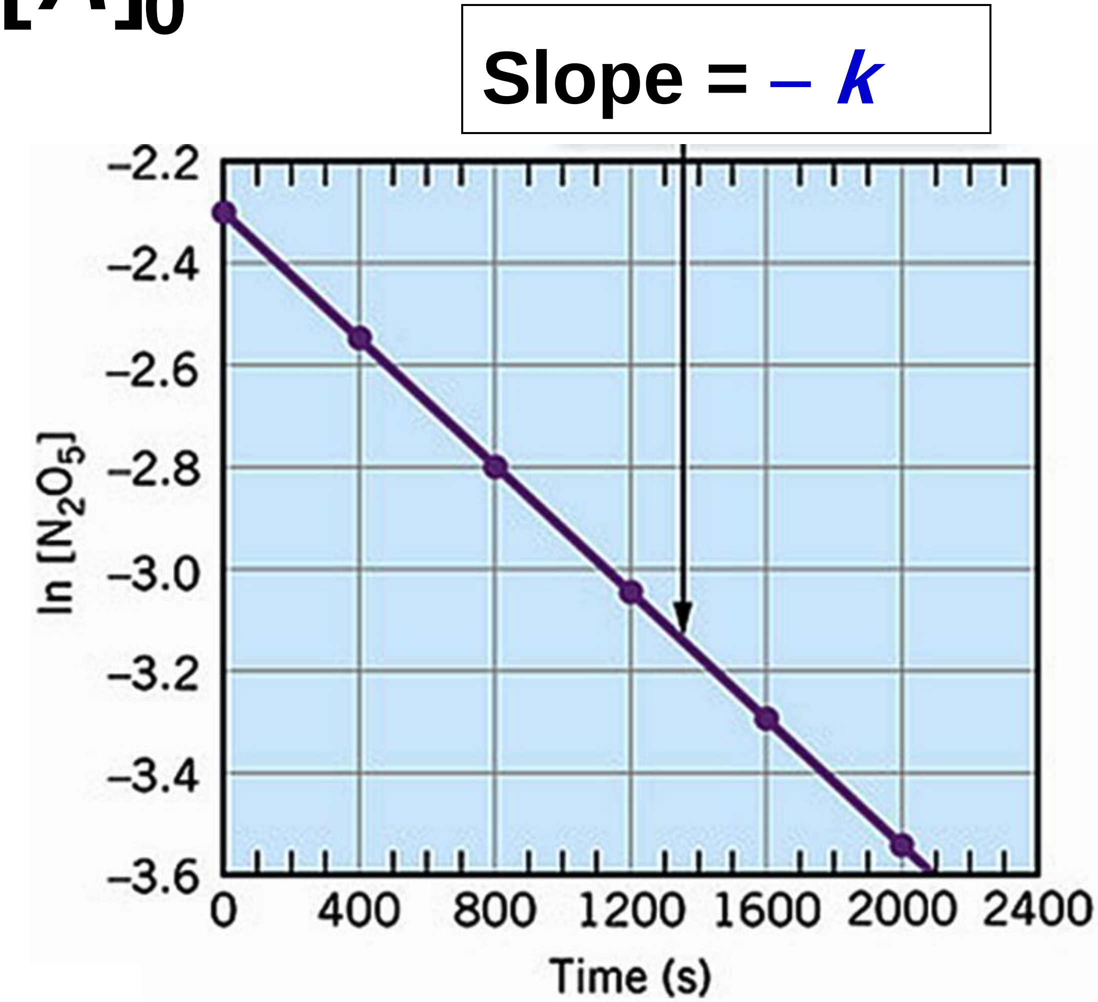
$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k[A]$$

- Corresponding to reactions
  - $A \rightarrow products$
- Integrating we get $$\ln\frac{[A]_0}{[A]_t} = kt$$
- Rearranging gives $$\ln[A]_t = -kt + \ln[A]_0$$
- Equation of line $$y = mx + b$$

Plot $\ln[A]_t$ (y axis) vs. t (x axis)

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

- Yields straight line
  - Indicative of 1st order kinetics
  - slope = $-k$
  - intercept = $\ln[A]_0$
    - If we don't know already

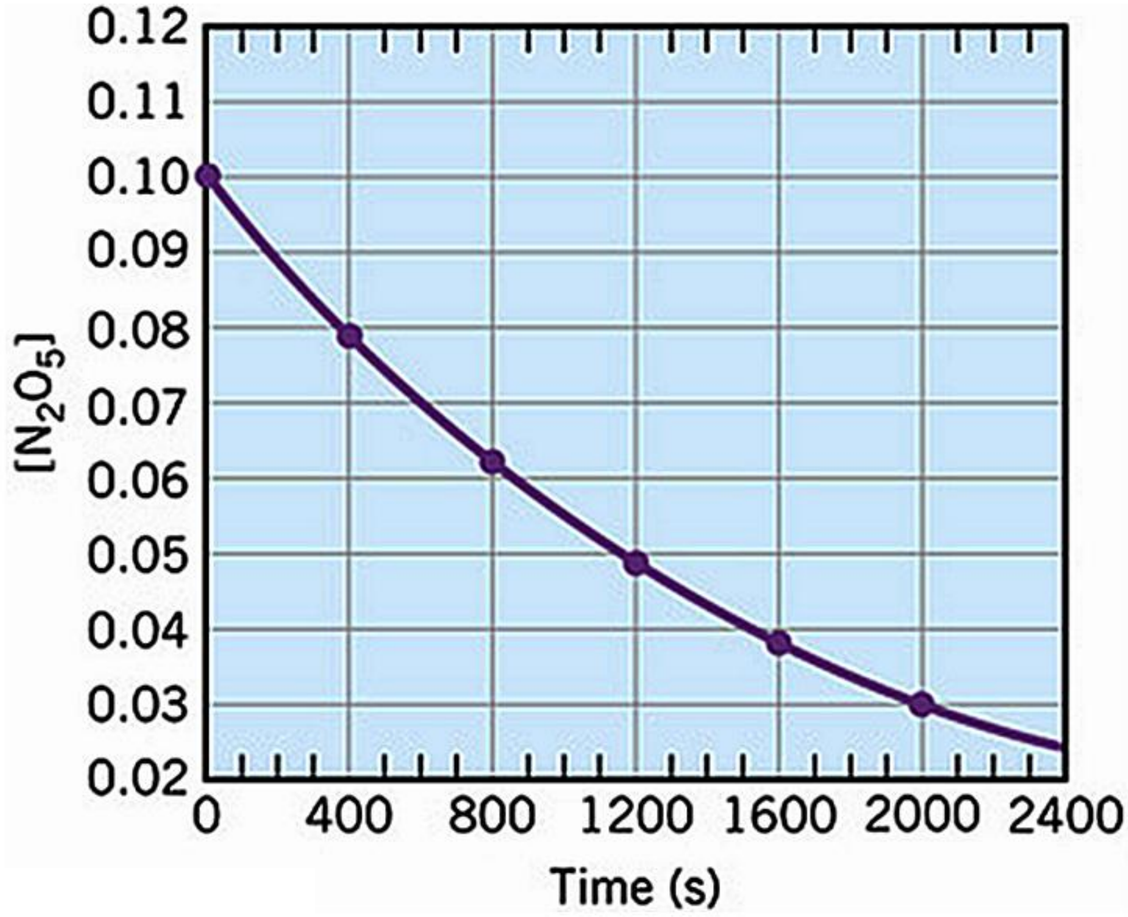


Slope = $-k$

First Order Kinetics Graph

- Plot of **[*A*]** vs. time gives an exponential decay

$$[A]_t = [A]_o e^{-kt}$$



Half-lives for 1st Order Reactions

- Half-life = $t_{1/2}$
- **First Order Reactions**
  - Set $$[A]_t = \frac{1}{2}[A]_0$$
  - Substituting into $$\ln\frac{[A]_0}{[A]_t} = kt$$
  - Gives $$\ln\frac{[A]_0}{\frac{1}{2}[A]_0} = kt_{1/2}$$
  - Canceling gives $\ln 2 = kt_{1/2}$
  - Rearranging gives $$t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1}$$

Half-life for 1st Order Reactions

Observe:

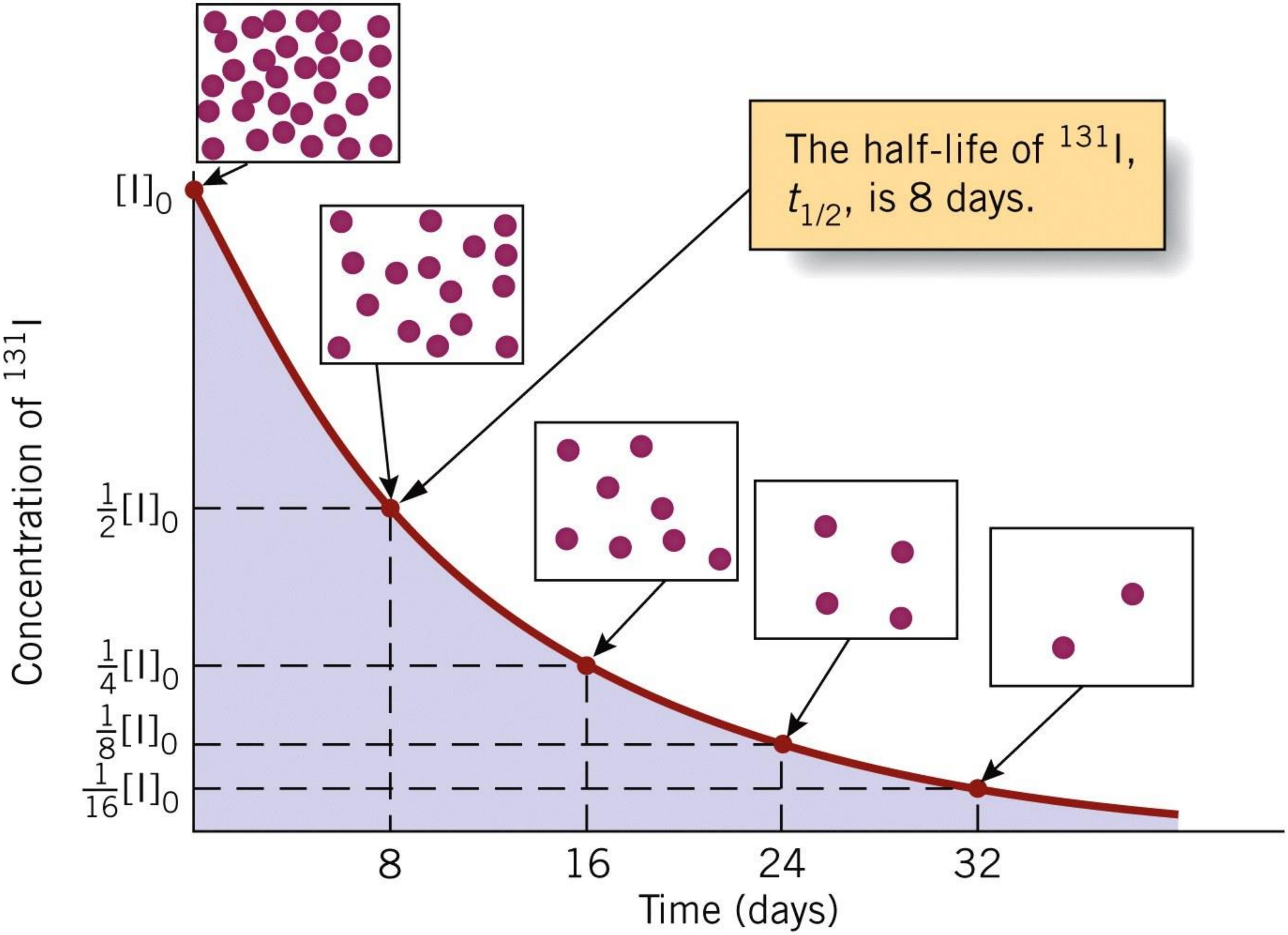
1. **$t_{1/2}$** is **independent** of **$[A]_o$**
   - For given reaction (and **T**)
   - Takes same time for concentration to fall from
     - 2 *M* to 1 *M* as from
     - 5.0×10^{-3} *M* to 2.5×10^{-3} *M*
2. **k_1** has units $(\text{time})^{-1}$, so ***$t_{1/2}$*** has units (time)
   - ***$t_{1/2}$*** called ***half-life***
     - Time for ½ of sample to decay

Half-life for 1st Order Reactions

Does this mean that all of sample is gone in two half-lives (2 x $t_{½}$)?

- **No!**
  - In **1st** $t_{½}$, it goes to **$½[A]_o$**
  - In **2nd** $t_{½}$, it goes to **$½(½[A]_o) = ¼[A]_o$**
  - In **3rd** $t_{½}$, it goes to **$½(¼[A]_o) = ⅛[A]_o$**
  - In **nth** $t_{½}$, it goes to **$[A]_o/2^n$**
- Existence of [X] independent ***half-life*** is property of exponential function
  - Property of 1st order kinetics

Half-Life Graph



Ex. Using Half-Life

- ^{131}I is used as a metabolic tracer in hospitals. It has a half-life, $t_{1/2}$ = 8.07 days. How long before the activity falls to 1% of the initial value?

$$N = N_o e^{-kt}$$

$$\ln\frac{N}{N_o} = -kt = \frac{-t\ln 2}{\tau_{1/2}}$$

$$t = -\frac{\tau_{1/2}\ln\frac{N}{N_o}}{\ln 2} = -\frac{(8.07\,days)\ln\left(\frac{1}{100}\right)}{\ln 2} = 53.6\,days$$

Learning Check

Ex. The radioactive decay of a new atom occurs so that after 21 days, the original amount is reduced to 33%. What is the rate constant for the reaction in s^{-1}?

$$\ln\left(\frac{A_0}{A}\right) = kt$$

$$\ln\left(\frac{100}{33}\right) = k(21\text{da})$$

$$k = 0.0528\ \text{da}^{-1}$$

$$k = 6.11 \times 10^{-7}\ \text{s}^{-1}$$

Learning Check

Ex. The half-life of I-132 is 2.295h. What percentage remains after 24 hours?

$$\frac{\ln(2)}{k} = t_{1/2} \qquad k = \frac{\ln 2}{2.295\text{h}} \qquad 0.302\ \text{h}^{-1} = k$$

$$\ln\left(\frac{A_o}{A}\right) = kt$$

$$\ln\left(\frac{A_o}{A}\right) = 0.302\text{h}^{-1} \times 24\text{h} = 7.248$$

$$A / A_o = .0711\ \%$$

Your Turn!

Ex. Which order has a half-life that is independent of the original amount?

A. Zero
B. First
C. Second
D. None depend on the original quantity

Theories about Reaction Rates

Reaction rate depends on [reactants] and T

- **Collision Theory**
  - Based on Kinetic Molecular Theory
  - Accounts for both effects on molecular level
  - Central Idea
    - Molecules must collide to react
    - Greater number of collision/sec = greater reaction rate

Theories about Reaction Rates

- **Collision Theory**
  - As [reactants] ↑
    - number of Collisions ↑
    - Reaction rate ↑
  - As T ↑
    - Molecular speed ↑
    - Molecules collide with more force (energy)
    - Reaction rate ↑

Collision Theory

- Rate of reaction proportional to number of effective collisions/sec among reactant molecules
- ***Effective collision***
  - that gives rise to product

1. Molecular Orientation

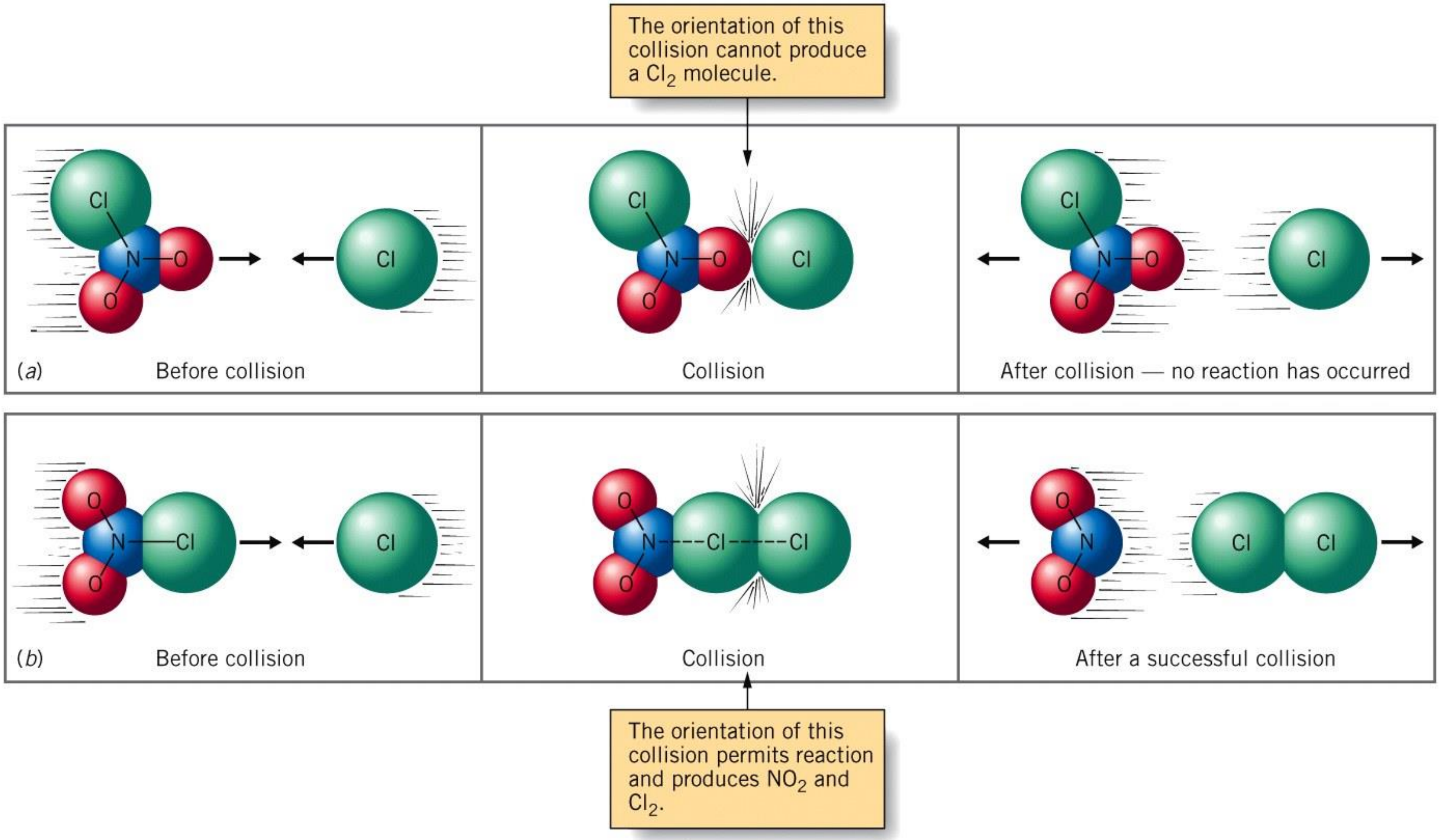
- Molecules must be oriented in a certain way during collisions for reaction to occur

Ex. $NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$

- Cl must come in pointing directly at another Cl atom for Cl_2 to form

Molecular Orientation

Wrong Orientation


The orientation of this collision cannot produce a Cl_2 molecule.

(*a*) Before collision

Collision

After collision — no reaction has occurred

(*b*) Before collision

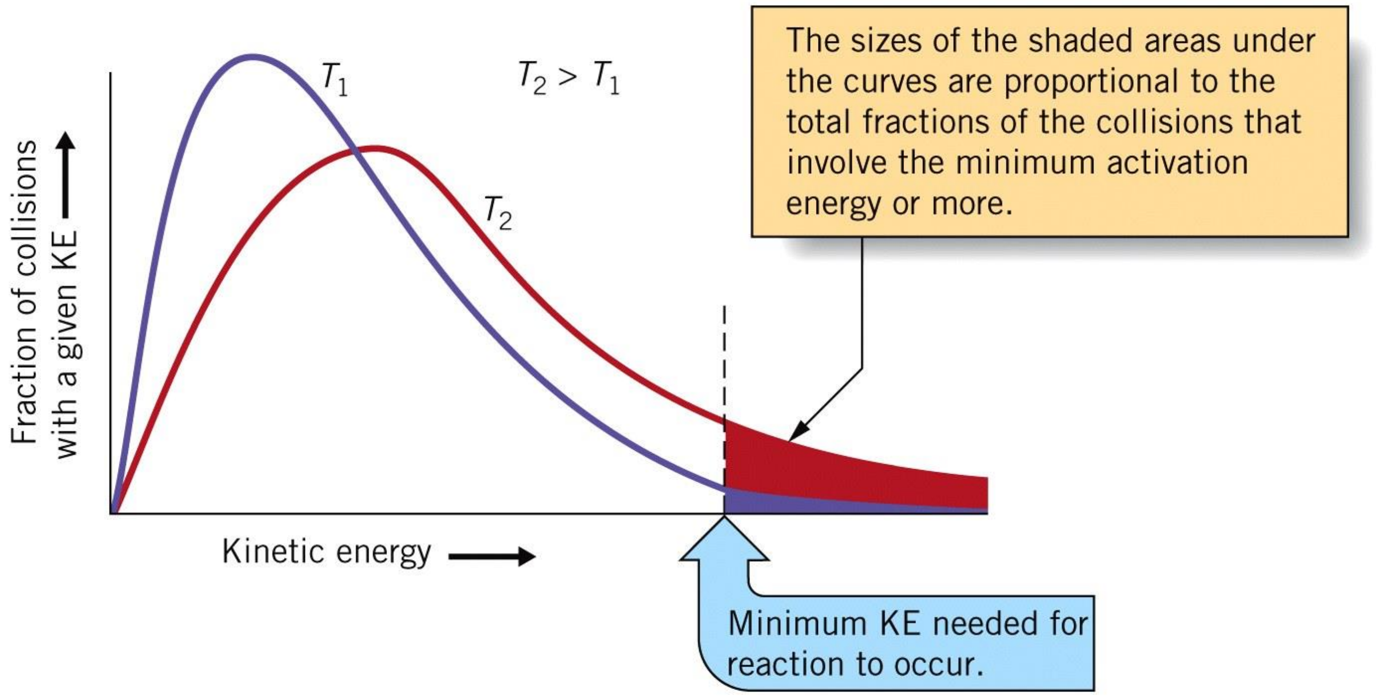
Collision

After a successful collision

The orientation of this collision permits reaction and produces NO_2 and Cl_2.

Correct Orientation

2. Temperature



- Over moderate **T** range, **E_a** unchanged
- As ↑ **T**,
  - More molecules have **E_a**
  - So more molecules undergo reaction
- Reaction rate ↑ as **T**↑

3. Activation Energy, E_a

- Molecules must possess certain amount of kinetic energy (KE) in order to react

Activation Energy, E_a

  - Minimum KE needed for reaction to occur

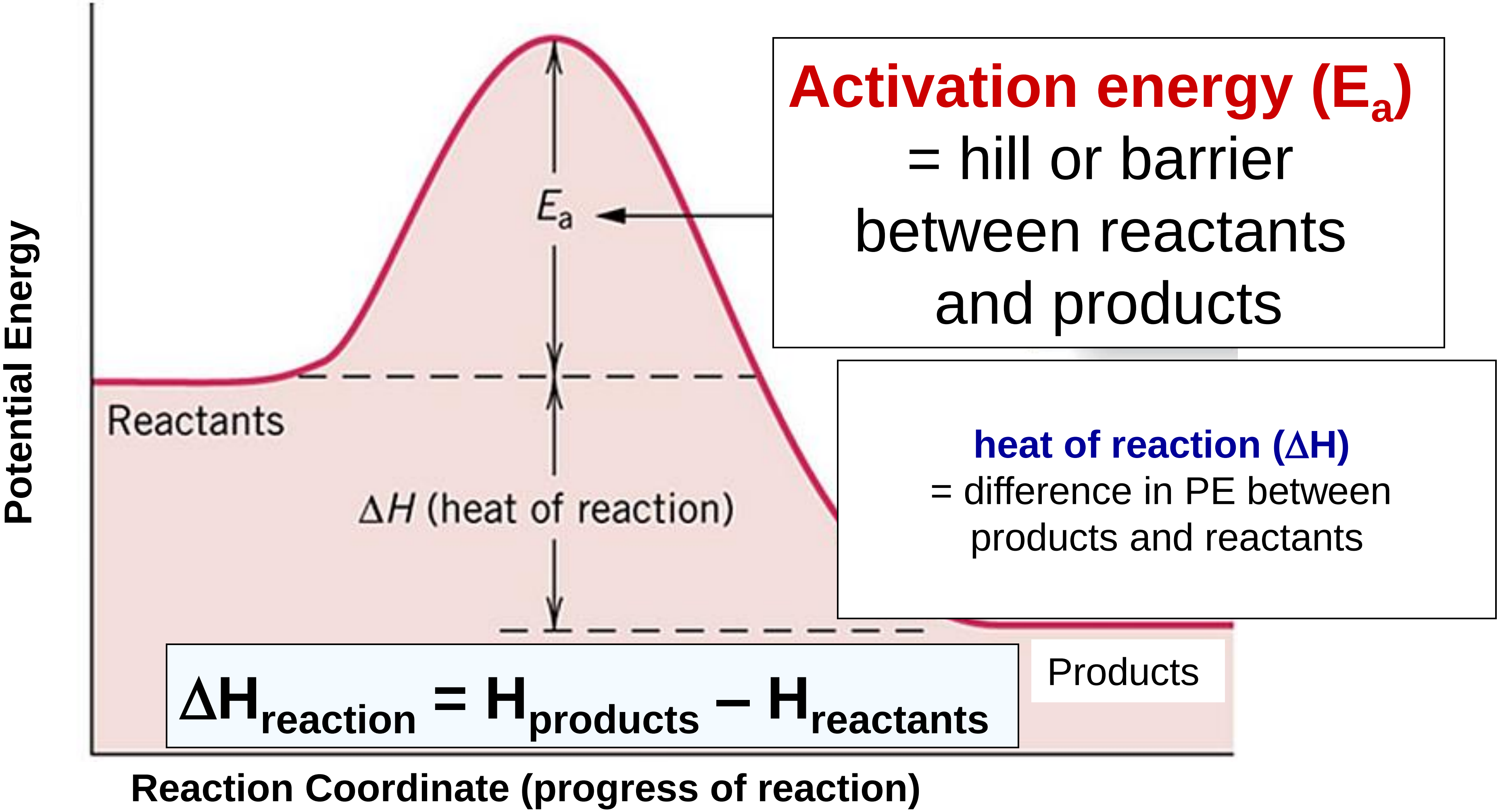
Transition State Theory

- Used to explain details of reactions
- What happens when reactant molecules collide

Potential Energy Diagram

- To visualize what actually happens during successful collision
- Relationship between E_a and developing Total PE

Potential Energy Diagram



Activation energy (E_a)
= hill or barrier between reactants and products

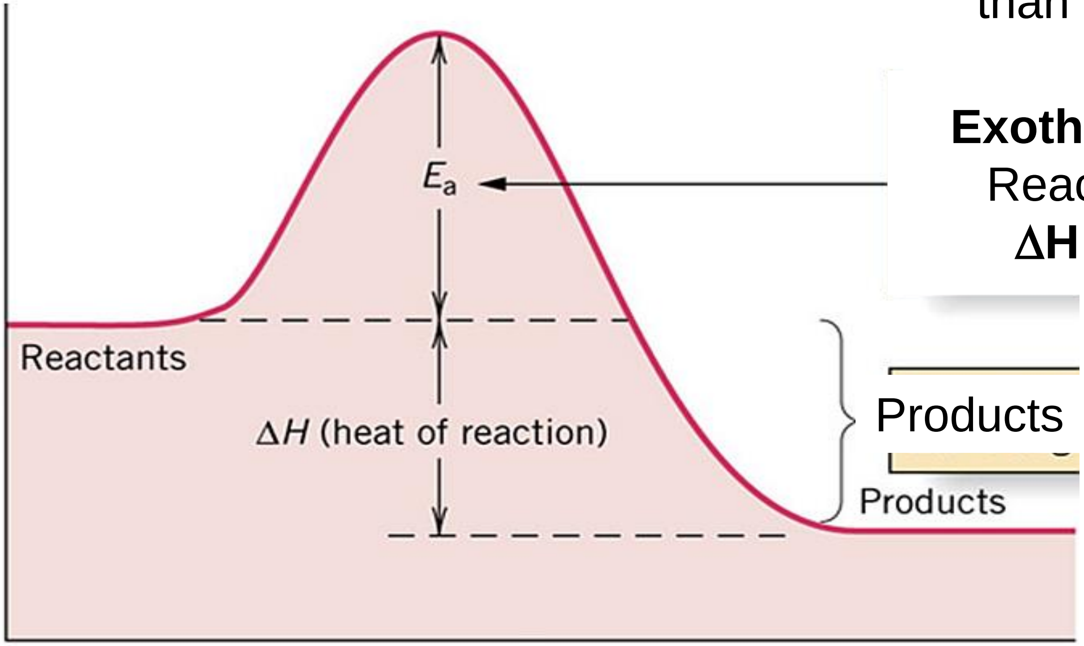
heat of reaction (ΔH)
= difference in PE between products and reactants

$$\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$$

Exothermic Reaction

- $\Delta H_{\text{reaction}} < 0$ **(–)**

Exothermic reaction
- Products *lower* PE than reactants



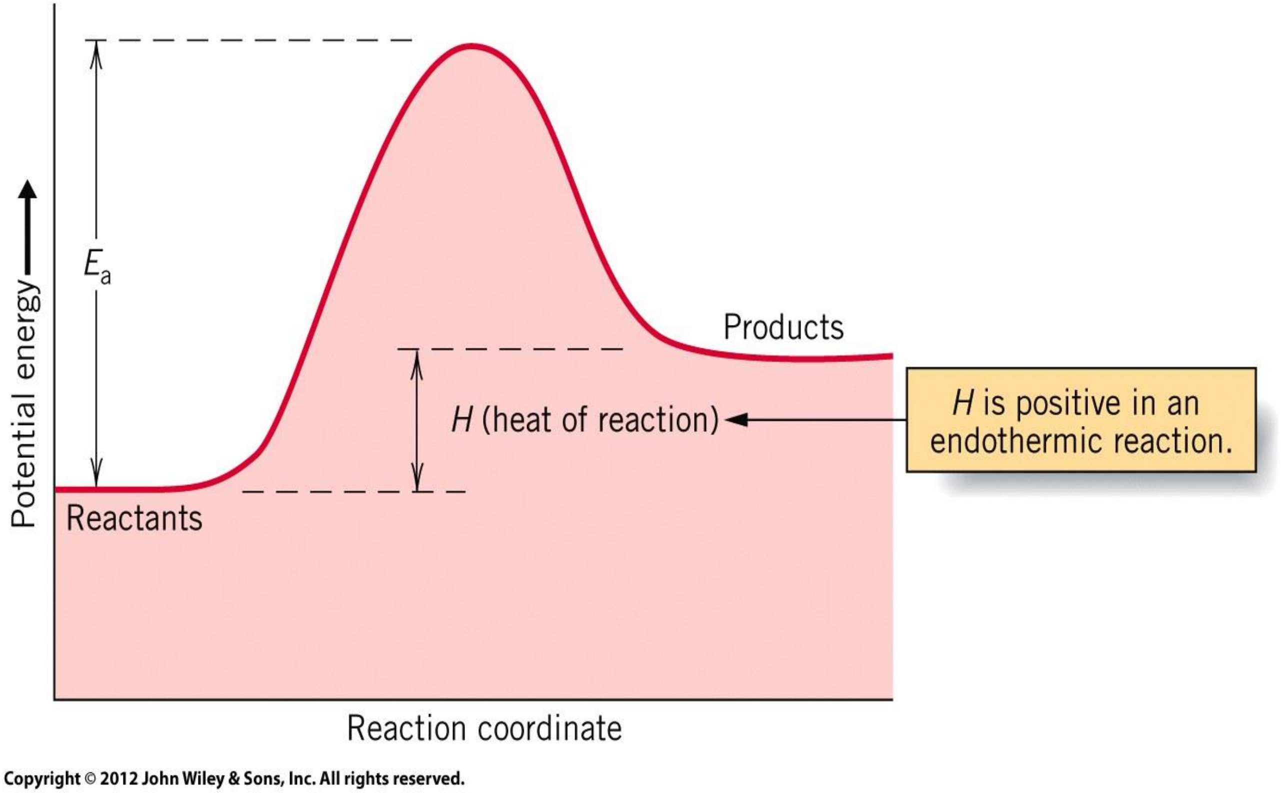
Exothermic
Reaction
ΔH = –

Products

- **E_a** could be high and reaction slow even if ΔH_{rxn} large and negative
- **E_a** could be low and reaction rapid

Endothermic Reaction

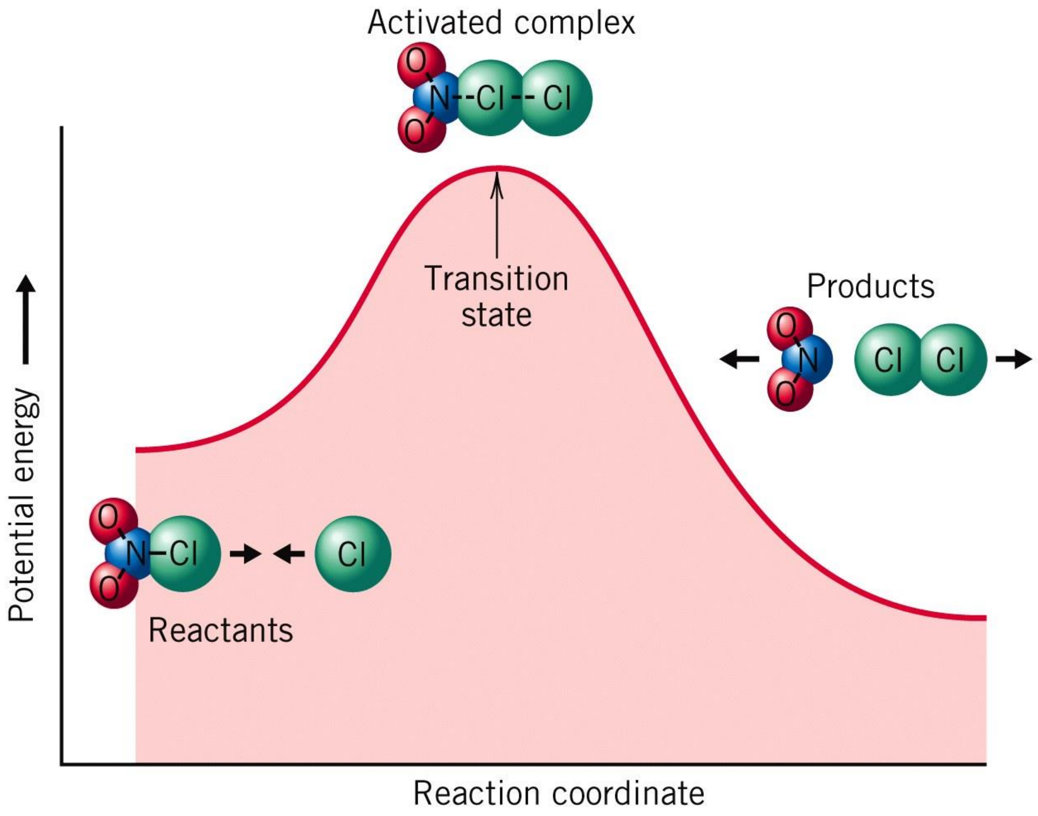
$\Delta H_{reaction} > 0 \quad (+)$



Endothermic
Reaction
$\Delta H = +$

$$\boxed{\Delta H_{reaction} = H_{products} - H_{reactants}}$$

Ex. $NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$



- As NO_2Cl and Cl come together
  - Start to form Cl····Cl bond
  - Start to break N····Cl bond
- Requires **E,** as must bring 2 things together
- In TS
  - N····Cl bond ½ broken
  - Cl····Cl bond ½ formed
- After TS
  - Cl—Cl bond forms
  - N····Cl breaks
- Releases E as products more stable

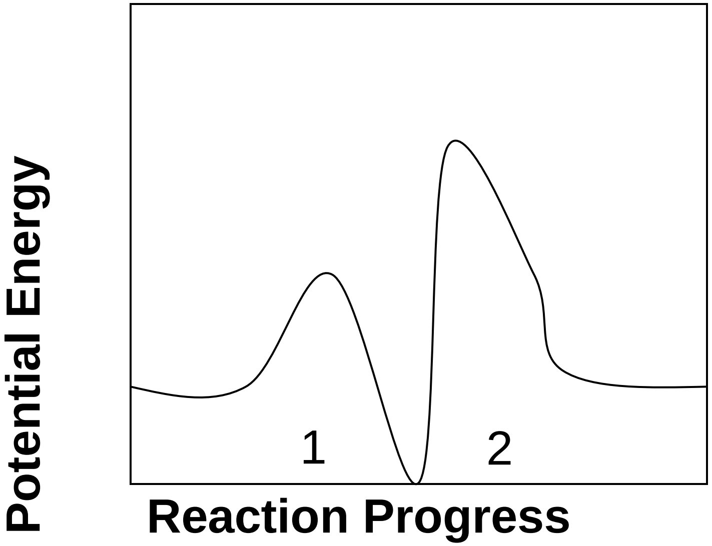
Your Turn!

Ex. Examine the potential energy diagram. Which is the Slowest (Rate Determining) Step?

A. Step 1

B. Step 2 Has greatest E_a

C. Can't tell from the given information



Measuring Activation Energy

- **Arrhenius Equation**
  - Equation expressing **T** dependence of ***k***

$$k = Ae^{-E_a/RT}$$

    - A = Frequency factor—has same units as ***k***
    - R = gas constant in energy units

      = 8.314 $J{\cdot}mol^{-1}{\cdot}K^{-1}$
    - E_a = Activation Energy—has units of ***J/mol***
    - T = Temperature in ***K***

How To Calculate Activation Energy

- **Method 1. Graphically**
- Take natural logarithm of both sides
- Rearranging

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) * \left(\frac{1}{T}\right)$$

- Equation for a line

$$y \quad = \quad b \qquad + \quad m \quad x$$

Arrhenius Plot

- Plot **ln *k*** (y axis) vs. ***1/T*** (x axis)

Method 2. van't Hoff Equation

- **van't Hoff Eq**
- **uation**

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

Using van't Hoff Equation

Ex. $CH_4 + 2\,S_2 \longrightarrow CS_2 + 2\,H_2S$

k (L/mol·s)	*T* (°C)	*T* (K)
1.1 = k_1	550	823 = T_1
6.4 = k_2	625	898 = T_2

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{-E_a}{8.3145 J/K\cdot mol}\left(\frac{1}{898K} - \frac{1}{823K}\right)$$

$$E_a = \frac{-(8.314 J/K\cdot mol)\ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{898K} - \frac{1}{823}\right)} = 1.4\times 10^5 J/mol$$

Learning Check

Ex. Given that *k* at 25°C is 4.61×10^{-1} M/s and that at 50°C it is 4.64×10^{-1} M/s, what is the activation energy for the reaction?

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-\mathrm{Ea}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}_2} - \frac{1}{\mathrm{T}_1}\right)$$

$$\ln\left(\frac{4.64 \times 10^{-1}\,\mathrm{M/s}}{4.61 \times 10^{-1}\,\mathrm{M/s}}\right) = \frac{-\mathrm{Ea}}{8.314\mathrm{J/(mol \cdot K)}}\left(\frac{1}{323\mathrm{K}} - \frac{1}{298\mathrm{K}}\right)$$

$$\mathrm{E_a} = 208\ \mathrm{J/mol}$$

Your Turn!

Ex. A reaction has an activation energy of 40 kJ/mol. What happens to the rate if you increase the temperature from 70 ^{o}C to 80 ^{0}C?

A. Rate increases approximately 1.5 times
B. Rate increases approximately 5000 times
C. Rate does not increase
D. Rate increases approximately 3 times

Your Turn! - Solution

Rate is proportional to the rate constant

$$\frac{k_2}{k_1} = \frac{e^{-\left(\frac{40000\ \text{J}}{8.314\frac{\text{J}}{\text{mol K}}\text{x}(80+273)\text{K}}\right)}}{e^{-\left(\frac{40000\ \text{J}}{8.314\frac{\text{J}}{\text{mol K}}\text{x}(70+273)\text{K}}\right)}} = 1.49$$

Homogeneous Catalyst

- Same phase as reactants

Consider : $\mathbf{S\ (g) + O_2\ (g) + H_2O\ (g) \longrightarrow H_2SO_4\ (g)}$

$S\ (g) + O_2\ (g) \longrightarrow SO_2\ (g)$

$\mathbf{NO_2\ (g)} + SO_2\ (g) \longrightarrow NO\ (g) + SO_3\ (g)$ Catalytic pathway

$SO_3\ (g) + H_2O\ (g) \longrightarrow H_2SO_4\ (g)$

$NO\ (g) + \frac{1}{2}O_2\ (g) \longrightarrow \mathbf{NO_2\ (g)}$ Regeneration of catalyst

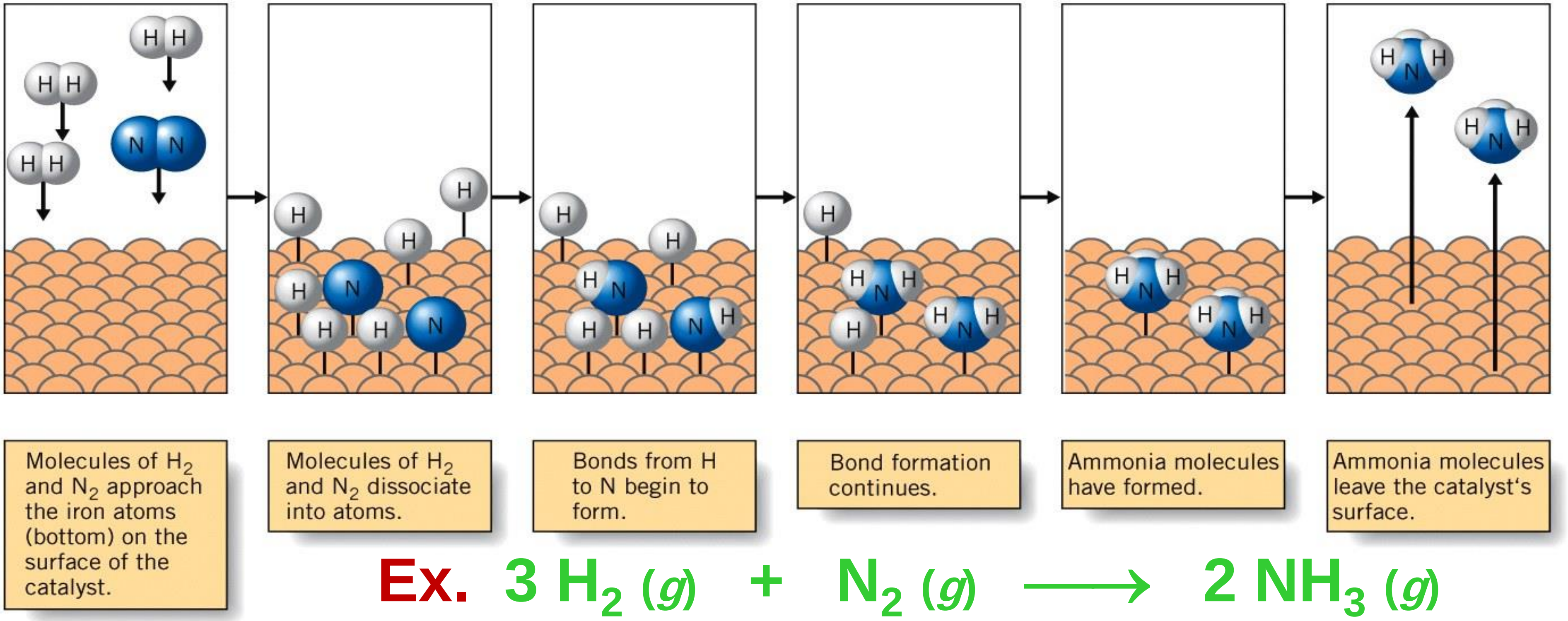
---

Net: $\mathbf{S\ (g) + O_2\ (g) + H_2O\ (g) \longrightarrow H_2SO_4\ (g)}$

- ***What is Catalyst?*** $NO_{2\ (g)}$
  - **Reactant** (used up) in early step
  - **Product** (regenerated) in later step
- ***Which are Intermediates?*** **NO and SO_2**

Heterogeneous Catalyst

Exists in separate phase from reactants



Molecules of H_2 and N_2 approach the iron atoms (bottom) on the surface of the catalyst.

Molecules of H_2 and N_2 dissociate into atoms.

Bonds from H to N begin to form.

Bond formation continues.

Ammonia molecules have formed.

Ammonia molecules leave the catalyst's surface.

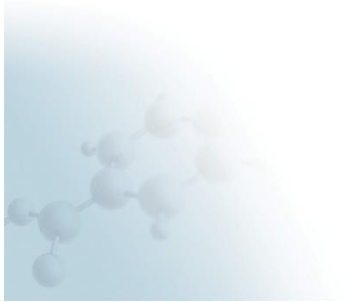
Ex. $3\ H_2\ (g) + N_2\ (g) \longrightarrow 2\ NH_3\ (g)$

H_2 & N_2 approach Fe catalyst	**H_2 & N_2 bind to Fe & bonds break**	**N—H bonds forming**	**N—H bonds forming**	**NH_3 formation complete**	**NH_3 dissociates**

Chapter 5
Properties of Solutions

Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop



Solutions

Solution

- Homogeneous mixture
- Composed of solvent and solute(s)

Solvent

- More abundant component of mixture

Solute(s)

- Less abundant or other component(s) of mixture

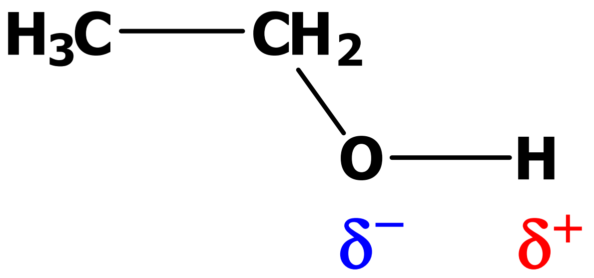
Ex. Lactated Ringer's solution

- NaCl, KCl, $CaCl_2$, $NaC_3H_5O_3$ in water

Rule of Thumb

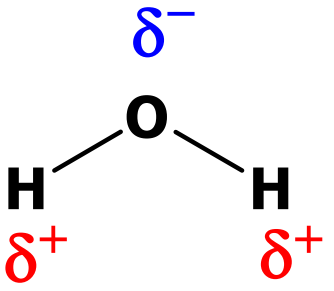
- **"Like dissolves Like"**
  - Use **polar** solvent for **polar** solute
  - Use **Nonpolar** solvent for **nonpolar** solute

- **Polar** solutes interact with and dissolve in **polar** solvents



Ex. Ethanol in water

- Both are polar molecules
- Both form hydrogen bonds



miscible Solution **Benzene in CCl_4**

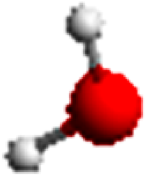
- CCl_4
  - Nonpolar
- Benzene, C_6H_6
  - Nonpolar
    - Similar in strength to CCl_4
- Does dissolve, solution forms

Immiscible Solution **Benzene in water**

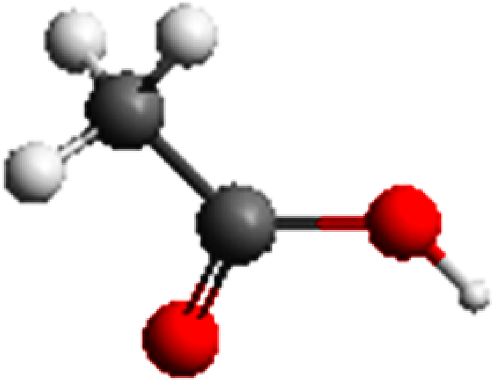
- Solvent and solute are very “different”
- No solution forms
  - 2 layers, Don’t Mix

Learning Check

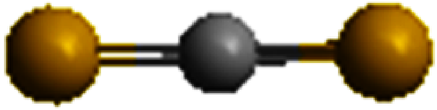
Ex. Which of the following are miscible in water?



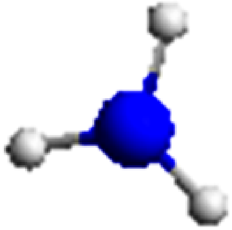
water



acetic acid



carbon
disulfide



ammonia

Your Turn!

Ex. Which of the following molecules is soluble in C_6H_6?

A. NH_3

B. CH_3NH_2

C. CH_3OH

D. CH_3CH_3

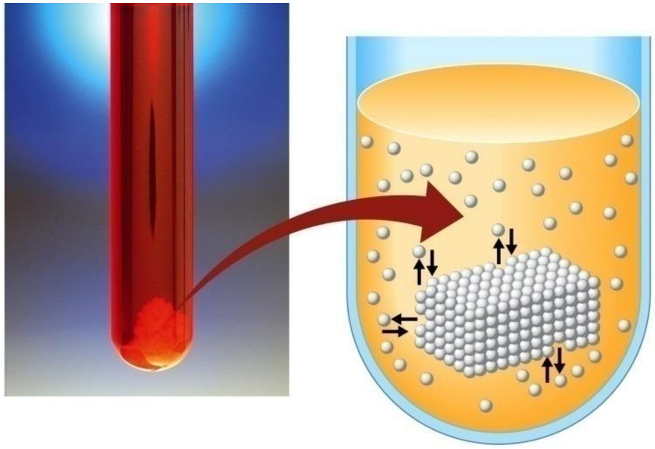
E. CH_3Cl

Solubility

- Mass of solute that forms *saturated solution* with given mass of solvent at specified temperature

$$\text{solubility} = \frac{g\ \text{solute}}{100g\ \text{solvent}}$$

- If extra solute added to saturated solution, extra solute will remain as separate phase
- $\text{solute}_{\text{undissolved}} \rightleftharpoons \text{solute}_{\text{dissolved}}$



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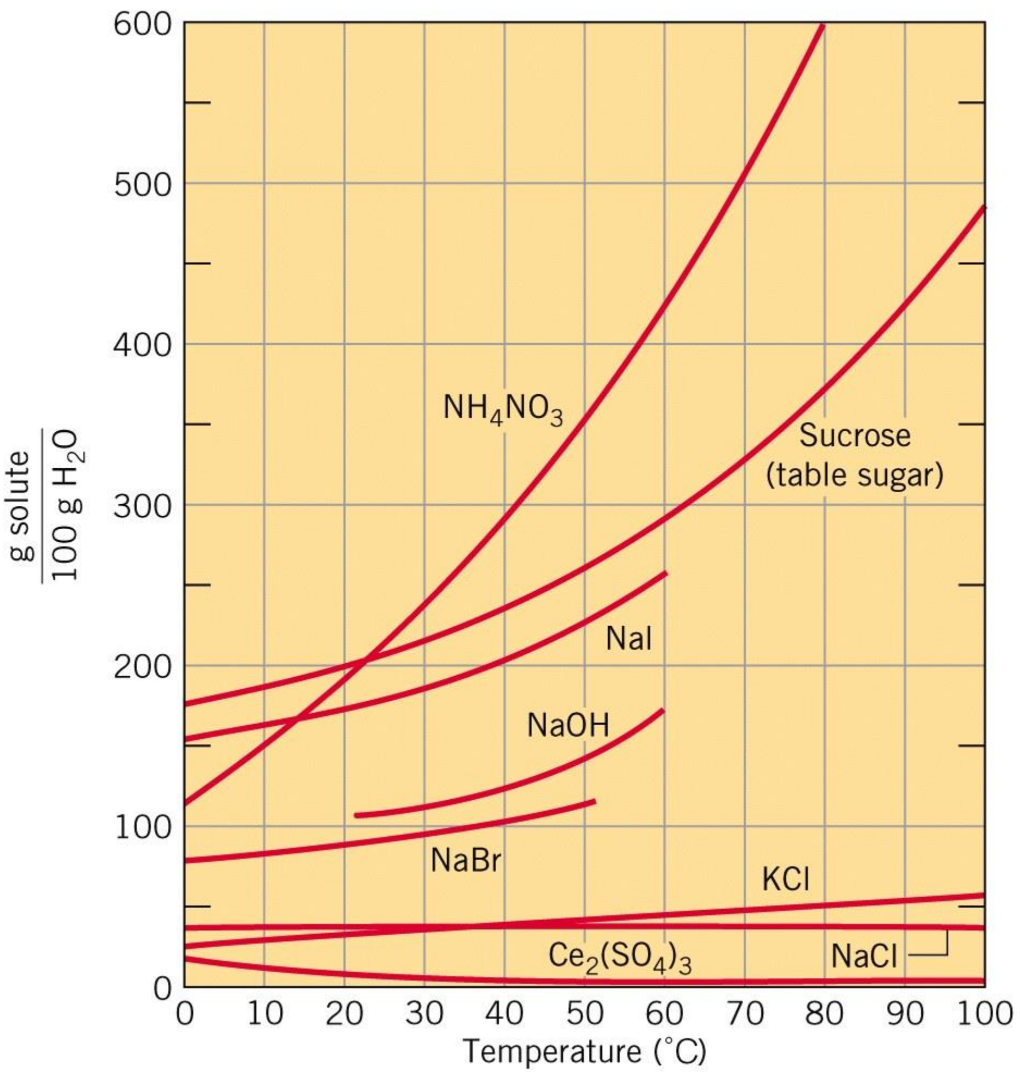
Effect of T on solid Solubility in Liquids



- Most substances become more soluble as T ↑
- Amount solubility ↑
  - Varies considerably
  - Depends on substance

Effect of T on Gas Solubility in Liquids

- **Solubility of gases usually ↓ as T ↑**

Table 13.2 Solubilities of Common Gases in Water

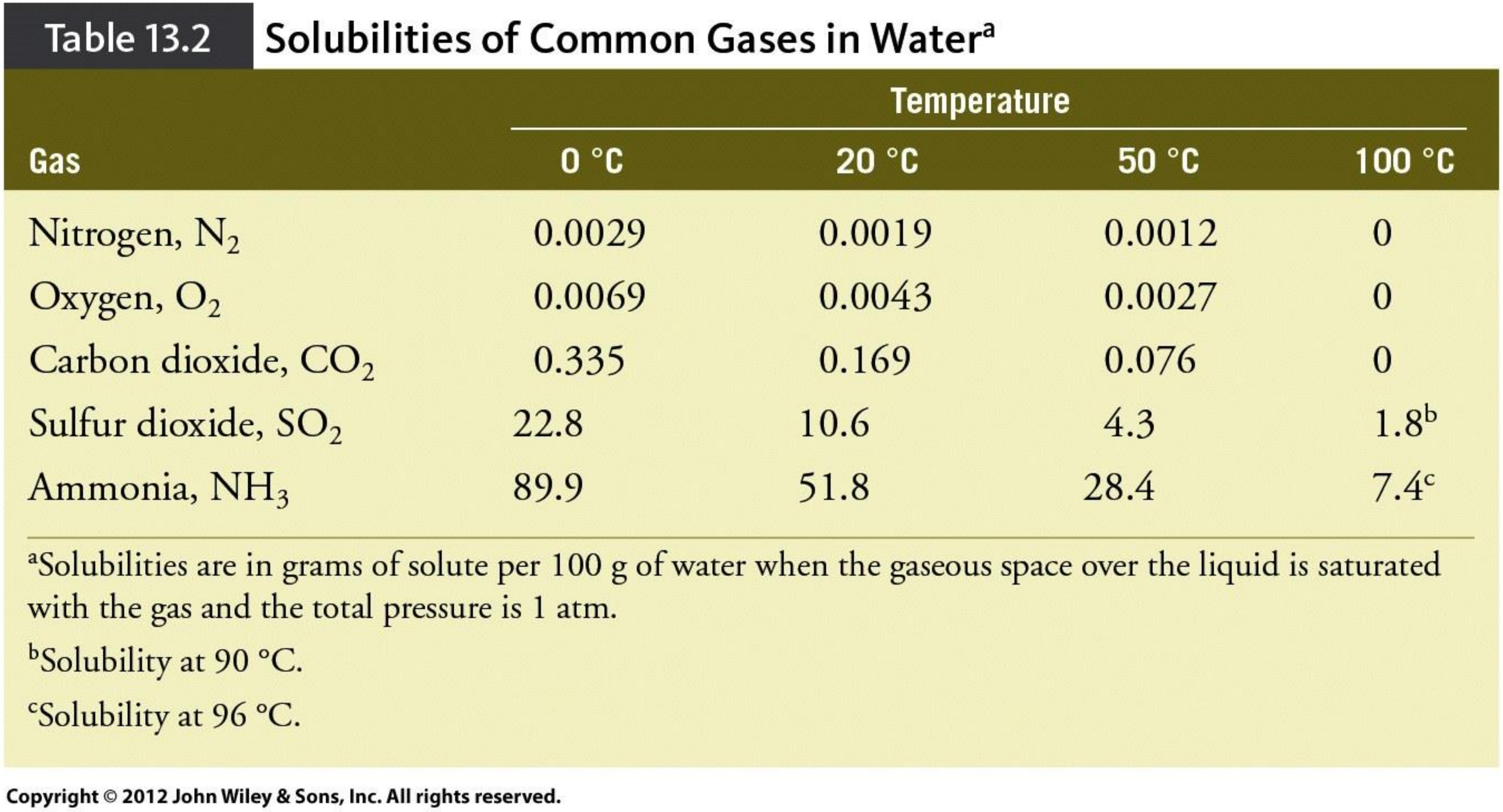


Table 13.2 Solubilities of Common Gases in Water[a]

Gas	Temperature			
	0 °C	20 °C	50 °C	100 °C
Nitrogen, N_2	0.0029	0.0019	0.0012	0
Oxygen, O_2	0.0069	0.0043	0.0027	0
Carbon dioxide, CO_2	0.335	0.169	0.076	0
Sulfur dioxide, SO_2	22.8	10.6	4.3	1.8[b]
Ammonia, NH_3	89.9	51.8	28.4	7.4[c]

[a] Solubilities are in grams of solute per 100 g of water when the gaseous space over the liquid is saturated with the gas and the total pressure is 1 atm.

[b] Solubility at 90 °C.

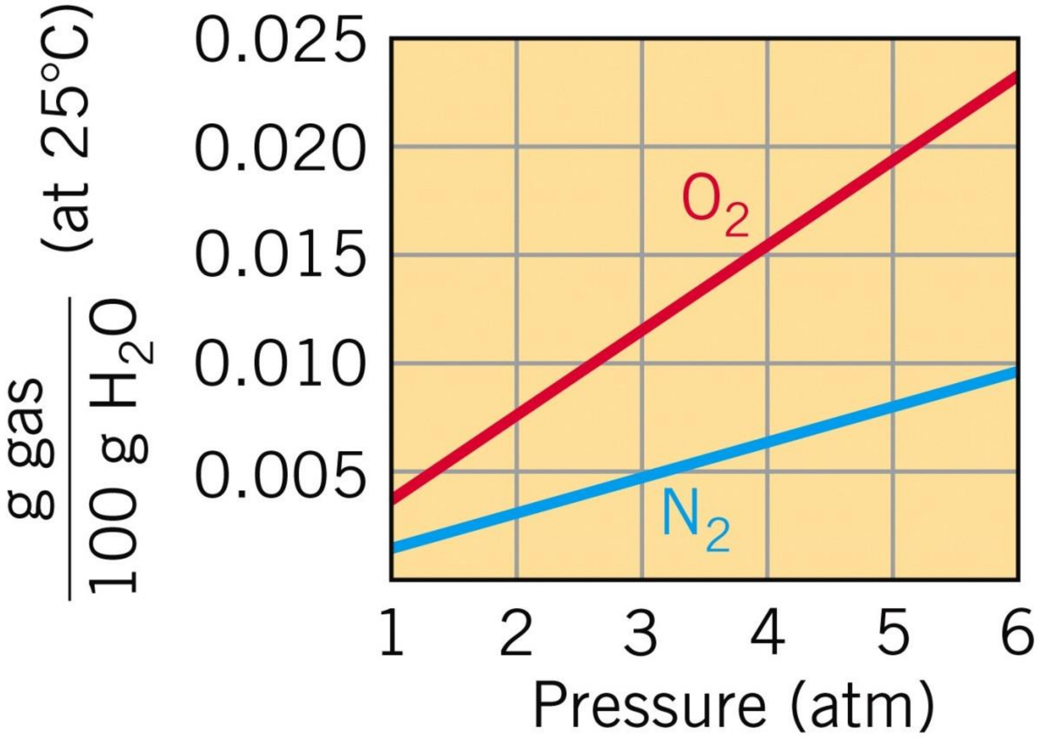
[c] Solubility at 96 °C.

Effect of Pressure on Gas Solubility

- **Solubility ↑ as P ↑**

Why?

- ↑ P means ↓ V above solution for gas
- Gas goes into solution
  - Relieves stress on system
- Conversely, solubility ↓ as P ↓
  - Soda in can



Gases are more soluble at low temperature and high pressure.

Effect of Pressure on Gas Solubility

A. At some P, equilibrium exists between vapor phase and solution

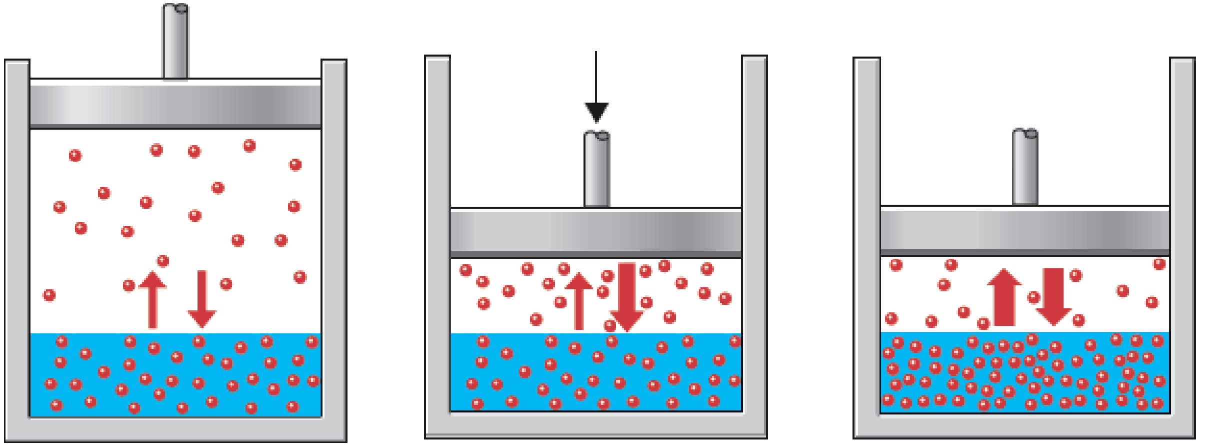
- **$rate_{in}$ = $rate_{out}$**

B. ↑ in P puts stress on equilibrium

- ↑ frequency of collisions so **$rate_{in}$ > $rate_{out}$**
- More gas molecules dissolve than are leaving solution

C. More gas dissolved

- $Rate_{out}$ will ↑ until $Rate_{out}$ = $Rate_{in}$ and equilibrium restored



Henry’s Law

- Pressure-Solubility Law
- “Concentration of gas in liquid at any given temperature is directly proportional to partial pressure of gas over solution”

$C_{gas} = k_H P_{gas}$ (T is constant)

C_{gas} = concentration of gas

P_{gas} = partial pressure of gas

k_H = Henry's Law constant

  - Unique to each gas
  - Tabulated

Henry's Law

- True only at low concentrations and pressures where gases do NOT react with solvent
- Alternate form

$$\frac{C_1}{P_1} = \frac{C_2}{P_2}$$

  - C_1 and P_1 refer to an initial set of conditions
  - C_2 and P_2 refer to a final set of conditions

Ex. Using Henry's Law

Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 5 atm over the liquid at 25 °C. The Henry's Law constant for CO_2 in water at this temperature is 3.12×10^{-2} mol/L·atm.

$$C_{CO_2} = k_H(CO_2)P_{CO_2}$$

$$= 3.12 \times 10^{-2} \text{ mol/L·atm} * 5.0 \text{ atm}$$

$$= 0.156 \text{ mol/L} \Rightarrow \mathbf{0.16 \text{ mol/L}}$$

When under 5.0 atm pressure

Ex. Using Henry's Law

Calculate the concentration of CO_2 in a soft drink after the bottle is opened and equilibrates at 25 °C under a partial pressure of CO_2 of 4.0×10^{-4} ·atm.

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} \qquad C_2 = \frac{P_2 C_1}{P_1}$$

$$C_2 = \frac{(0.156\,\text{mol/L})(4.0 \times 10^{-4}\ \text{atm})}{5.0\text{atm}}$$

$$\mathbf{C_2 = 1.2 \times 10^{-4} \cdot mol/L}$$

When open to air

Learning Check

Ex. What is the concentration of dissolved nitrogen in a solution that is saturated in N_2 at 2.0 atm? $k_H = 8.42 \times 10^{-7}$ ($\underline{M}$ / atm)

- $C_g = k_H P_g$
- $C_g = 8.42 \times 10^{-7}$ ($\underline{M}$ / atm) × 2.0 atm
- $C_g = 1.7 \times 10^{-6}$ $\underline{M}$

Your Turn!

Ex. How many grams of oxygen gas at 1.0 atm will dissolve in 10.0 L of water at 25 °C if Henry's constant is 1.3×10^{-3} M atm^{-1} at this temperature?

A. 0.42 g

B. 0.013 g

C. 0.042 g

D. 0.21 g

E. 2.4 g

Colligative Properties

- Physical properties of solutions
- Depend mostly on relative populations of **particles** in mixtures
- Don’t depend on their chemical identities

Effects of Solute on Vapor Pressure of Solvents

- Solutes that can’t evaporate from solution are called **nonvolatile solutes**

Fact: All solutions of **nonvolatile solutes** have lower vapor pressures than their pure solvents

Raoult's Law

- Vapor pressure of solution, ***P_{soln}***, equals product of mole fraction of solvent, ***$X_{solvent}$***, and its vapor pressure when pure, ***$P_{solvent}$***
- Applies for dilute solutions

$$\boxed{P_{solution} = X_{solvent} P^{\circ}_{solvent}}$$

$P_{solution}$ = vapor pressure of the solution

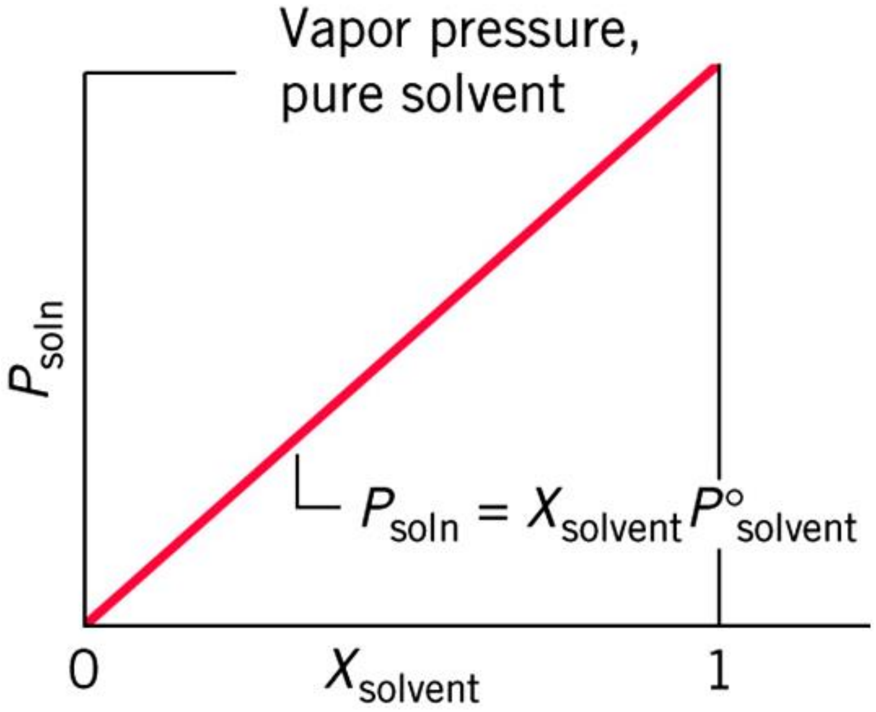
$X_{solvent}$ = mole fraction of the solvent

$P^{\circ}_{solvent}$ = vapor pressure of pure solvent

Alternate form of Raoult's Law

- Plot of P_{soln} vs. $X_{solvent}$ should be **linear**
  - ***Slope*** = $P^{\circ}_{solvent}$
  - ***Intercept*** = 0
- Change in vapor pressure can be expressed as

$$\Delta P = \textbf{change in } P = (P^{\circ}_{solvent} - P_{solution})$$



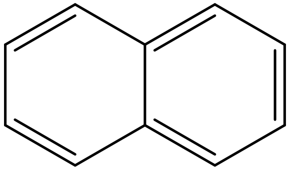
- Usually more interested in how solute's mole fraction changes the vapor pressure of solvent

$$\boxed{\Delta P = X_{solute} P^{\circ}_{solvent}}$$

Learning Check

Ex. The vapor pressure of 2-methylhexane is 37.986 torr at 15°C. What would be the pressure of the mixture of 78.0 g 2-methylhexane and 15 g naphthalene, which is nearly non-volatile at this temperature?

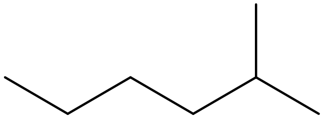
$$\mathbf{P_{solution} = X_{solvent}P^{o}_{solvent}}$$



naphthalene
$C_{10}H_8$
MM 128.17

$$\text{mole naphthalene} = \frac{15\text{ g}}{128.17\text{ g/mol}} = 0.1\underline{1}7\text{ mol}$$

$$\text{mole 2-methylhexane} = \frac{78.0\text{ g}}{100.2\text{ g/mol}} = 0.77\underline{8}4\text{ mol}$$



2-methylhexane
C_7H_{16}
MM 100.2

$$X_{2-\text{methylhexane}} = \frac{0.77\underline{8}4\text{ mol}}{0.77\underline{8}4\text{ mol} + 0.1\underline{1}7\text{ mol}} = 0.8\underline{6}9$$

$$P = (0.8\underline{6}9 \times 37.986\text{ torr})$$

$$= 3\underline{3}.02\text{ torr} \;\mathbf{= 33\text{ torr}}$$

Solutions That Contain Two or More Volatile Components

- Now vapor contains molecules of both components
  - Partial pressure of each component A and B is given by Raoult’s Law

$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

  - Total pressure of solution of components A and B given by Dalton’s Law of Partial Pressures

$$P_{total} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

Ex. Benzene and Toluene

- Consider a mixture of benzene, C_6H_6, and toluene, C_7H_8, containing 1.0 mol benzene and 2.0 mol toluene. At 20 °C, the vapor pressures of the pure substances are:
  $P°_{\text{benzene}} = 75$ torr
  $P°_{\text{toluene}} = 22$ torr
- what is the total pressure above this solution?

Ex. Benzene and Toluene (cont.)

1. **Calculate mole fractions of A and B**

$$X_{benzene} = \frac{1.0 mol}{(1.0 + 2.0) mol} = 0.33 \text{ benzene}$$

$$X_{toluene} = \frac{2.0 mol}{(1.0 + 2.0) mol} = 0.67 \text{ toluene}$$

2. **Calculate partial pressures of A and B**

$$P_{benzene} = X_{benzene} * P^{\circ}_{benzene} = 0.33 \times 75 torr = 25 torr$$

$$P_{toluene} = X_{toluene} * P^{\circ}_{toluene} = 0.67 \times 22 torr = 15 torr$$

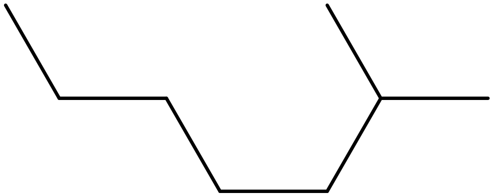
3. **Calculate total pressure**

$$P_{total} = P_{benzene} + P_{toluene}$$

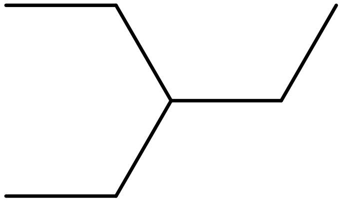
$$= (25 + 15) torr = 40 torr$$

Learning Check

Ex. The vapor pressure of 2-methylheptane is 233.95 torr at 55°C. 3-ethylpentane has a vapor pressure of 207.68 at the same temperature. What would be the pressure of the mixture of 78.0g 2-methylheptane and 15 g 3-ethylpentane?



2-methylheptane
C_8H_{18}
MM 114.23 g/mol



3-ethylpentane
C_7H_{16}
MM 100.2 g/mol

$$P_{solution} = X_A P^o_A + X_B P^o_B$$

Learning Check

$$\text{mole 2-methylheptane} = \frac{78.0\ \text{g}}{114.23\ \text{g/mol}} = 0.68\underline{2}8\ \text{mol}$$

$$\text{mole 3-ethylpentane} = \frac{15\ \text{g}}{100.2\ \text{g/mol}} = 0.1\underline{4}97\ \text{mol}$$

$$X_{\text{2-methylpentane}} = \frac{0.68\underline{2}83\ \text{mol}}{(0.68\underline{2}83\ \text{mol} + 0.14\underline{\ }97\ \text{mol})} = 0.8\underline{2}7$$

$$X_{\text{3-ethylpentane}} = \frac{0.1\underline{4}97\ \text{mol}}{(0.68\underline{2}83\ \text{mol} + 0.1\underline{4}97\ \text{mol})} = 0.1\underline{7}3$$

$$P = (0.8\underline{2}7 \times 233.95\,\text{torr}) + (0.1\underline{7}3 \times 207.68\,\text{torr})$$

P = 230 torr

Your Turn!

Ex. If the vapor pressure of pure hexane is 151.28 mmHg, and heptane is 45.67 mm Hg at 25º, which equation is correct if the mixture's vapor pressure is 145.5 mmHg?

A. X(151.28 mmHg) = 145.5 mmHg
B. X(151.28 mmHg) + (X)(45.67 mm Hg) = 145.5 mmHg
C. X(151.28 mmHg) + (1 – X)(45.67 mm Hg) = 145.5 mm Hg
D. None of these

Solutes also Affect Freezing and Boiling Points of Solutions

- **Freezing Point** of solution always **Lower** than pure solvent
- **Boiling Point** of solution always **Higher** than pure solvent

Colligative properties

- **Boiling Point Elevation (ΔT_b)**
  - ↑ in boiling point of solution vs. pure solvent
- **Freezing Point Depression (ΔT_f)**
  - ↓ in freezing point of solution vs. pure solvent

Freezing Point Depression (ΔT_f)

$$\boxed{\Delta T_f = K_f\, m}$$

where

$\Delta T_f = (T_{fp} - T_{soln})$

m = concentration in Molality

K_f = molal freezing point depression constant

Units of °C/molal, Depend on solvent.

Boiling Point Elevation (ΔT_b)

$$\boxed{\Delta T_b = K_b\, m}$$

where

$\Delta T_b = (T_{soln} - T_{bp})$

m = concentration in Molality

K_b = molal boiling point elevation constant

Units of °*C/m,* Depend on solvent.

Values of K_f and K_b for solvents

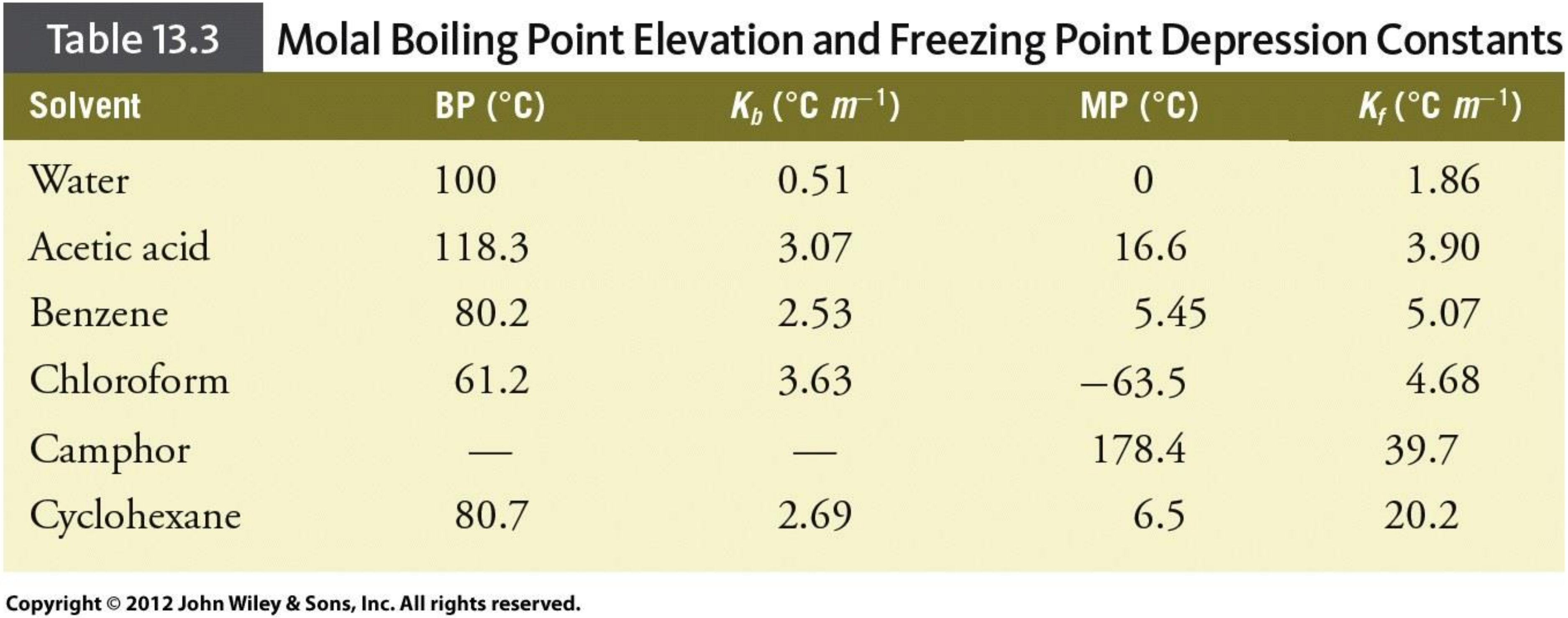


Table 13.3 Molal Boiling Point Elevation and Freezing Point Depression Constants

Solvent	BP (°C)	K_b (°C m^{-1})	MP (°C)	K_f (°C m^{-1})
Water	100	0.51	0	1.86
Acetic acid	118.3	3.07	16.6	3.90
Benzene	80.2	2.53	5.45	5.07
Chloroform	61.2	3.63	−63.5	4.68
Camphor	—	—	178.4	39.7
Cyclohexane	80.7	2.69	6.5	20.2

Ex. Freezing Point Depression

Estimate the freezing point of solution contain 100.0 g ethylene glycol, $C_2H_6O_2$, (MM = 62.07) and 100.0 g H_2O (MM = 18.02).

$$100.0\,g\ C_2H_6O_2 \times \frac{1\,mol\ C_2H_6O_2}{62.07\,g\ C_2H_6O_2} = 1.611\,mol\ C_2H_6O_2$$

$$m = \frac{mol\ \text{solute}}{kg\ \text{solvent}} = \frac{1.611\,mol\ C_2H_6O_2}{0.100\,kg\ \text{water}} = 16.11\,m\ C_2H_6O_2$$

$$\Delta T_f = K_f m = (1.86\ °\text{C}/m) \times 16.11\,m = 30.0\ °\text{C}$$

$$\Delta T_f = (T_{fp} - T_{soln})$$

$$30.0\ °\text{C} = 0.0\ °\text{C} - T_{soln}$$

$$T_{soln} = 0.0\ °\text{C} - 30.0\ °\text{C} \quad \mathbf{= -30.0\ °C}$$

Your Turn!

- Ex. When 0.25 g of an unknown organic compound is added to 25.0 g of cyclohexane, the freezing point of cyclohexane is lowered by 1.6 °C. K_f for the solvent is 20.2 °C m^{-1}. Determine the molar mass of the unknown.

A. 505 g/mol

B. 32 g/mol

C. 315 g/mol

D. 126 g/mol

$$\Delta T_f = K_f m$$

$$1.6\,^{\circ}\mathrm{C} = 20.2\,\frac{^{\circ}\mathrm{C}}{m} \times \frac{\left[\dfrac{0.250\ \mathrm{g}}{MW}\right]}{0.025\ \mathrm{kg}}$$

$$MW = 126\ \mathrm{g/mol}$$

Ex. Boiling Point Elevation

A 2.00 *g* biomolecule sample was dissolved in 15.0 *g* of CCl_4. The boiling point of this solution was determined to be 77.85 *°C*. Calculate the molar mass of the biomolecule. For CCl_4, the $\boldsymbol{K_b}$ = 5.07 *°C/m* and BP_{CCl4} = 76.50 *°C*.

$$\Delta \boldsymbol{T_b} = \boldsymbol{K_b m} \qquad m = \frac{\Delta T_b}{K_b} = \frac{(77.85 - 76.50)^\circ C}{5.07^\circ C / m} = 0.26\underline{8}4 m$$

$$m = \frac{mol \text{ solute}}{kg \text{ solvent}} \qquad mol \text{ solute} = 0.26\underline{8}4 m \times 0.0150 kg \text{ CCl}_4$$

$$= 4.0\underline{2}6 \times 10^{-3} mol$$

$$MM_{\text{biomolecule}} = \frac{2.00 g \text{ biomoleucle}}{4.0\underline{2}6 \times 10^{-3} mole} = 497 g / mol$$

Osmosis

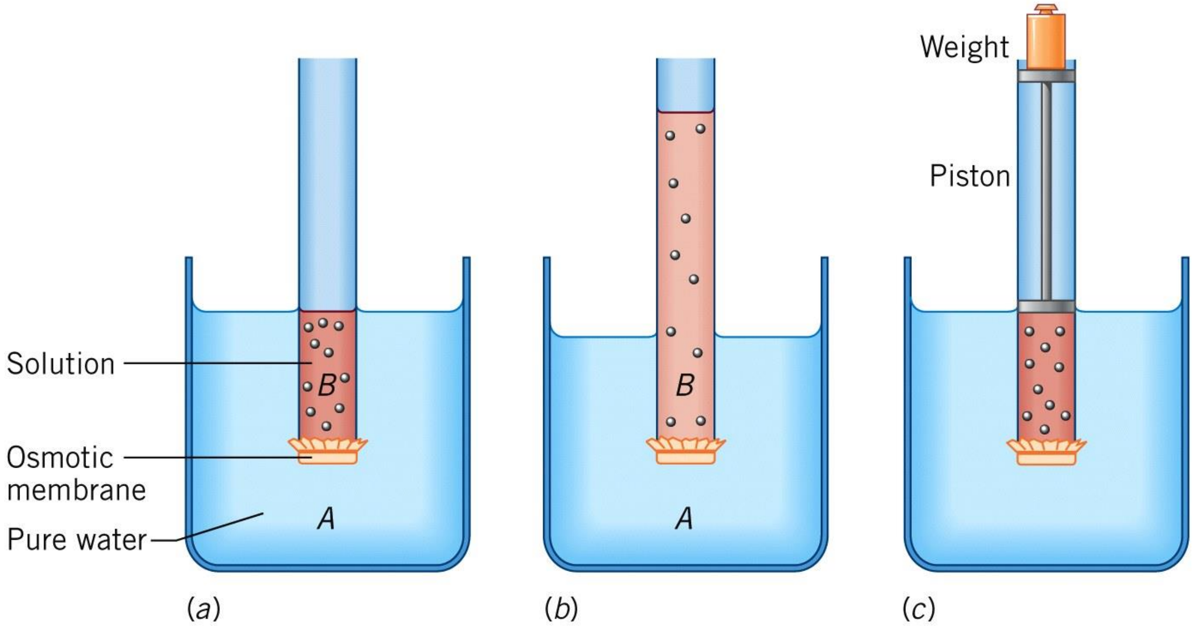
Osmotic Membrane

- Semipermeable membrane that lets only solvent molecules through

Osmosis

- Net shift of solvent molecules (usually water) through an osmotic membrane
- Direction of flow in osmosis,
  - Solvent flows *from dilute to more* concentrated side
  - Flow of solvent molecules across osmotic membrane
    - ↑ concentration of solute on *dilute* side
    - ↓ concentration of solute on *more concentrated* side

Osmosis and Osmotic Pressure



A. Initially, Soln B separated from pure water, A, by osmotic membrane. No osmosis occurred yet

B. After a while, volume of fluid in tube higher. Osmosis has occurred.

C. Need back pressure to prevent osmosis = **osmotic pressure**.

Equation for Osmotic Pressure

- Assumes dilute solutions

$$\Pi = MRT$$

  - Π = osmotic pressure
  - **M** = molarity of solution
  - **T** = Kelvin Temperature
  - **R** = Ideal Gas constant
    = $0.082057\ \text{L·atm·mol}^{-1}\text{K}^{-1}$

Ex. Using Π to determine MM

A solution contained 3.50 *mg* of protein in sufficient H_2O to form 5.00 *mL* of solution. The measured osmotic pressure of this solution was 1.54 *torr* at 25 *°C*. Calculate the molar mass of the protein.

$$M = \frac{\Pi}{RT} = \frac{1.54 torr\left(\frac{1 atm}{760 torr}\right)}{\left(0.08206\frac{L \cdot atm}{K \cdot mol}\right)298K} = 8.28 \times 10^{-5}\,\frac{mol}{L}$$

$$mol = M * L = \left(8.28 \times 10^{-5}\,M\right) * 5.00 \times 10^{-3}\,L = 4.14 \times 10^{-7}\,mol$$

$$MM = \frac{g}{mol} = \frac{3.50 \times 10^{-3}\,g}{4.14 \times 10^{-7}\,mol} = 8.45 \times 10^{3}\,g/mol$$

Learning Check

Ex. For a typical blood plasma, the osmotic pressure at body temperature (37°C) is 5409 mm Hg. If the dominant solute is serum protein, what is the concentration of serum protein?

$$\Pi = MRT$$

$$\frac{5409\,\text{mm Hg}}{} \times \frac{1\,\text{atm}}{760\,\text{mm Hg}} = \Pi$$

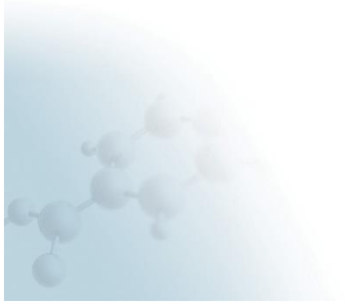
$$7.117\,\text{atm} = \frac{?\,\text{mol}}{\text{L}} \times \frac{0.082057\,\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 310.\underline{1}5\,\text{K}$$

M = 0.280 *M*

Chapter 6
Chemical Equilibrium

Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop



Dynamic Equilibrium in Chemical Systems

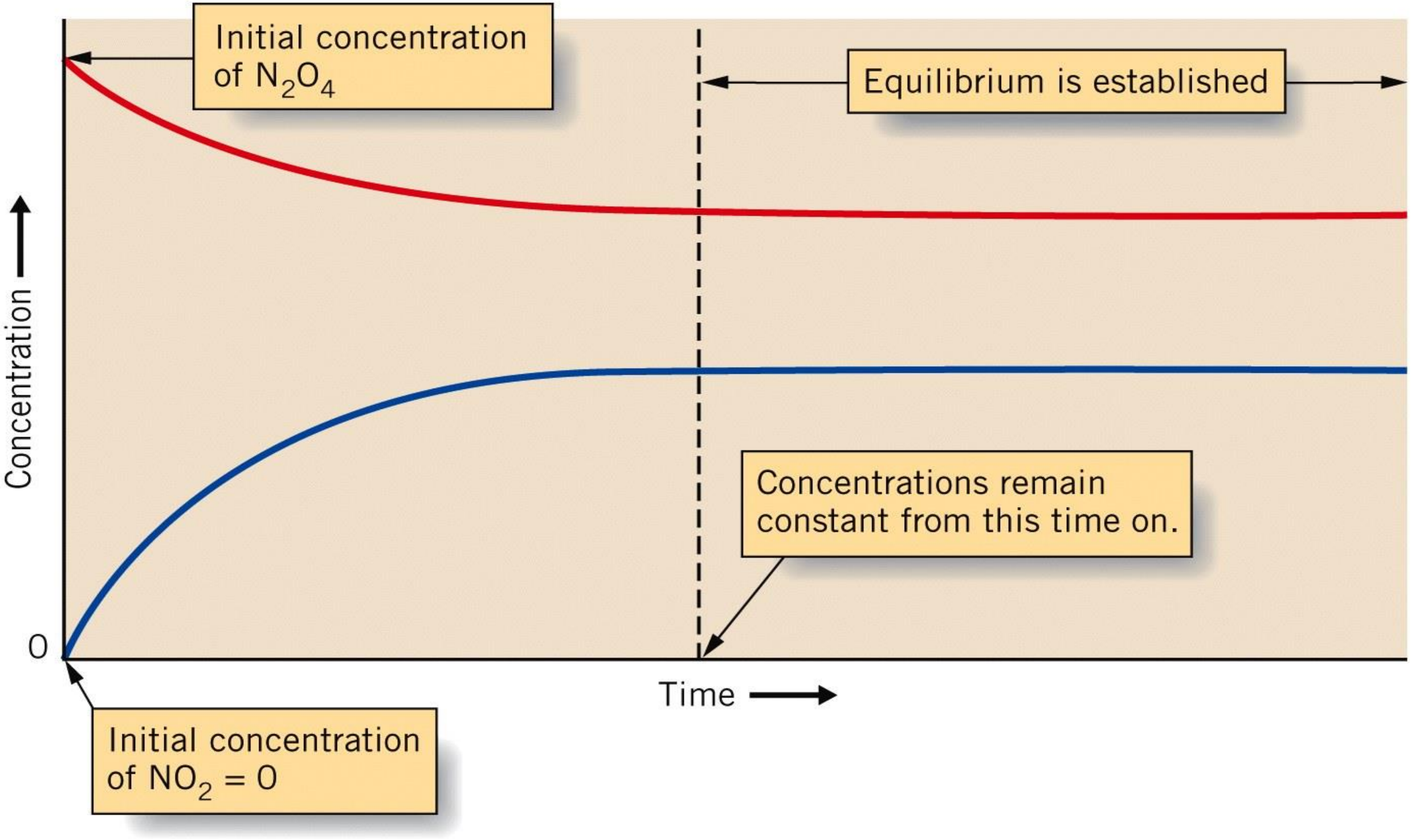
- Chemical equilibrium exists when
  - Rates of forward and reverse reactions are equal
  - Reaction appears to stop
  - [**reactants**] and [**products**] don't change over time
    - Remain constant
    - Both forward and reverse reaction never cease
- Equilibrium signified by double arrows ($\rightleftharpoons$) or equal sign (=)

Dynamic Equilibrium

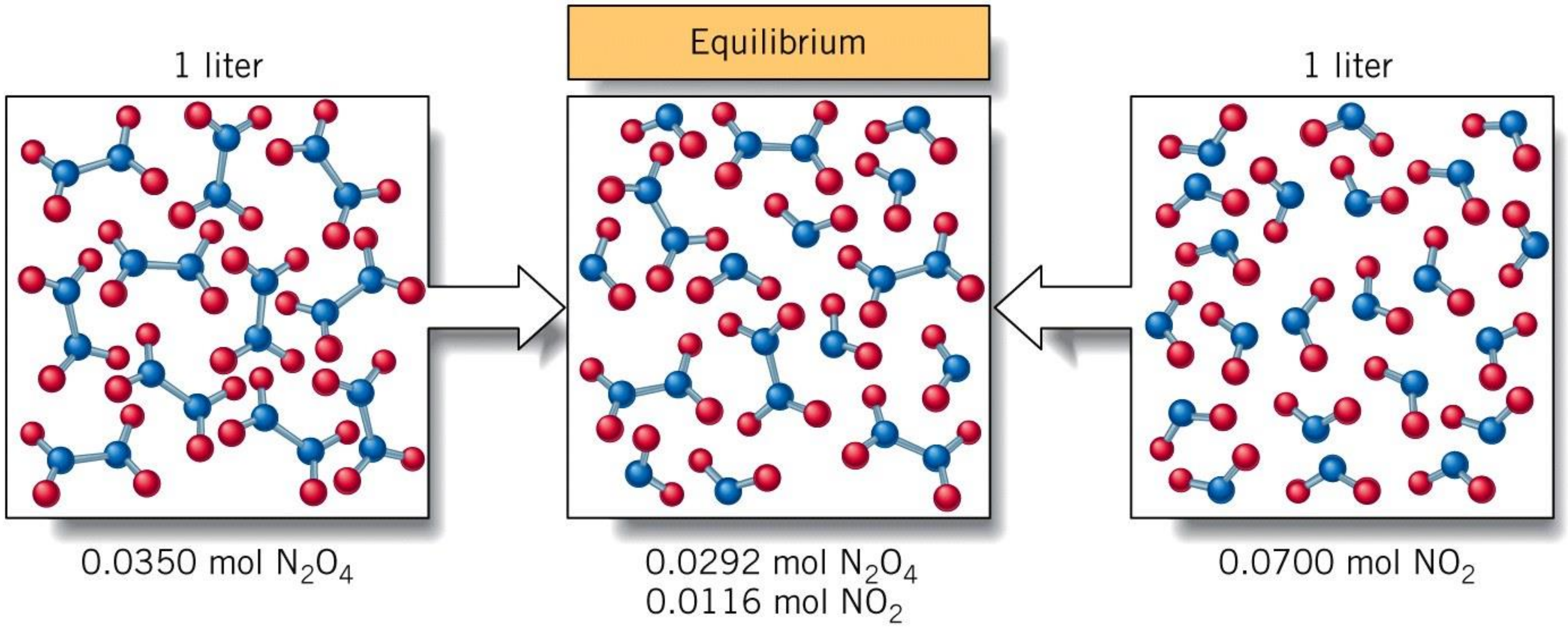
$\mathbf{N_2O_4 \rightleftharpoons 2\ NO_2}$

- Initially forward reaction rapid
    - As some reacts ↓[$\mathbf{N_2O_4}$] so rate forward ↓
- Initially Reverse reaction slow
    - No products
- As $\mathbf{NO_2}$ forms
    - ↑ Reverse rate
    - Ions collide more frequently as [ions] ↑
- Eventually $\boldsymbol{rate_{forward}} = \boldsymbol{rate_{reverse}}$
    - Equilibrium

Dynamic Equilibrium



Reactants **Equilibrium** **Products**



$$\mathbf{N_2O_4 \rightleftharpoons 2\,NO_2}$$

- For given overall system composition
- Always reach same equilibrium concentrations
- Whether equilibrium is approached from **forward** or **reverse** direction

Equilibrium

- Simple relationship among [**reactants**] and [**products**] for any chemical system at equilibrium
- Called = **mass action expression**
  - Derived from thermodynamics
- Forward reaction: **A** $\rightarrow$ **B** **Rate = k_f[A]**
- Reverse reaction: **A** $\leftarrow$ $\overset{k_f}{k_r}$**B** **Rate = k_r[B]**
- At equilibrium: **A** $\rightleftharpoons$ **B** **k_f[A] = k_r[B]**
  - **rate forward = rate reverse**
- rearranging:

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{k_f}{k_r} = \underline{\text{constant}}$$

Mass Action Expression (MAE)

- Uses stoichiometric coefficients as exponent for each reactant
- For reaction: **aA + bB** $\rightleftharpoons$ **cC + dD**

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Reaction quotient

  - Numerical value of mass action expression
  - Equals "**Q**" at any time, **and**
  - Equals "**K**" only when reaction is known to be at equilibrium

Mass Action Expression

$$Q = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \text{same for all data sets at equilibrium}$$

Exp't	Equilibrium Concentrations (M) $[H_2]$	$[I_2]$	$[HI]$	$Q = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}$
I	0.0222	0.0222	0.156	$\frac{(0.156)^2}{(0.0222)(0.0222)} = 49.4$
II	0.0350	0.0450	0.280	$\frac{(0.280)^2}{(0.0350)(0.0450)} = 49.8$
III	0.0150	0.0135	0.100	$\frac{(0.100)^2}{(0.0150)(0.0135)} = 49.4$
IV	0.0442	0.0442	0.311	$\frac{(0.311)^2}{(0.0442)(0.0442)} = 49.5$
				Average = 49.5

Equilibrium Law

- For reaction at equilibrium write the following

Equilibrium Law (at 440 °C)

$$K_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H}_2][\mathrm{I}_2]} = 49.5$$

- **Equilibrium constant** = ***K_c*** = constant at given T
- Use ***K_c*** since usually working with concentrations in **mol/L**
- For chemical **equilibrium** to exist in reaction mixture, reaction quotient **Q must be equal to** equilibrium constant, **K_c**

$Q = K_c$

Predicting Equilibrium Law

For general chemical reaction:

$$dD + eE \rightleftharpoons fF + gG$$

- Where ***D***, ***E***, ***F***, and ***G*** represent chemical formulas
- ***d***, ***e***, ***f***, and ***g*** are coefficients

- Mass action expression = $\dfrac{[F]^f[G]^g}{[D]^d[E]^e}$
- ***Note:*** **Exponents** in mass action expression are **stoichiometric coefficients** in balanced equation.
- **Equilibrium law** is: $K_c = \dfrac{[F]^f[G]^g}{[D]^d[E]^e}$

Ex. Equilibrium Law

$$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$$

- $K_c = 4.26 \times 10^8$ at 25 °C
- What is equilibrium law?

$$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]} = 4.26 \times 10^8$$

Learning Check

Ex. Write mass action expressions for the following:

- **$2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$**

$$Q = \frac{[N_2O_4]}{[NO_2]^2}$$

- **$2CO\ (g) + O_2\ (g) \rightleftharpoons 2\ CO_2\ (g)$**

$$Q = \frac{[CO_2]^2}{[CO]^2[O_2]}$$

Manipulating Equations for Chemical Equilibria

Various operations can be performed on equilibrium expressions

1. When **direction** of equation is **reversed**, new **equilibrium constant** is **reciprocal** of original

$$\mathbf{A + B \rightleftharpoons C + D}$$

$$K_c = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$

$$\mathbf{C + D \rightleftharpoons A + B}$$

$$K'_c = \frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{C}][\mathrm{D}]} = \frac{1}{K_c}$$

Ex. Manipulating Equilibria 1

1. When **direction** of equation is **reversed**, new **equilibrium constant** is **reciprocal** of original

$$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g) \quad \text{at } 25°\text{C}$$

$$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]} = 4.26 \times 10^8$$

$$2\,NH_3(g) \rightleftharpoons 3\,H_2(g) + N_2(g) \quad \text{at } 25°\text{C}$$

$$K_c' = \frac{[H_2]^3[N_2]}{[NH_3]^2} = \frac{1}{K_c} = \frac{1}{4.26 \times 10^8} = 2.35 \times 10^{-9}$$

Manipulating Equilibria 2

2. When coefficients in equation are **multiplied by a factor**, equilibrium constant is **raised to a power** equal to that factor.

$A + B \rightleftharpoons C + D$

$$K_c = \frac{[C][D]}{[A][B]}$$

$3A + 3B \rightleftharpoons 3C + 3D$

$$K_c'' = \frac{[C]^3[D]^3}{[A]^3[B]^3} = \frac{[C][D]}{[A][B]} \times \frac{[C][D]}{[A][B]} \times \frac{[C][D]}{[A][B]} = K_c^3$$

Manipulating Equilibria 2

2. When coefficients in equation are ***multiplied by factor***, equilibrium constant is ***raised to power*** equal to that factor

$3\ H_2(g)\ +\ N_2(g) \leftrightarrows 2\ NH_3(g)$ at 25°C

$$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]} = 4.26 \times 10^8$$

multiply by 3

$9\ H_2(g) + 3\ N_2(g) \leftrightarrows 6\ NH_3(g)$

$$K_c'' = \frac{[NH_3]^6}{[H_2]^9[N_2]^3} = K_c^3$$

Manipulating Equilibria 3

3. When chemical **equilibria** are **added**, their **equilibrium constants** are **multiplied**

$A + B \rightleftharpoons C + D$

$$K_{c_1} = \frac{[C][D]}{[A][B]}$$

$C + E \rightleftharpoons F + G$

$$K_{c_2} = \frac{[F][G]}{[C][E]}$$

$A + B + E \rightleftharpoons D + F + G$

$$K_{c_3} = \frac{\cancel{[C]}[D]}{[A][B]} \times \frac{[F][G]}{\cancel{[C]}[E]} = \frac{[D][F][G]}{[A][B][E]} = K_{c_1} \times K_{c_2}$$

Manipulating Equilibria 3

3. When chemical **equilibria** are **added**, their **equilibrium constants** are **multiplied**

$2\,NO_2(g) \rightleftharpoons NO_3(g) + NO(g)$ $\qquad K_{c_1} = \dfrac{[NO][NO_3]}{[NO_2]^2}$

$NO_3(g) + CO(g) \rightleftharpoons NO_2(g) + CO_2(g)$ $\qquad K_{c_2} = \dfrac{[NO_2][CO_2]}{[NO_3][CO]}$

$NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g)$ $\qquad K_{c_3} = \dfrac{[NO][CO_2]}{[NO_2][CO]}$

$$\frac{[NO]\cancel{[NO_3]}}{[NO_2]^{\cancel{2}}} \times \frac{\cancel{[NO_2]}[CO_2]}{\cancel{[NO_3]}[CO]} = \frac{[NO][CO_2]}{[NO_2][CO]}$$

Therefore $\qquad K_{c_1} \times K_{c_2} = K_{c_3}$

Learning Check

Ex. $\mathbf{N_2(\mathit{g}) + 3\,H_2(\mathit{g}) \rightleftharpoons 2\,NH_3(\mathit{g})}$

$\mathbf{K_c = 500}$ at a particular temperature.

What would be $\mathbf{K_c}$ for following?

- $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$

$$K_c' = \frac{1}{K_c} = \frac{1}{500} = \mathbf{0.002}$$

- $\frac{1}{2}\,N_2(g) + 3/2\,H_2(g) \rightleftharpoons NH_3(g)$

$$K_c'' = K_c^{1/2} = \sqrt{500} = \mathbf{22.4}$$

Equilibrium Constant, K_c

- Constant value equal to ratio of product concentrations to reactant concentrations raised to their respective exponents

$$K_c = \frac{[\text{products}]^f}{[\text{reactants}]^d}$$

- Changes with temperature (van’t Hoff Equation)
- Depends on solution concentrations
- Assumes reactants and products are in solution

Equilibrium Constant, K_p

- Based on reactions in which substances are gaseous
- Assumes gas quantities are expressed in atmospheres in mass action expression
- Use partial pressures for each gas in place of concentrations
- Ex. $\mathbf{N_2\,(\mathit{g}) + 3\,H_2\,(\mathit{g}) \leftrightarrows 2\,NH_3\,(\mathit{g})}$

$$K_P = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

How are K_p and K_c Related?

- Start with Ideal Gas Law

$$PV=nRT$$

- Substituting **P/RT** for molar concentration into K_c results in pressure-based formula
- **Δn** = moles of gas in product – moles of gas in reactant

$$K_p = K_c(RT)^{\Delta n}$$

For gaseous reactions, use either K_P or K_C
For solution reactions, must use K_C

Learning Check

Ex. Consider the reaction: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

If $\mathbf{K_p}$ = 0.480 for the reaction at 25°C, what is value of $\mathbf{K_c}$ at same temperature?

- $\Delta n = n_{products} - n_{reactants} = 1 - 2 = -1$

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{0.480}{(0.0821 \times 298K)^{-1}}$$

$\mathbf{K_c = 11.7}$

Your Turn!

Ex. Consider the reaction **A(*g*) + 2B(*g*)** $\rightleftharpoons$ **4C(*g*)**

If the K_c for the reaction is 0.99 at 25ºC, what would be the K_p?

A. 0.99

B. 2.0

C. 24.

D. 2400

E. None of these

Δn=(4 – 3)=1

$K_p = K_c(RT)^{\Delta n}$

$K_p = 0.99*(0.082057*298.15)^1$

$K_p = 24$

Homogeneous reaction/equilibrium

- All reactants and products in same phase
- Can mix freely

Heterogeneous reaction/equilibrium

- Reactants and products in different phases
- Can't mix freely
- Solutions are expressed in *M*
- Gases are expressed in *M*
- Governed by K_c

Heterogeneous Equilibria

$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$

- Equilibrium Law =

$$K = \frac{[\cancel{Na_2CO_3(s)}][H_2O(g)][CO_2(g)]}{[\cancel{NaHCO_3(s)}]^2}$$

- Can write in simpler form
- For any pure liquid or solid, ratio of moles to volume of substance (M) is constant
  - Ex. 1 mol $NaHCO_3$ occupies 38.9 cm^3
    2 mol $NaHCO_3$ occupies 77.8 cm^3

$$M = \frac{2\text{ mol NaHCO}_3}{0.0778\text{ L}} = 25.7M$$

$$M = \frac{1\text{ mol NaHCO}_3}{0.0389\text{ L}} = 25.7M$$

Heterogeneous Equilibria

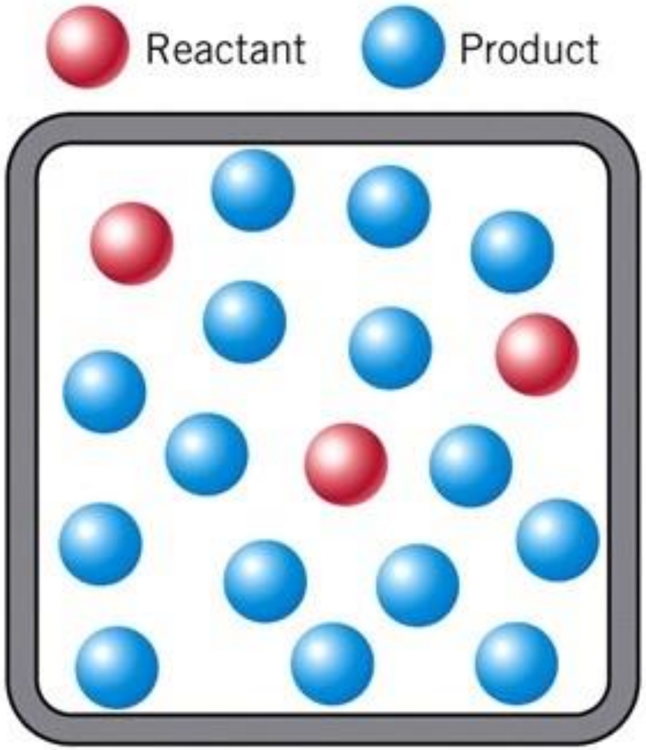
$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

- concentrations of pure solids and liquids can be incorporated into equilibrium constant, K_c
- Equilibrium law for heterogeneous system written without concentrations of pure solids or liquids

$$K_c = K\frac{[Na_2CO_3(s)]}{[NaHCO_3(s)]^2} = [H_2O(g)][CO_2(g)]$$

Interpreting K_c

- **Large K (K>>1)**
  - Means product rich mixture
  - Reaction goes far toward completion



Ex.

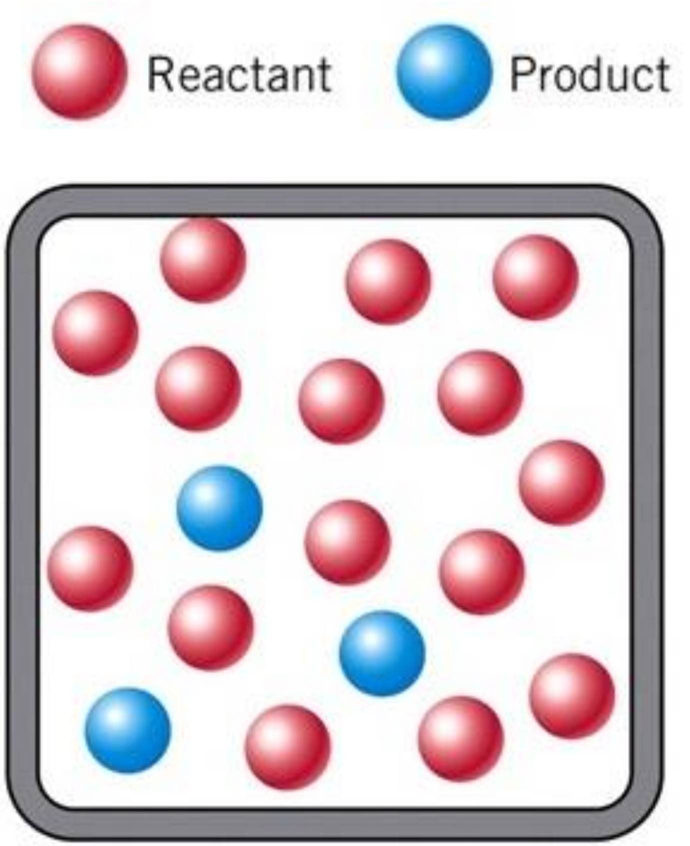
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$K_c = 7.0 \times 10^{25}$ at 25 ° C

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{7.0 \times 10^{25}}{1}$$

Interpreting K_c

- **Small K (K<<1)**
  - Means reactant rich mixture
  - Only very small amounts of product formed



Ex.

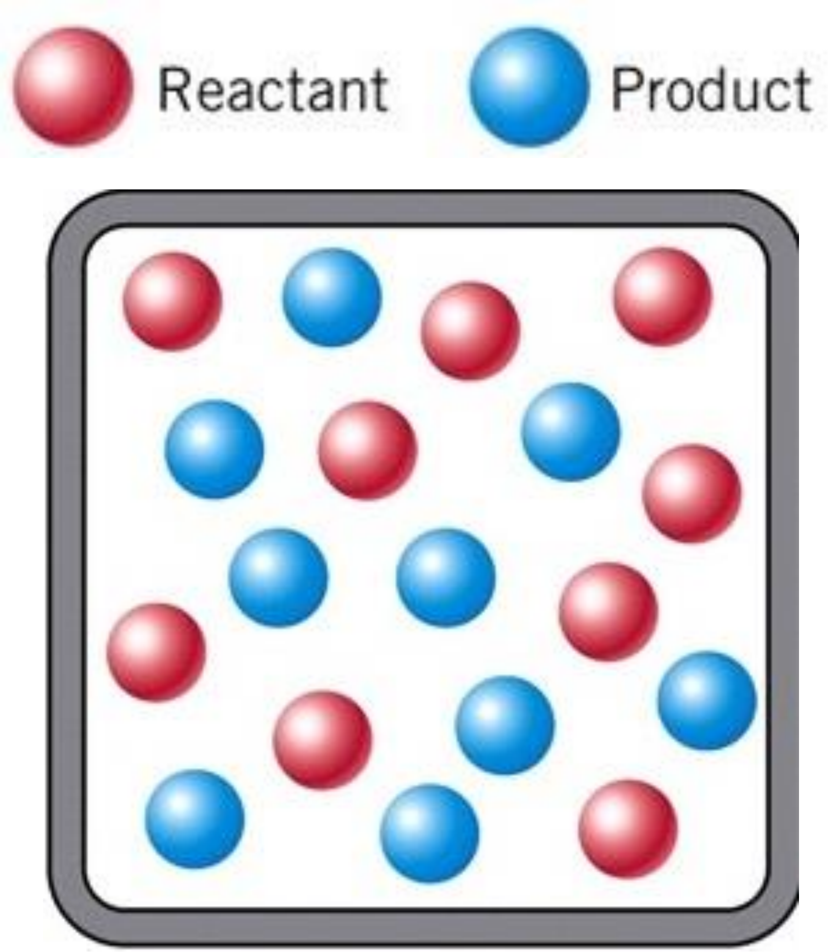
$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

$K_c = 1.4 \times 10^{-21}$ at 25 °C

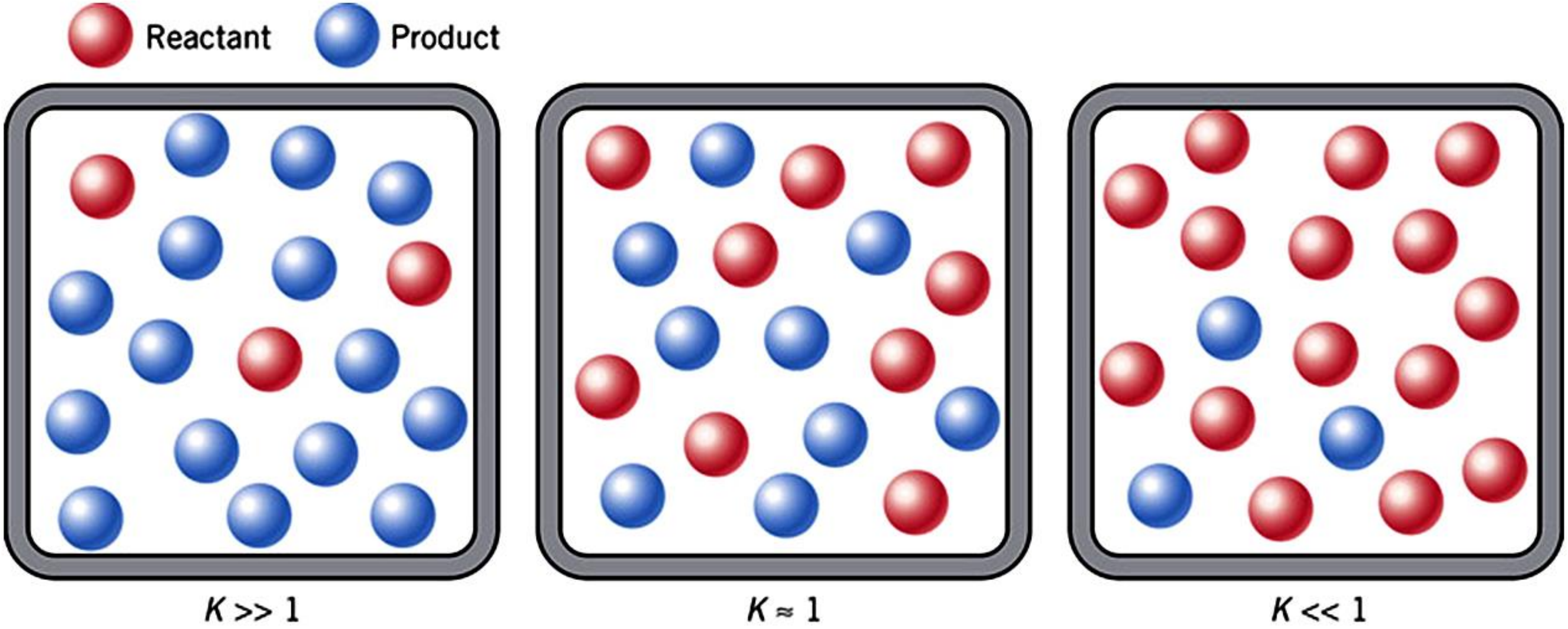
$$K_c = \frac{[HBr]^2}{[H_2][Br_2]} = \frac{1.4 \times 10^{-21}}{1}$$

Interpreting K_c

- **K ≈ 1**
  - Means product and reactant concentrations close to equal
  - Reaction goes only ~ halfway



- **Size of K gives measure of how reaction proceeds**



- **K >> 1** [products] >> [reactants]
- **K = 1** [products] = [reactants]
- **K << 1** [products] << [reactants]

Learning Check

Ex. Consider the reaction of $2NO_2(g) \rightleftharpoons N_2O_4(g)$

If $K_p = 0.480$ at 25°C, does the reaction favor product
or reactant?

K is small (**K < 1**)

Reaction favors **reactant**

Since K is close to 1, significant amounts of ***both*** reactant and product are present

Equilibrium Positions and "Shifts"

- **Equilibrium positions**
  - Combination of concentrations that allow **$Q = K$**
  - Infinite number of possible equilibrium positions
- **Le Châtelier's principle**
  - System at equilibrium (**$Q = K$**) when upset by disturbance (**$Q \neq K$**) will shift to offset stress
    - System said to **"shift to right"** when ***forward*** reaction is dominant (**$Q < K$**)
    - System said to **"shift to left"** when ***reverse*** direction is dominant (**$Q > K$**)

Relationship Between Q and K

- **$Q = K$ reaction at equilibrium**
- **$Q < K$ reactants → products**
  - Too many reactants
  - Must convert some reactant to product to move reaction toward equilibrium
- **$Q > K$ reactants ← products**
  - Too many products
  - Must convert some product to reactant to move reaction toward equilibrium

Examples of Le Châtelier's Principle

Let's see how this works with changes in

1. Concentration
2. Pressure and volume
3. Temperature
4. Catalysts
5. Adding inert gas to system at constant volume

Effect of Change in Concentration

- Ex. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
- $K_c = 2.4 \times 10^{-3}$ at 700 °C
- Which direction will the reaction move if 0.125 moles of O_2 is added to an equilibrium mixture ?
- A. Towards the products
- B. Towards the reactants
- C. No change will occur

Effect of Change in Concentration

- When changing concentrations of reactants or products
  - Equilibrium shifts to **remove** reactants or products that have been **added**
  - Equilibrium shifts to **replace** reactants or products that have been **removed**

Effect of Pressure and Volume Changes

Ex. Consider gaseous system at constant **T** and **n**

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_P = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

- If reduce volume (**V**↓)
  - Expect Pressure to increase (**P**↑)
  - To reduce pressure, look at each side of reaction
  - Which has less moles of gas
  - Reactants = 3 + 1 = 4 moles gas
  - Products = 2 moles gas
  - Reaction favors products (shifts to right)

Effect of P and V Changes

Consider gaseous system at constant **T** and **n**

Ex. $\mathbf{H_2(\mathit{g}) + I_2(\mathit{g}) \rightleftharpoons 2\,HI(\mathit{g})}$

$$K_P = \frac{P_{\mathrm{HI}}^2}{P_{\mathrm{H_2}} P_{\mathrm{I_2}}}$$

- If pressure is increased, what is the effect on equilibrium?
  - $n_{\text{reactant}} = 1 + 1 = 2$
  - $n_{\text{product}} = 2$
  - Predict no change or shift in equilibrium

Effect of P and V Changes

$$2NaHSO_3(s) \rightleftharpoons NaSO_3(s) + H_2O(g) + SO_2(g)$$

$$K_P = P_{H_2O} P_{SO_2}$$

- If you decrease volume of reaction, what is the effect on equilibrium?
  - Reactants: no moles gas = all solids
  - Products: 2 moles gas
  - ↓V, causes ↑P
  - Reaction shifts to left (reactants), as this has fewer moles of gas

Effect of P and V Changes

- Reducing volume of gaseous reaction mixture causes reaction to decrease number of molecules of gas, if it can
  - Increasing pressure
- Moderate pressure changes have negligible effect on reactions involving only liquids and/or solids
  - Substances are already almost incompressible
- Changes in V, P and [X] effect position of equilibrium (Q), but not K

Effect of Temperature Changes

$H_2O(s) \rightleftharpoons H_2O(\ell)$ $\Delta H° = +6\ \text{kJ (at 0 °C)}$

- Energy + $H_2O(s) \rightleftharpoons H_2O(\ell)$

$$\xrightarrow{\hspace{10cm}}$$

- Energy is reactant
- Add heat, shift reaction right

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H_f° = -47.19\ \text{kJ}$

- $3\ H_2(g) + N_2(g) \rightleftharpoons 2\ NH_3(g)$ + energy

$$\xleftarrow{\hspace{10cm}}$$

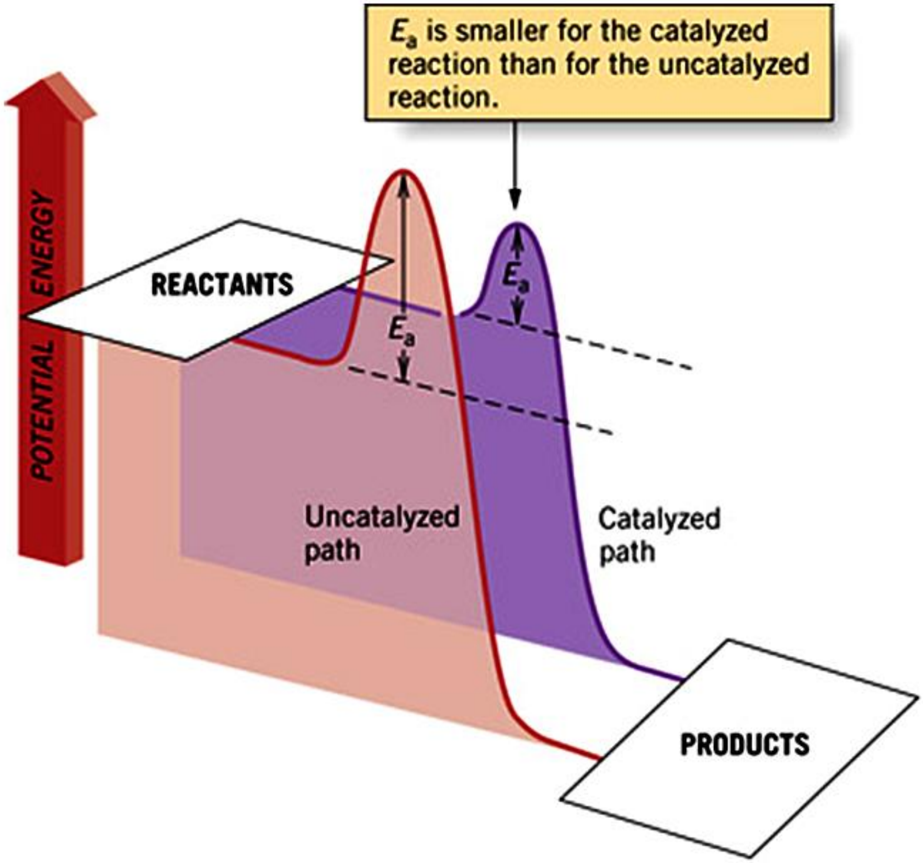
- Energy is product
- Add heat, shift reaction left

Effect of Temperature Changes

- ↑ **T** shifts reaction in direction that produces **endothermic** (heat absorbing) change
- ↓ **T** shifts reaction in direction that produces **exothermic** (heat releasing) change
- Changes in T change value of mass action expression at equilibrium, so K changed
  - K depends on T
  - ↑T of exothermic reaction makes K smaller
    - More heat (product) forces equilibrium to reactants
  - ↑T of endothermic reaction makes K larger
    - More heat (reactant) forces equilibrium to products

Catalysts And Equilibrium

- Catalyst lowers E_a for both forward and reverse reaction
- Change in E_a affects rates k_r and k_f equally
- Catalysts have no effect on equilibrium



Effect of Adding Inert Gas

Inert gas

  - One that does not react with components of reaction

  Ex. Argon, Helium, Neon, usually N_2

- Adding inert gas to reaction at fixed **V** (n and T), ↑ **P** of all reactants and products
- Since it doesn't react with anything
  - No change in concentrations of reactants or products
  - No net effect on reaction

Your Turn!

Ex. The following are equilibrium constants for the reaction of acids in water, K_a. Which is the most acid dissociated reaction?

A. $K_a = 2.2 \times 10^{-3}$

B. $K_a = 1.8 \times 10^{-5}$

C. $K_a = 4.0 \times 10^{-10}$

D. $K_a = 6.3 \times 10^{-3}$

Calculating K_c Given Equilibrium Concentrations

Ex. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

- If you place 0.0350 mol N_2O_4 in 1 L flask at equilibrium, what is K_C?
- $[N_2O_4]_{eq} = 0.0292$ M
- $[NO_2]_{eq} = 0.0116$ M

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_c = \frac{[0.0116]^2}{[0.0292]}$$

$$K_c = 4.61 \times 10^{-3}$$

Your Turn!

Ex. For the reaction: **$2A(aq) + B(aq) \rightleftharpoons 3C(aq)$** the equilibrium concentrations are: A = 2.0 M, B = 1.0 M and C = 3.0 M. What is the expected value of K_c at this temperature?

A. 14

B. 0.15

C. 1.5

D. 6.75

$$K_c = \frac{[C]^3}{[A]^2[B]}$$

$$K_c = \frac{[3.0]^3}{[2.0]^2[1.0]}$$

Calculating K_c Given Initial Concentrations and One Final Concentration

Ex. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

- 1.000 mol SO_2 and 1.000 mol O_2 are placed in a 1.000 L flask at 1000 K. At equilibrium 0.925 mol SO_3 has formed. Calculate K_C for this reaction.
- 1st calculate concentrations of each
    - Initial

$$[SO_2] = [O_2] = \frac{1.00mol}{1.00L} = 1.00M$$

    - Equilibrium

$$[SO_3] = \frac{0.925mol}{1.00L} = 0.925M$$

Set up Concentration Table

	$2SO_2(g)$	$+$ $O_2(g)$	$\rightleftharpoons$ $2SO_3(g)$
Initial Conc. (M)	1.000	1.000	0.000
Changes in Conc. (M)	**–0.925**	**–0.462**	**+0.925**
Equilibrium Conc. (M)	**0.075**	**0.538**	**0.925**

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$K_c = \frac{[0.925]^2}{[0.075]^2[0.538]}$$

$$\mathbf{K_c = 2.8 \times 10^2 = 280}$$

Calculate $[X]_{\text{equilibrium}}$ from K_c and $[X]_{\text{initial}}$

Ex. $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

- At 1500 °C, $K_c = 5.67$. An equilibrium mixture of gases had the following concentrations: $[CH_4] = 0.400$ M and $[H_2] = 0.800$M and $[CO] = 0.300$M. What is $[H_2O]$ at equilibrium ?

Calculate $[X]_{\text{equilibrium}}$ from K_c and $[X]_{\text{initial}}$

Ex. $\mathbf{CH_4(\mathit{g}) + H_2O(\mathit{g}) \rightleftharpoons CO(\mathit{g}) + 3H_2(\mathit{g})}$ $K_c = 5.67$

$[CH_4] = 0.400\ M$; $[H_2] = 0.800M$; $[CO] = 0.300M$

- What is $[H_2O]$ at equilibrium?
- First, set up equilibrium

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]} \qquad [H_2O] = \frac{[CO][H_2]^3}{[CH_4]K_c}$$

- Next, plug in equilibrium concentrations and $\boldsymbol{K_c}$

$$[H_2O] = \frac{[0.300][0.800]^3}{[0.400](5.67)} = \frac{0.154}{2.27}$$

$[H_2O] = 0.0678\ M$

Calculate $[X]_{equilibrium}$ from $[X]_{initial}$ and K_C

Ex. **$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 425 °C**

$K_C = 55.64$

- If one mole each of **H_2 and I_2** are placed in a 0.500 L flask at 425 °C, what are the equilibrium concentrations of H_2, I_2 and HI?
- **Step 1. Write Equilibrium Law**

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 55.64$$

Ex. Step 2. Concentration Table

Conc (M)	$H_2(g)$ +	$I_2(g) \rightleftharpoons$	$2HI(g)$
Initial	2.00	2.00	0.000
Change	**– x**	**– x**	**+2x**
Equil'm	**2.00 – x**	**2.00 – x**	**+2x**

- Initial $[H_2] = [I_2]$ = 1.00 mol/0.500L =2.00M
- Amt of H_2 consumed = Amt of I_2 consumed = x
- Amt of HI formed = 2x

$$55.64 = \frac{(2x)^2}{(2.00 - x)(2.00 - x)} = \frac{(2x)^2}{(2.00 - x)^2}$$

Ex. Step 3. Solve for x

- Both sides are squared so we can take square root of both sides to simplify

$$\sqrt{K} = \sqrt{55.64} = \sqrt{\frac{(2x)^2}{(2.00 - x)^2}}$$

$$7.459 = \frac{2x}{(2.00 - x)} \qquad 7.459(2.00 - x) = 2x$$

$$14.918 - 7.459x = 2x \qquad 14.918 = 9.459x$$

$$x = \frac{14.918}{9.459} = 1.58$$

Ex. Step 4. Equilibrium Concentrations

Conc (M)	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI\,(g)$
Initial	2.00		2.00		0.00
Change	**– 1.58**		**– 1.58**		**+3.16**
Equil'm	**0.42**		**0.42**		**+3.16**

- $[H_2]_{equil} = [I_2]_{equil} = 2.00 - 1.58 = 0.42$ M
- $[HI]_{equil} = 2x = 2(1.58) = 3.16$

Your Turn!

Ex. $N_2(g) + O_2(g) \rightarrow 2NO(g)$

$K_c = 0.0123$ at 3900 ^oC

If 0.25 moles of N_2 and O_2 are placed in a 250 mL container, what are the equilibrium concentrations of all species ?

- A. 0.0526 M, 0.947 M, 0.105 M
- B. 0.947 M, 0.947 M, 0.105 M
- C. 0.947 M 0.105 M, 0.0526 M
- D. 0.105 M, 0.105 M, 0.947 M

Your Turn! - Solution

Ex. Conc (M)	$N_2(g)$	$+O_2(g) \rightleftharpoons$	$2NO(g)$
Initial	1.00	1.00	0.00
Change	**– x**	**– x**	**+ 2x**
Equil	1.00 **– x**	1.00 **– x**	**+ 2x**

$$[N_2] = [O_2] = \frac{0.250 \text{ mol}}{0.250 \text{ L}} = 1.00\,M$$

$$0.0123 = \frac{(2x)^2}{(1-x)^2} \qquad \sqrt{0.0123} = \frac{2x}{1-x}$$

$$x = 0.0526M \quad [\text{NO}] = 2x = 0.105M$$

Learning Check

EX. For the reaction **$2A_{(g)} \leftrightarrows B_{(g)}$**

given that $K_p = 3.5\times10^{-16}$ at 25°C, and we place 0.2 atm A into the container, what will be the pressure of B at equilibrium?

	2A	↔	**B**
I	0.2		0 atm
C	−2x		+x
E	0.2 − 2x		x

$$3.5\times10^{-16} = \frac{x}{(0.2)^2}$$

$x = 1.4\times10^{-17}$

$[B] = 1.4\times10^{-17}$ M

Calculating K_C Given Initial Concentrations and One Final Concentration

Ex. $H_2(g) + I_2(g) \leftrightarrows 2HI(g)$ @ 450 °C

- Initially H_2 and I_2 concentrations are 0.200 mol each in 2.00 L At equilibrium, HI concentration is 0.160 M. Calculate K_C

$$[I_2] = [H_2] = 0.100M$$

$H_2(g)$	+	$I_2(g)$	$\leftrightarrows 2HI(g)$ @ 450 °C
0.100M		**0.100M**	**0**
-x		**-x**	**2x**
0.100-x		**0.100-x**	**2x**
			2x=0.160

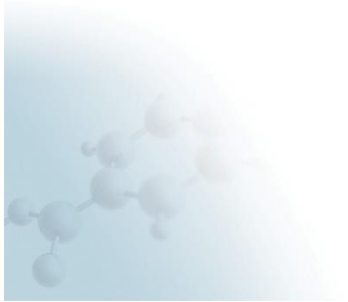
- **X=0.08 M**
- **$[I_2] = [H_2] = 0.100-0.08=0.020$ M**
- **$K_\mathrm{C} = (0.160)^2 / (0.020)^2 = 64$**

Chapter 7

Acids and Bases

Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop



Arrhenius Acids and Bases

Acid produces H_3O^+ in water

Base gives OH^-

Acid-base neutralization

- Acid and base combine to produce water and a salt.

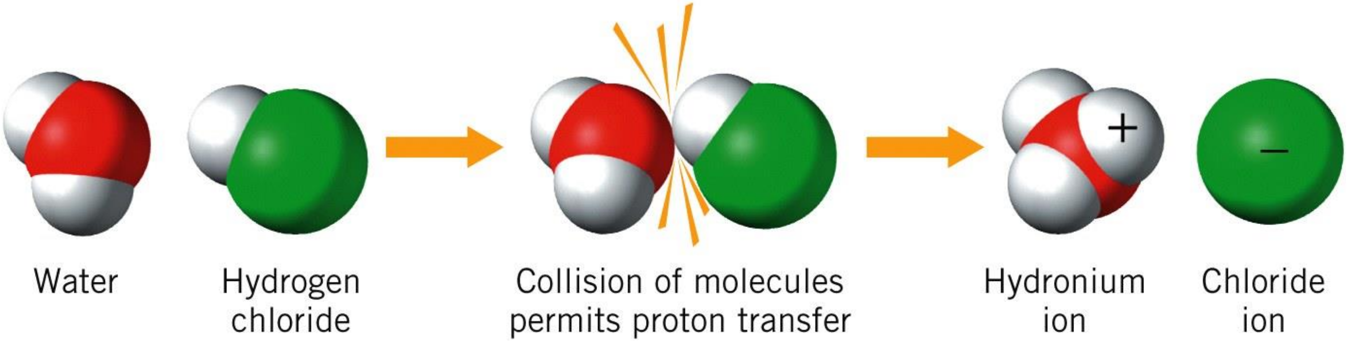
Ex. $HCl(aq) + NaOH(aq) \rightarrow H_2O + NaCl(aq)$

$$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow 2H_2O + Cl^-(aq) + Na^+(aq)$$

- Many reactions resemble this without forming H_3O^+ or OH^- in solution

Brønsted-Lowry Definition

- **Acid** = proton donor
- **Base** = proton acceptor
- Allows for gas phase acid-base reactions



Ex. $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

- **HCl = acid**
  - Donates H^+
- **Water = base**
  - Accepts H^+

Conjugate Acid-Base Pair

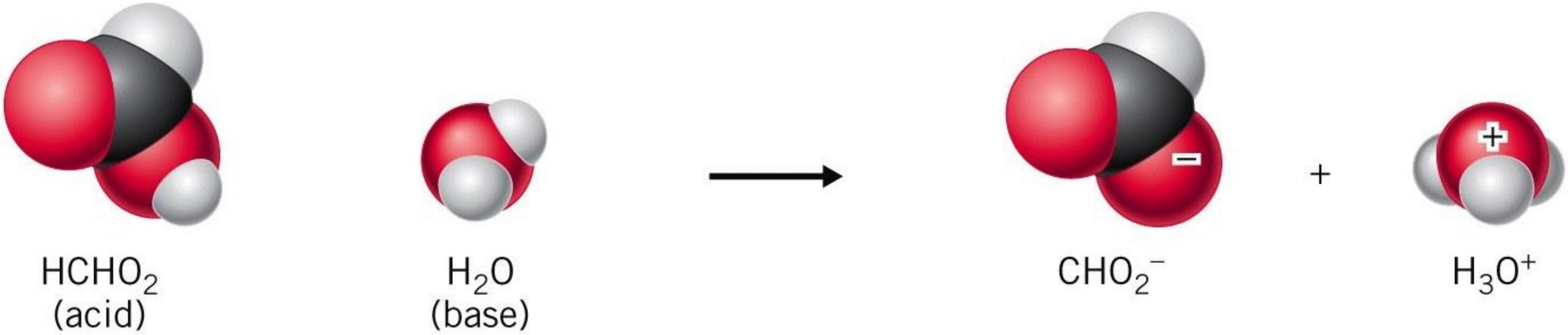
- Species that differ by H^+

Ex. $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

- **HCl = acid**
- **Water = base**
- **H_3O^+**
  - Conjugate acid of H_2O
- **Cl^-**
  - Conjugate base of HCl

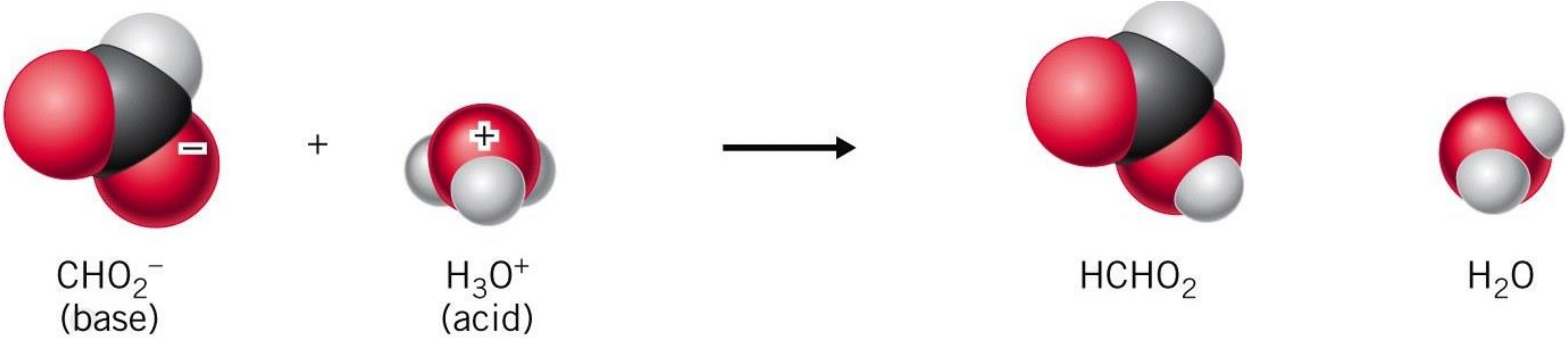
Formic Acid is Bronsted Acid

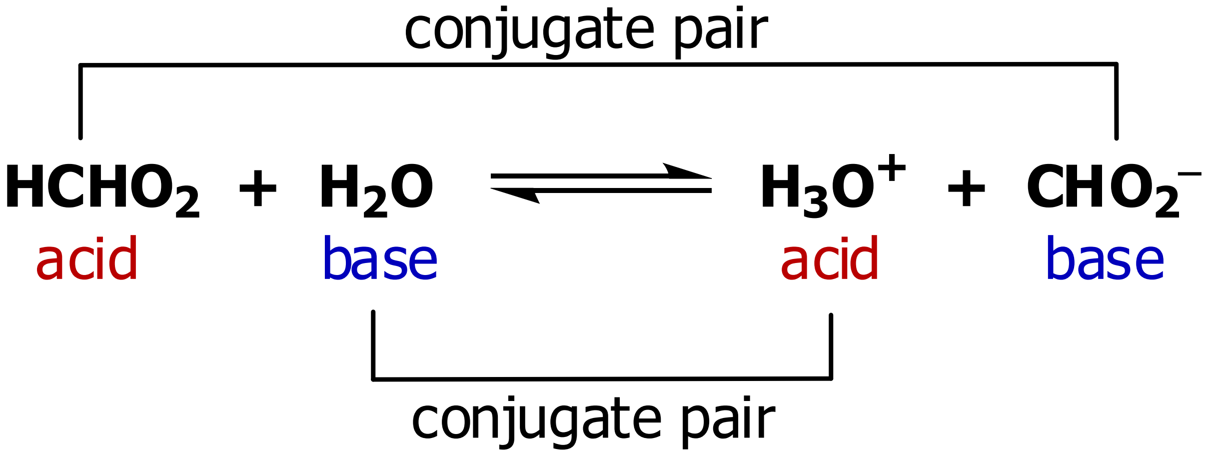
- Formic acid ($HCHO_2$) is a weak acid
- Must consider equilibrium
  - $\mathbf{HCHO_2(\mathit{aq}) + H_2O \rightleftharpoons CHO_2^-(\mathit{aq}) + H_3O^+(\mathit{aq})}$
- Focus on forward reaction



Formate Ion is Bronsted Base

- Now consider reverse reaction
- Hydronium ion transfers H^+ to CHO_2^-





conjugate pair

$$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$$

acid base acid base

conjugate pair

Learning Check

- Identify the Conjugate Partner for Each

conjugate base	**conjugate acid**
Cl^-	HCl
NH_3	**NH_4^+**
$C_2H_3O_2^-$	$HC_2H_3O_2$
CN^-	**HCN**
F^-	HF

Learning Check

- Write a reaction that shows that HCO_3^- is a Brønsted **acid** when reacted with OH^-
- $HCO_3^-(aq) + OH^-(aq) \rightleftharpoons H_2O(\ell) + CO_3^{2-}(aq)$
- Write a reaction that shows that HCO_3^- is a Brønsted **base** when reacted with $H_3O^+(aq)$
- $HCO_3^-(aq) + H_3O^+(aq) \rightleftharpoons H_2CO_3(aq) + H_2O(\ell)$

Your Turn!

Ex. In the following reaction, identify the acid/base conjugate pair.

$(CH_3)_2NH + H_2SO_4 \rightarrow (CH_3)_2NH_2^+ + HSO_4^-$

A. $(CH_3)_2NH$ / H_2SO_4 ; $(CH_3)_2NH^+$ / HSO_4^-

B. $(CH_3)_2NH$ / $(CH_3)_2N^{+2}$; H_2SO_4 / SO_4^{2-}

C. H_2SO_4 / HSO_4^- ; $(CH_3)_2NH_2^+$ / $(CH_3)_2NH$

D. H_2SO_4 / $(CH_3)_2NH$; $(CH_3)_2NH^+$ / HSO_4^-

Amphoteric Substances

- Can act as either acid or base
  - Also called **amphiprotic**
  - Can be either molecules or ions

Ex. hydrogen carbonate ion:

- **Acid**:

$$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(\ell)$$

- **Base:**

$$HCO_3^-(aq) + H_3O^+(aq) \rightarrow H_2CO_3(aq) + H_2O(\ell)$$

$$\rightarrow 2H_2O(\ell) + CO_2(g)$$

Your Turn!

Ex. Which of the following can act as an amphoteric substance?

A. CH_3COOH

B. HCl

C. NO_2^-

D. HPO_4^{2-}

Strengths of Acids and Bases

Strength of Acid

- Measure of its ability to transfer H^+
- **Strong acids**
  - React completely with water **Ex.** HCl and HNO_3
- **Weak acids**
  - Less than completely ionized **Ex.** CH_3COOH and CHOOH

Strength of Base classified in similar fashion:

- **Strong bases**
  - React completely with water **Ex.** Oxide ion (O^{2-}) and OH^-
- **Weak bases**
  - Undergo incomplete reactions

  Ex. NH_3 and NRH_2 (NH_2CH_3, methylamine)

Reactions of Strong Acids and Bases

In water

- **Strongest acid** = hydronium ion, H_3O^+
  - If more powerful H^+ donor added to H_2O
  - Reacts with H_2O to produce H_3O^+

Similarly,

- **Strongest base** is hydroxide ion (OH^-)
  - More powerful H^+ acceptors
  - React with H_2O to produce OH^-

Position of Acid-Base Equilibrium

- Acetic acid ($HC_2H_3O_2$) is **weak acid**
  - Ionizes only slightly in water

$$HC_2H_3O_2(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

weaker acid weaker base stronger acid stronger base

- Hydronium ion
  - **Better** H^+ donor than acetic acid
  - **Stronger acid**
- Acetate ion
  - **Better** H^+ acceptor than water
  - **Stronger base**
- Position of equilibrium **favors weaker** acid and base

Your Turn!

Ex. In the reaction:

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

which species is the weakest base ?

A. HCl

B. H_2O

C. H_3O^+

D. Cl^-

In General

- **Stronger** acids and bases tend to react with each other to produce their **weaker** conjugates
  - ***Stronger*** Brønsted acid has ***weaker*** conjugate base
  - ***Weaker*** Brønsted acid has ***stronger*** conjugate base

Autoionization of water

- **Trace ionization ≡ self-ionization of water**
- $\mathbf{H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(}aq\mathbf{) + OH^-(}aq\mathbf{)}$

  acid **base** **acid** **base**

- Equilibrium law is: $K_c = \dfrac{[H_3O^+][OH^-]}{[H_2O]^2}$
- But $[H_2O]_{pure} = \dfrac{\dfrac{1000\,g}{18.0\,g/mol}}{1.00\,L}$ = **55.6 *M***
- $[H_2O]$ = constant

Autoionization of water

$$\mathbf{H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(\mathit{aq}) + OH^-(\mathit{aq})}$$

- Since ∴ $[\mathbf{H_2O}]$ = constant
- Equilibrium law simplifies to

$$K_c \times [\mathrm{H_2O}]^2 = \boxed{[\mathrm{H^+}][\mathrm{OH^-}] = K_\mathrm{w}}$$

- Where $\boldsymbol{K_w}$ = ion product constant for water
- Often omit 2nd H_2O molecule and write
- $\mathbf{H_2O(\ell) \rightleftharpoons H^+(\mathit{aq}) + OH^-(\mathit{aq})}$

$$\boxed{K_\mathrm{w} = [\mathrm{H^+}][\mathrm{OH^-}]}$$

Autoionization of water

H_2O (l) $\leftrightarrows$ **H^+** (aq) **+** **OH^-** (aq)

- for pure H_2O at 25 °C
- $[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$
- $K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = \mathbf{1.0 \times 10^{-14}}$

H_2O auto-ionization occurs in any solution

- **$K_w = [H^+]\cdot[OH^-] = 1.0 \times 10^{-14}$ at** 25 °C

Self-Ionization of Water

- In aqueous solution,
- **Product of [H^+] and [OH^-] equals K_w**
- **[H^+] and [OH^-]** may not actually equal each other

Solution Classification

Neutral	$[H_3O^+] = [OH^-]$
Acidic	$[H_3O^+] > [OH^-]$
Basic	$[H_3O^+] < [OH^-]$

Learning Check

Ex. In a sample of blood at 25 °C, $[H^+] = 4.6 \times 10^{-8}$ *M*. Find $[OH^-]$ and determine if the solution is acidic, basic or neutral.

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-8}} = 2.2 \times 10^{-7}$$

- So $2.2 \times 10^{-7}\ M > 4.6 \times 10^{-8}\ M$
- **$[OH^-] > [H_3O^+]$**
- Solution slightly **basic**

The pH Concept

- In general

$$\boxed{\mathbf{pH} = -\log[\mathbf{H}^+]}$$

$$\boxed{[\mathbf{H}^+] = \mathbf{10}^{-\mathbf{pH}}}$$

$$\mathbf{pX} = -\log \mathbf{X}$$

$$\mathbf{pOH} = -\log[\mathbf{OH}^-]$$

$$\mathbf{p}K_\mathbf{w} = -\log K_\mathbf{w} = \mathbf{14.00}$$

Using Logarithms

$$K_w = [H^+][OH^-]$$

$$-\log([H^+][OH^-]) = -\log K_w = -\log(1.0 \times 10^{-14})$$

$$-\log[H^+] - \log[OH^-] = -\log K_w = -(-14.00)$$

$$\boxed{pH + pOH = pK_w = 14.00}$$

Redefine Acidic, Basic and Neutral Solutions in terms of pH!

- As **pH** ↑, [H^+] ↓; **pOH** ↓, and [OH^-] ↑
- As **pH** ↓, [H^+] ↑; **pOH** ↑, and [OH^-] ↓

Neutral	**pH = 7.00**
Acidic	**pH < 7.00**
Basic	**pH > 7.00**

Your Turn!

Ex. K_w increases with increasing temperature. At 50 ^oC, $K_w = 5.476 \times 10^{-14}$. What is the pH of a neutral solution at 50 ^oC ?

A. 7.00

B. 6.63

C. 7.37

D. 15.3

$[H^+] = [OH^-] = (5.476 \times 10^{-14})^{1/2} = 2.34 \times 10^{-7}$

$pH = -\log[H^+] = -\log 2.34 \times 10^{-7} = 6.63$

Learning Check

Ex. What are $[H^+]$ and $[OH^-]$ of **pH = 3.00** solution?

- **$[H^+]$** = $10^{-3.00} = 1.0 \times 10^{-3}$ *M*
- **$[OH^-]$** = $\dfrac{\mathbf{1.0 \times 10^{-14}}}{\mathbf{1.0 \times 10^{-3}}} = \boxed{\mathbf{1.0 \times 10^{-11}\ \mathit{M}}}$

Ex. What are $[H^+]$ and $[OH^-]$ of **pH = 4.00** solution?

- **pH** = 4.00 **$[H^+]$** = 1.0×10^{-4} *M*
- **$[OH^-]$** = $\dfrac{\mathbf{1.0 \times 10^{-14}}}{\mathbf{1.0 \times 10^{-4}}} = \boxed{\mathbf{1.0 \times 10^{-10}\ \mathit{M}}}$
- ***Or*** **pH** 4.00 solution has 10 times less H^+ than **pH** 3.00 solution

Sample pH Calculations

Ex. Calculate pH and pOH of blood where

$$[H^+] = 4.6 \times 10^{-8}\ M$$

$$[OH^-] = 2.2 \text{ x } 10^{-7}\ M$$

$$\textbf{pH} = -\log(4.6 \text{ x } 10^{-8}) = 7.34$$

$$\textbf{pOH} = -\log(2.2 \text{ x } 10^{-7}) = \underline{\ 6.66}$$

$$14.00 = \text{p}\boldsymbol{K_w}$$

Or

$$\textbf{pOH = 14.00 – pH} = 14.00 - 7.34 = \textbf{6.66}$$

Sample pH Calculations (cont'd)

Ex. What is the pH of NaOH solution at 25 °C in which the OH^- concentration is 0.0026 *M*?

- **$[OH^-]$** = 0.0026 *M*
- **pOH** = –log(0.0026) = 2.59
- **pH = 14.00 – pOH**
- = 14.00 – 2.59
- = $\boxed{\mathbf{11.41}}$

Your Turn!

Ex. A sample of juice has a pH of 3.76. Calculate $[H^+]$.

A. 7.6×10^{-3} *M*

B. 3.76 *M*

C. 10.24 *M*

D. 5.9×10^{-9} *M*

E. 1.7×10^{-4} *M*

$$[H^+] = 10^{-pH}$$

$$= 10^{-3.76}$$

$$= \mathbf{1.7 \times 10^{-4}}\ \boldsymbol{M}$$

Learning Check

Ex. What is the $[H_3O^+]$ and pH of a solution that has $[OH^–] = 3.2 \times 10^{–3}$ M?

- $[H_3O^+][OH^-] = 1 \text{ x } 10^{-14}$
- $[H_3O^+] = 1 \text{ x } 10^{-14}/3.2 \text{ x } 10^{-3} = 3.1 \text{ x } 10^{-12}$ M
- $\text{pH} = -\log [H_3O^+] = -\log(3.1 \text{ x } 10^{-12}) = 11.50$

Your Turn!

Ex. What is the $[OH^-]$ and pH of a solution that has $[H_3O^+] = 2.3 \times 10^{-5}$ M?

	$[H_3O^+]$	pH
A.	2.3×10^{-5} M	9.40
B.	1.0×10^{-14} M	14.00
C.	4.3×10^{-10} M	4.60
D.	7.7×10^{-9} M	5.23
E.	1.0×10^{-7} M	7.00

Learning Check

Ex. What is the pOH and the $[H_3O^+]$ of a solution that has a pH of 2.33?

pOH = 11.67

$[H_3O^+] = 4.7 \times 10^{-3}$

Your Turn!

Ex. What is the pH and the $[H_3O^+]$ of a solution that has a pOH of 1.89?

	$[H_3O^+]$	pH
A.	1.29×10^{-2} M	1.89
B.	1.0×10^{-14} M	14.00
C.	1.50×10^{-11} M	10.82
D.	7.8×10^{-13} M	12.11
E.	1.0×10^{-7} M	7.00

pOH= 1.89
$[OH^-]$ = Shift log –pOH
$[OH^-]$ =0.0129
$[H^+]=10^{-14} / 0.0129=7.8 \times 10^{-13}$
pH= -log H^+ = -log 7.8×10^{-13}
pH=12.11

Strong Acids: pH of Dilute Solutions

- Assume 100% dissociated in solution
  - Good ~ if dilute
- Makes calculating $[H^+]$ and $[OH^-]$ easier
- **1 mole H^+ for every 1 mole HA**
  - So **$[H^+] = [HA]$** for strong acids
- Thus, if 0.040 M $HClO_4$
- $[H^+] = 0.040$ M
- And **pH = – log (0.040) = 1.40**

Strong Acids

HCl

HBr

HI

HNO_3

H_2SO_4

$HClO_3$

$HClO_4$

pH of Dilute Solutions of Strong Bases

Strong Bases

NaOH
KOH
LiOH

- 1 mole OH^- for every 1 mole ***B***
- $[OH^-] = [$***B***$]$ for strong bases

$Ca(OH)_2$
$Ba(OH)_2$
$Sr(OH)_2$

- 2 mole OH^- for every 1 mole ***B***
- $[OH^-] = 2*[$***B***$]$ for strong bases

Learning Check

Ex. Calculate the pH of 0.011 M $Ca(OH)_2$.

$$\mathbf{Ca(OH)_2(\mathit{s}) + H_2O \rightarrow Ca^{2+}(\mathit{aq}) + 2\ OH^{-}(\mathit{aq})}$$

- $\mathbf{[OH^-]} = 2*[Ca(OH)_2] = 2*0.011\mathit{M} = 0.022\mathit{M}$
- $\mathbf{pOH} = -\log(0.022) = 1.66$
- $\mathbf{pH} = 14.00 - \mathbf{pOH}$
- $= 14.00 - 1.66 = \boxed{\mathbf{12.34}}$
- What is this in the $[H^+]$ of the solution?
- $\mathbf{[H^+]} = 10^{-12.34} = 4.6 \times 10^{-13}\ \mathit{M}$

Learning Check

Ex. What is the pH of 0.1M HCl?

- Assume 100% dissociation

$$\mathbf{HCl}(aq) + \mathbf{H_2O}(\ell) \rightarrow \mathbf{H^+}(aq) + \mathbf{OH^-}(aq)$$

I	0.1	N/A	0	0
C	-0.1	-0.1	0.1	0.1
End	0	N/A	0.1	0.1

pH = –log(0.1) = **1**

Learning Check

Ex. What is the pH of 0.5M $Ca(OH)_2$?

- Assume 100% dissociation

$$Ca(OH)_2\ (aq) \rightarrow Ca^{2+}\ (aq) + 2\ OH^{-}\ (aq)$$

	$Ca(OH)_2$	Ca^{2+}	OH^{-}
I	0.5	0	0
C	-0.5	+0.5	$+0.5\times2$
E	0	0.5	1.0

$$pOH = -\log(1.0) = 0$$

$$pH = 14.00 - pOH = 14.00 - 0 = \mathbf{14}$$

Weak Acids and Bases

- Incompletely ionized
- Molecules and ions exist in equilibrium
- **Reaction of a Weak Acid with Water**

$CH_3COOH(aq) + H_2O(l) \leftrightarrows CH_3COO^-(aq) + H_3O^+(aq)$

$HSO_3^-(aq) + H_2O(l) \leftrightarrows SO_3^{2-}(aq) + H_3O^+(aq)$

$NH_4^+(aq) + H_2O(l) \leftrightarrows NH_3(aq) + H_3O^+(aq)$

Weak Acid/Base Equilibria

Acid + Water ⇆ Conjugate Base + Hydronium Ion

Or generally

$$\mathbf{HA}(aq) \quad + \quad \mathbf{H_2O}(l) \leftrightarrows \mathbf{A^-}(aq) \quad + \quad \mathbf{H_3O^+}(aq)$$

$$K'_c = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

- But $[H_2O]$ = constant (55.6 M) so rewrite as

$$K'_c \times [H_2O] = \frac{[A^-][H_3O^+]}{[HA]} = K_a$$

- Where K_a = **acid ionization constant**

Weak Acid/Base Equilibria

- Often simplify as
- $\mathbf{HA}\ (aq) \leftrightarrows \mathbf{A^-}\ (aq) + \mathbf{H^+}\ (aq)$

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

$$pK_a = -\log K_a$$

$$K_a = 10^{-pK_a}$$

Table 17.2 Weak Monoprotic Acids at 25 °C

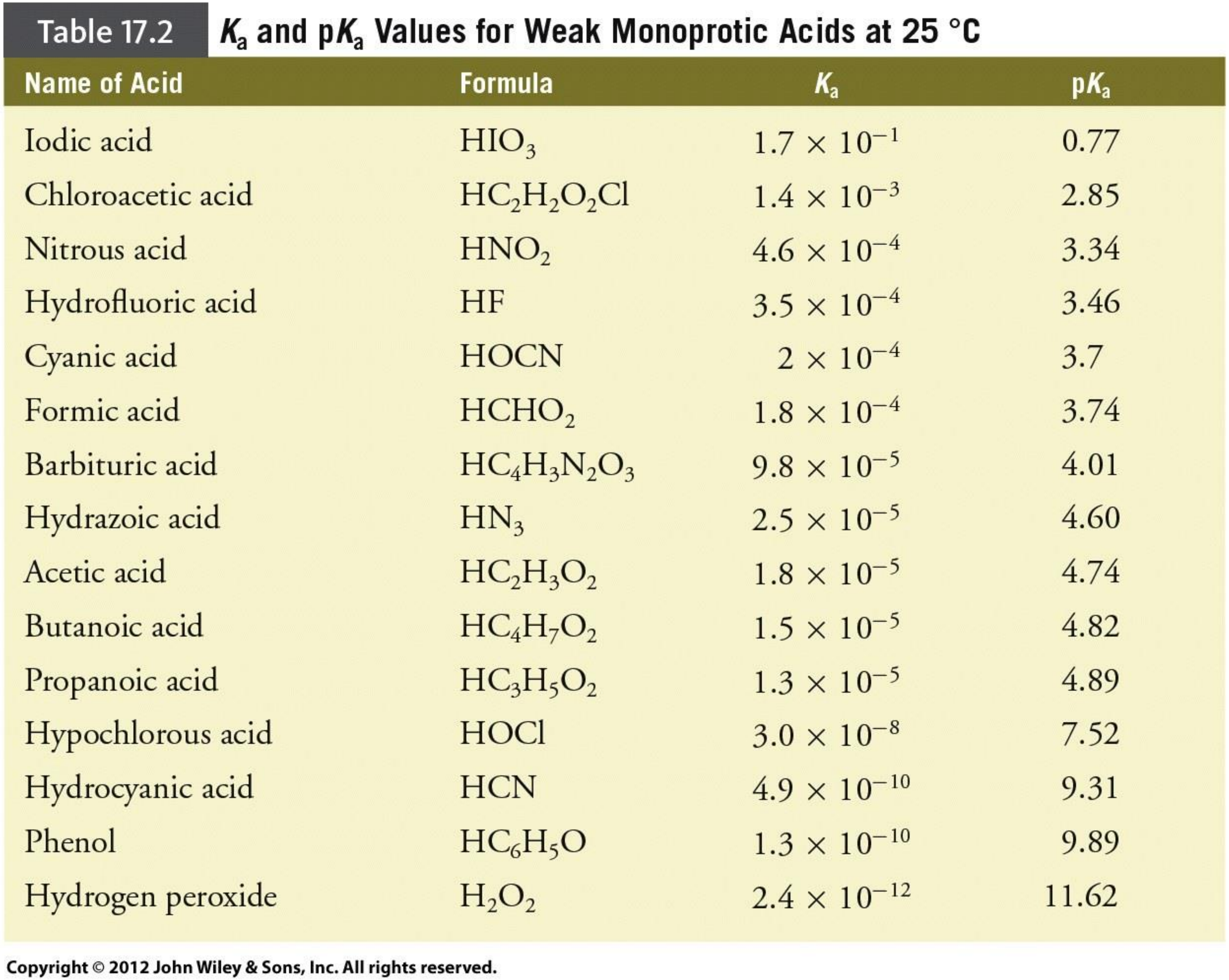


Table 17.2 K_a and pK_a Values for Weak Monoprotic Acids at 25 °C

Name of Acid	Formula	K_a	pK_a
Iodic acid	HIO_3	1.7×10^{-1}	0.77
Chloroacetic acid	$HC_2H_2O_2Cl$	1.4×10^{-3}	2.85
Nitrous acid	HNO_2	4.6×10^{-4}	3.34
Hydrofluoric acid	HF	3.5×10^{-4}	3.46
Cyanic acid	$HOCN$	2×10^{-4}	3.7
Formic acid	$HCHO_2$	1.8×10^{-4}	3.74
Barbituric acid	$HC_4H_3N_2O_3$	9.8×10^{-5}	4.01
Hydrazoic acid	HN_3	2.5×10^{-5}	4.60
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}	4.74
Butanoic acid	$HC_4H_7O_2$	1.5×10^{-5}	4.82
Propanoic acid	$HC_3H_5O_2$	1.3×10^{-5}	4.89
Hypochlorous acid	$HOCl$	3.0×10^{-8}	7.52
Hydrocyanic acid	HCN	4.9×10^{-10}	9.31
Phenol	HC_6H_5O	1.3×10^{-10}	9.89
Hydrogen peroxide	H_2O_2	2.4×10^{-12}	11.62

Learning Check

Ex. What is the pK_a of HOAC if $K_a = 3.5 \times 10^{-4}$?

$$\mathbf{HOCN}(aq) + \mathbf{H_2O}(l) \leftrightarrows \mathbf{OCN^-}(aq) + \mathbf{H_3O^+}(aq)$$

or

$$\mathbf{HOCN}(aq) \leftrightarrows \mathbf{OCN^-}(aq) + \mathbf{H^+}(aq)$$

$$K_a = \frac{[\mathrm{OCN}^-][\mathrm{H}^+]}{[\mathrm{HOCN}]} = 3.5 \times 10^{-4}$$

$$\mathrm{p}K_a = -\log K_a = -\log(3.5 \times 10^{-4}) = \mathbf{3.46}$$

Reaction of a Weak Base with Water

$$CH_3COO^-(aq) + H_2O(l) \leftrightarrows CH_3COOH(aq) + OH^-(aq)$$

$$NH_3(aq) + H_2O(l) \leftrightarrows NH_4^+(aq) + OH^-(aq)$$

- Or generally

$$B(aq) + H_2O(l) \leftrightarrows BH^+(aq) + OH^-(aq)$$

$$K_c' = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

But $[H_2O]$ = constant so can rewrite as

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Where K_b = base ionization constant

$$pK_b = -\log K_b \qquad K_b = 10^{-pK_b}$$

Learning Check

Ex. What is the pK_b of C_5H_5Nif K_a = 3.5 x $10^{–4}$?

$$C_5H_5N(aq) + H_2O(\ell) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]} \quad = 1.7 \times 10^{-9}$$

$$pK_b = -\log K_b = -\log(1.7 \times 10^{-9}) = \mathbf{8.76}$$

Table 17.3 Weak Bases at 25 °C

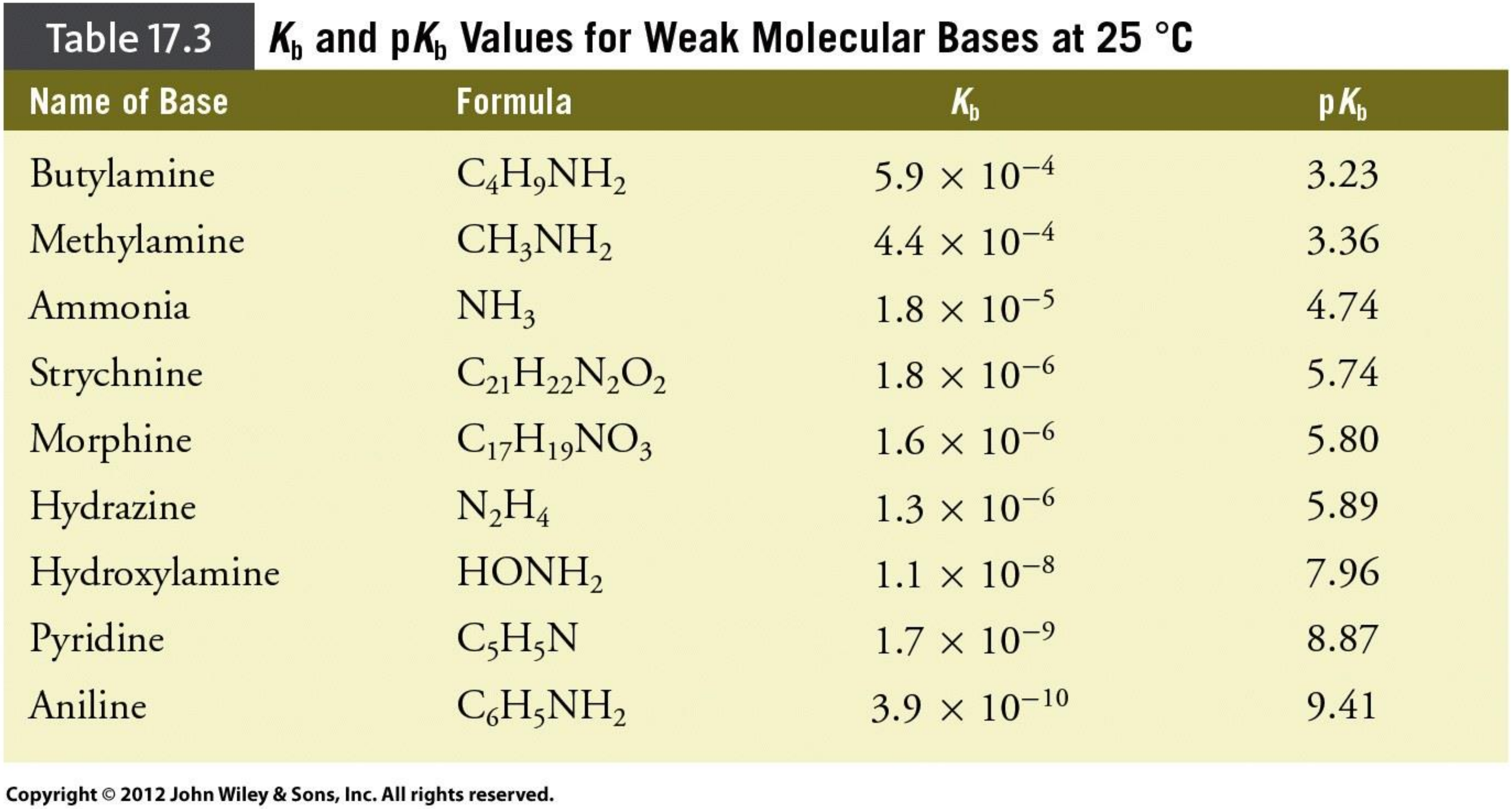


Table 17.3 K_b and pK_b Values for Weak Molecular Bases at 25 °C

Name of Base	Formula	K_b	pK_b
Butylamine	$C_4H_9NH_2$	5.9×10^{-4}	3.23
Methylamine	CH_3NH_2	4.4×10^{-4}	3.36
Ammonia	NH_3	1.8×10^{-5}	4.74
Strychnine	$C_{21}H_{22}N_2O_2$	1.8×10^{-6}	5.74
Morphine	$C_{17}H_{19}NO_3$	1.6×10^{-6}	5.80
Hydrazine	N_2H_4	1.3×10^{-6}	5.89
Hydroxylamine	$HONH_2$	1.1×10^{-8}	7.96
Pyridine	C_5H_5N	1.7×10^{-9}	8.87
Aniline	$C_6H_5NH_2$	3.9×10^{-10}	9.41

Conjugate Acid-Base Pairs and Values of K_a and K_b

$$K_a \times K_b = \frac{[A^-][H^+]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H^+][OH^-] = K_w$$

For any conjugate acid base pair:

$$K_a \times K_b = K_w = 1.0 \times 10^{-14} \qquad \text{(at 25 °C)}$$

$$\mathbf{pK_a + pK_b = pK_w = 14.00}$$

Ex. Niotinic acid (niacin) is a monoprotic acid with the formula $HC_6H_4NO_2$. A solution that is 0.012 *M* in nicotinic acid has a pH of 3.39 at 25 °C. What are the acid-ionization constant, $\boldsymbol{K_a}$, and $\mathbf{p}\boldsymbol{K_a}$ for this acid at 25 °C? What is the degree of ionization of nicotinic acid in this solution? Let **HNic** = nicotinic acid and **Nic⁻** = anion.

$$\mathbf{HNic}(aq) + \mathbf{H_2O}(l) \leftrightarrows \mathbf{Nic^-}(aq) + \mathbf{H_3O^+}(aq)$$

Ex. (cont)

$$K_a = \frac{[\text{Nic}^-][\text{H}^+]}{[\text{HNic}]}$$

	[HNic] (*M*)	**[Nic⁻] (*M*)**	**[H_3O^+] (*M*)**
I	0.012	0	0
C	$-x$	$+x$	$+x$
E	$0.012 - x$	x	x

What is value of *x*?

- Only source of H^+ is ionization of **HNic**, then can get x from $[H^+]$
- x = antilog(–pH) = 10^{-pH} = $10^{-3.39}$
  = **4.1×10^{-4}** = $[H^+]$

Ex. (cont)

- **Since Nic$^-$ is formed in 1:1 ratio with H$^+$, then**
  - **[Nic$^-$]** = $\boldsymbol{x}$ = 4.1 x 10^{-4}
- Finally only reason **HNic** disappears is because it ionizes, so loss of **[HNic] = $-\boldsymbol{x}$**

$$K_\text{a} = \frac{[\text{Nic}^-][\text{H}^+]}{[\text{HNic}]} = \frac{x * x}{0.012 - x} = \frac{x^2}{0.012 - x}$$

- But we know **[Nic$^-$]**, so can put into concentration table and solve for each

Ex. (cont)

$$K_a = \frac{[\text{Nic}^-][\text{H}^+]}{[\text{HNic}]}$$

	[HNic] (*M*)	[Nic⁻] (*M*)	[H⁺] (*M*)
I	**0.0120**	**0**	**0**
C	**– 0.00041**	**+ 0.00041**	**+ 0.00041**
E	0.0120 – 0.00041 = 0.01159 ≈**0.012**	**0.00041**	**0.00041**

- Notice if $c >> K_a$, then equilibrium concentration of acid is approximated as initial concentration

Ex. (cont)

- Now ready to calculate K_a.

$$K_a = \frac{x^2}{0.012 - x} \cong \frac{x^2}{0.012} = \frac{(0.00041)^2}{0.012} = 1.4 \times 10^{-5}$$

$$pK_a = -\log(1.4 \times 10^{-5}) = 4.85$$

% ionization

$$\%\ \text{ionization} = \frac{\text{moles ionized per liter}}{\text{moles available per liter}} \times 100\%$$

$$= \frac{x}{c} = \frac{0.00041}{0.012} \times 100\% = 3.4\%$$

Your Turn!

Ex. The base ionization constant for methylamine is 4.4 x 10^{-4}. What is the pH of a 0.050 *M* solution of this base ?

A. 1.03

B. 2.33

C. 11.67

D. 12.97

Your Turn! - Solution

$$K_b = 4.4 \text{ x } 10^{-4} = \frac{\left[CH_3NH_3^{+}\right]\left[OH^{-}\right]}{\left[CH_3NH_2\right]} = \frac{x^2}{0.05 - x}$$

Assume x is small

$$4.4 \text{ x } 10^{-4} = \frac{x^2}{0.05 - x} \qquad x^2 = 2.2 \text{ x } 10^{-5}$$

$$x = 4.69 \text{ x } 10^{-3} \qquad \text{pOH} = -\log\left(4.69 \text{ x } 10^{-3}\right) = 2.33$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.33 = 11.67$$