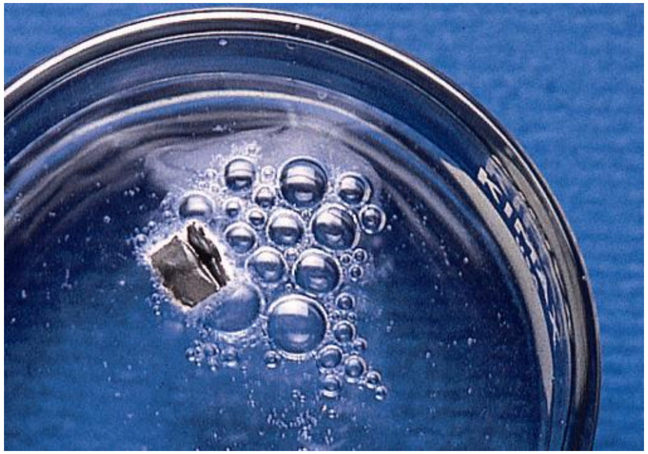
Mass Relationships in Chemical Reactions

Chapter 3



Micro World → Macro World

atoms & molecules → grams

Atomic number: number of protons which equal the number of electrons in neutral atom

Atomic mass is the mass of an atom in atomic mass units (amu) (1amu=1.6 x10^{-24}g)

amu: *define as mass exactly equal to 1/12 of the mass of Carbon-12 ……*

By definition:
1 atom ^{12}C "weighs" 12 amu

On this scale

^{1}H = 1.00794 amu

^{16}O = 15.9994 amu

Ex sulfer-36 has mass of 35.967 amu, which is around 3 times the mass of C-12 [35.967/12=2.99]

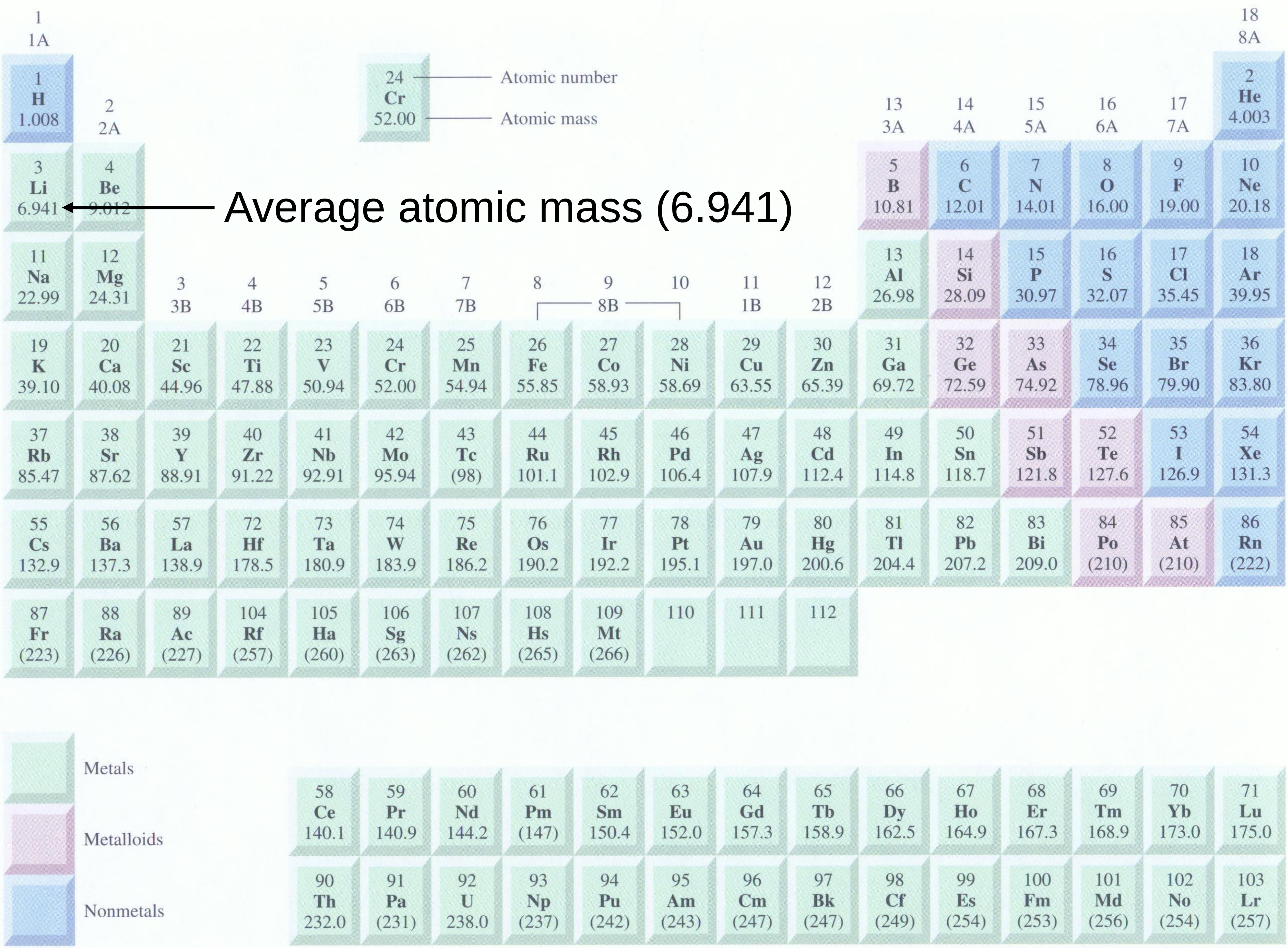
- When express the mass in amu, mass of atom is approximately equal the number of protons and neutrons.

Average atomic mass: is the weighted average of all the naturally occurring isotopes

Ex: Natural lithium is:7.42% ^{6}Li (6.015 amu) and 92.58% ^{7}Li (7.016 amu)

Average atomic mass of lithium=

[(7.42/100) x 6.015] + [(92.58/100) x 7.016] = 6.941 amu



24
Cr
52.00

Atomic number

Atomic mass

Average atomic mass (6.941)

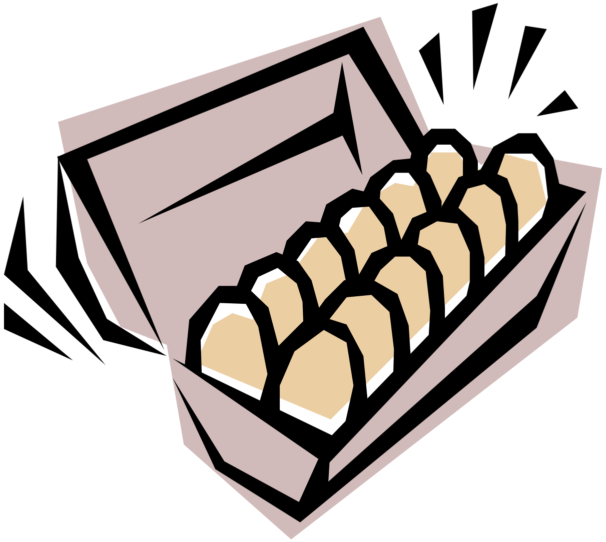
1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (210)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (257)	105 **Ha** (260)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110	111	112						
				58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (147)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
				90 **Th** 232.0	91 **Pa** (231)	92 **U** 238.0	93 **Np** (237)	94 **Pu** (242)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (249)	99 **Es** (254)	100 **Fm** (253)	101 **Md** (256)	102 **No** (254)	103 **Lr** (257)

🟩 Metals

🟪 Metalloids

🟦 Nonmetals

Dozen = 12



Pair = 2

Mole = **6.022 × 10^{23} units**

The mole ***(mol)*** is a unit to account the number of particles(atoms, molecules,…)

- Number of atoms in exactly 12 grams of ^{12}C = **6.022 × 10^{23} atoms** **(**experimentally**)**

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

Avogadro's number = N_A

  – Number of atoms, molecules or particles in one mole

1 mole of X = 6.022 × 10^{23} units of X

- 1 mole Xe = 6.022×10^{23} Xe atoms
- 1 mole NO_2 = 6.022×10^{23} NO_2 molecules

Molar mass: ($\mathcal{M}$), defined as the mass (in grams or kilograms) of 1 mole of units (such as atoms or molecules) of a substance

1 mole ^{12}C atoms = 12.00 g = 6.022 x 10^{23} atoms

1 mole lithium atoms = 6.941 g of Li

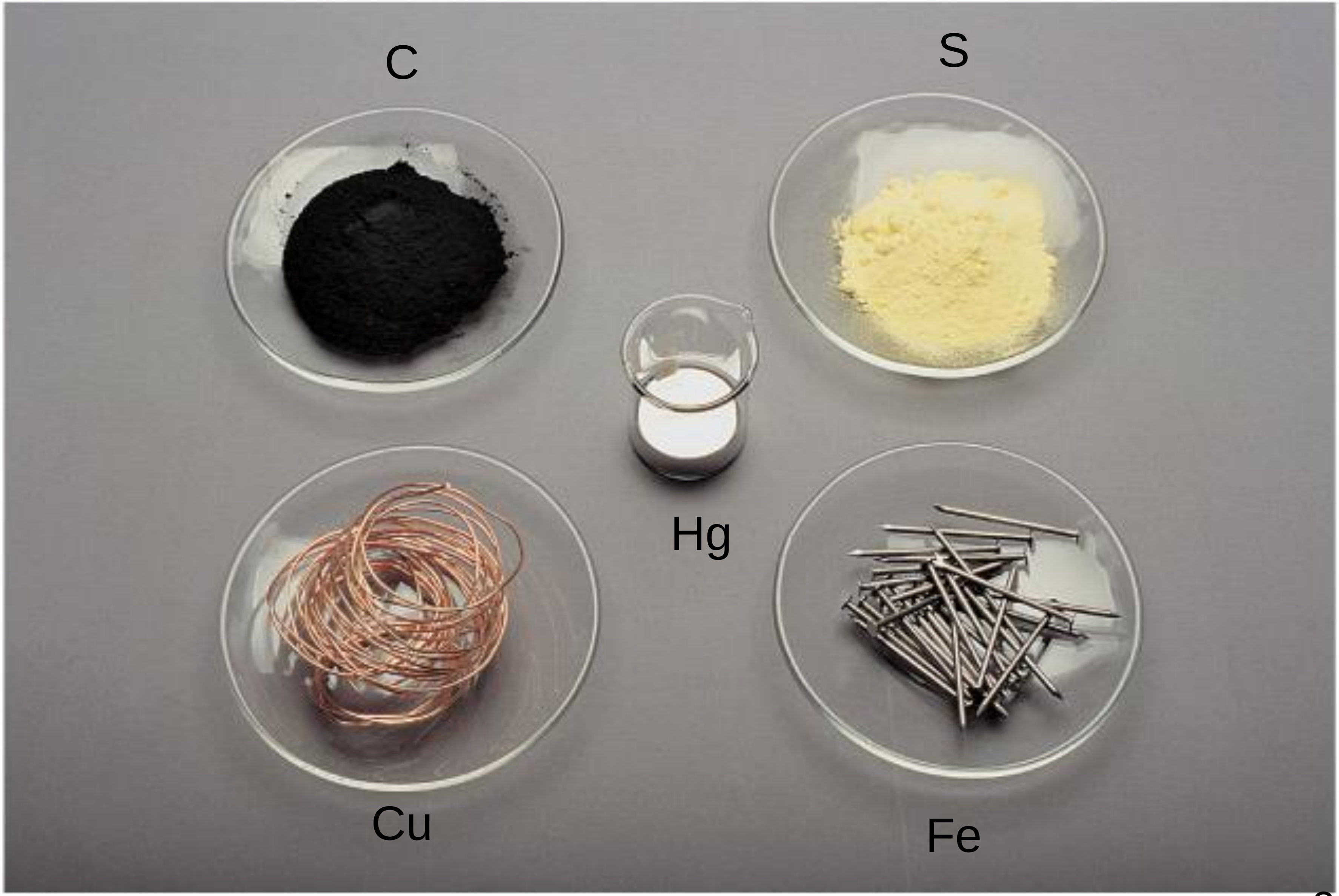
For any element

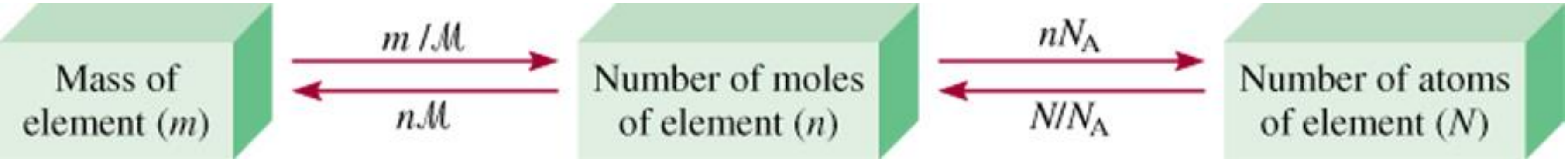
atomic mass (amu) = molar mass (grams/mol)
from periodic table

Atomic mass of O=16 amu

Molar mass of O = 16g/mol

One Mole of:





$\mathcal{M}$ = molar mass in g/mol ,n = mole

N_A = Avogadro's number

Two main rules

1- mole=mass/molar mass

$$\boldsymbol{n} = \frac{\boldsymbol{m}}{\boldsymbol{\mu}}$$

2- number of atoms (or molecules)= moles x Avogadro's #

$$N = n.N_A$$

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

End

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

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

Or using direct way

$$n = \frac{m}{\mu} = \frac{15.34}{55.85} = \mathbf{0.2747\ mole\ Fe}$$

Ex: How many potassium atoms are in 0.551 g of potassium (K) ?

1 mol of K = 39.10 g of K

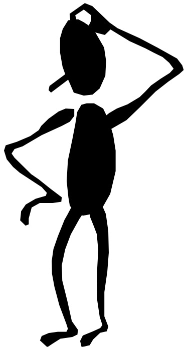
$$N = n.N_A = \left(\frac{0.551}{39.10}\right).(6.022\ \text{x}10^{23}) = 8.49\ \text{x}\ 10^{21}\ \text{atoms of K}$$

Ex: calculate the mass of one atom of Na (Na=23g/mol)

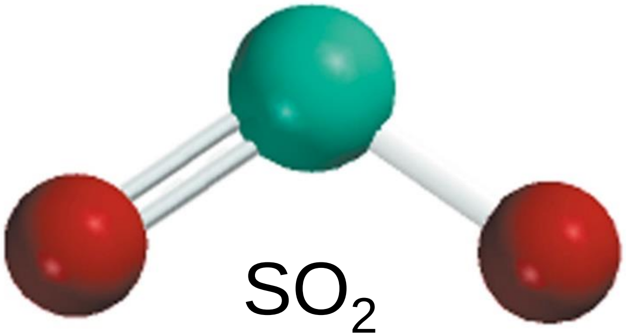
$$\boldsymbol{N = n.N_A}$$

$$1 = \left(\frac{m}{23}\right).(6.022\text{x}10^{23})$$

$$m = 3.82\text{x}10^{-23}\text{g}$$



Molecular mass (or molecular weight) is the sum of the atomic masses (in amu) in a molecule.



SO_2

1S	32.07 amu
2O	+ 2 x 16.00 amu
SO_2	64.07 amu

For any molecule

molecular mass in amu = molar mass in grams

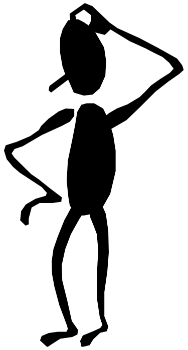
1 molecule of SO_2 weighs 64.07 amu

1 mole of SO_2 weighs 64.07 g

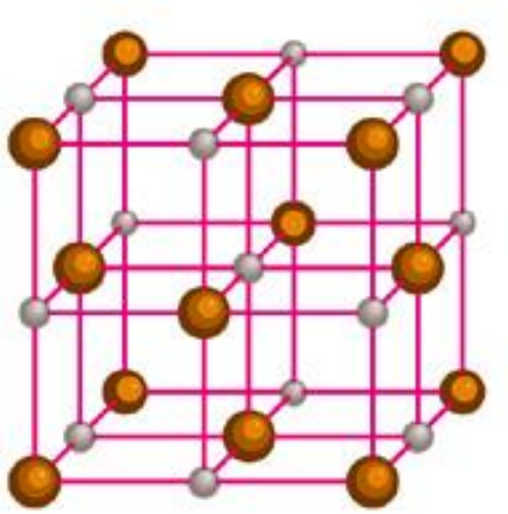
Ex How many H atoms are in 72.5 g of C_3H_8O ?

$$N = (n)_{molecule} . N_A . (\# \; of \; H \; per \; molecule)$$

$$N = \left(\frac{72.5}{60.09}\right) . (6.022x10^{23}) . (8) =$$ 5.82×10^{24} H atoms



Formula mass is the sum of the atomic masses (in amu) in a formula unit of an ionic compound.



NaCl

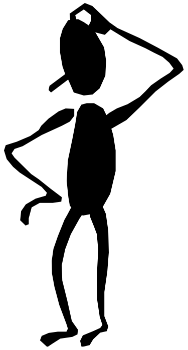
$$\begin{array}{ll} 1\text{Na} & 22.99\ \text{amu} \\ 1\text{Cl} & \underline{+\ \ 35.45\ \text{amu}} \\ \text{NaCl} & 58.44\ \text{amu} \end{array}$$

For any ionic compound

formula mass (amu) = molar mass (gram/mol)

1 formula unit of NaCl = 58.44 amu

1 mole of NaCl = 58.44 g of NaCl



Do You Understand Formula Mass?

What is the formula mass of $Ca_3(PO_4)_2$?

1 formula unit of $Ca_3(PO_4)_2$

3 Ca		3 x 40.08 g/mol
2 P		2 x 30.97 g/mol
8 O	+	8 x 16.00 g/mol
		310.18 g/mol

Units of grams per mole are the most practical for chemical calculations!

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

$$N = n.N_A$$

$$1.53\text{x}10^{23} = \left(\frac{m}{162}\right)\text{x}(6.022\text{x}10^{23})$$

$$m = 41.21g$$

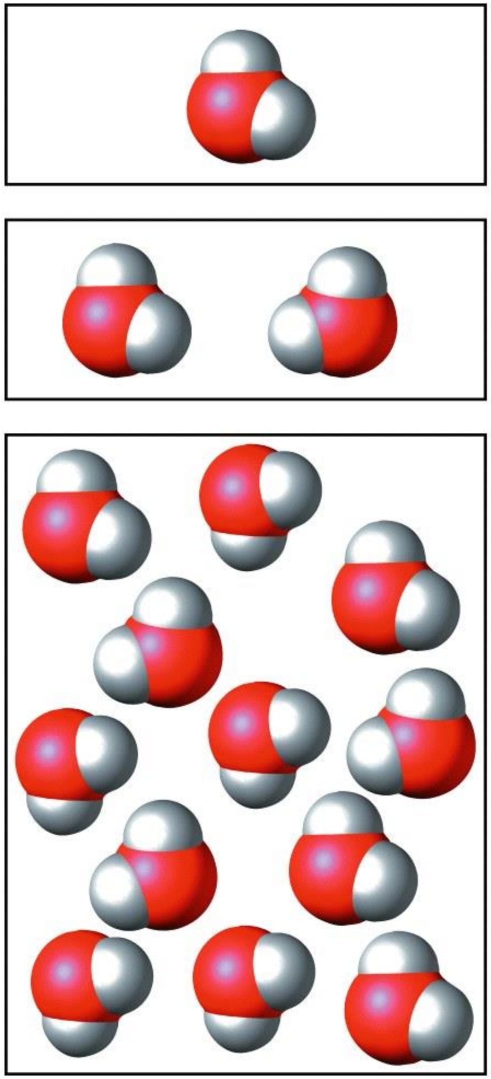
Ex Calculate the number of formula units of Na_2CO_3 in 1.29 moles of Na_2CO_3

$$\mathrm{N} = \mathrm{n}.\mathrm{N_A}$$

$$N = (1.29)\text{x}(6.022\text{x}10^{23}) = 7.77\times10^{23} \text{ particles } Na_2CO_3$$

Mole-to-Mole Conversion Factors

- Can use chemical formula to relate amou of each atom to amount of compound
- In H_2O there are 3 relationships:
  - 2 mol H ⇔ 1 mol H_2O
  - 1 mol O ⇔ 1 mol H_2O
  - 2 mol H ⇔ 1 mol O
- Can also use these on atomic scale
  - 2 atom H ⇔ 1 molecule H_2O
  - 1 atom O ⇔ 1 molecule H_2O



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

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

3 mol Ca ⇔ 1 mol $Ca_3(PO_4)_2$

$$2.53\ \cancel{\text{mol Ca}_3(\text{PO}_4)_2}\left(\frac{3\ \text{mol Ca}}{1\ \cancel{\text{mol Ca}_3(\text{PO}_4)_2}}\right)$$

= 7.59 mol Ca

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

- **mass O → mol O → mol Fe → mass Fe**

25.6 g O → ? g Fe

3 mol O ⇔ 2 mol Fe

$- n_O = \frac{25.6}{16} = 1.6\, mol$ O

3 mol O ⇔ 2 mol Fe

1.6 ⇔ ?? mol Fe

$- n_{Fe}$=(1.6 x 2)/3

=1.06

- mass of Fe = 1.06 x 55.85 =59.2 g of Fe

Determining Empirical & Molecular Formulas

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

Molecular Formula (MF)

- – Exact composition of one molecule
- – Exact whole # ratio of atoms of each element in molecule(**Ex** :**MF of glucose is $C_6H_{12}O_6$)**

Empirical Formula (EF)

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

Ex **EF of glucose is CH_2O**

Ex what is the EF of pentane (C_5H_{12})

EF is C_5H_{12} same as molecular formula

Three Ways to Calculate Empirical Formulas

1. **From Masses of Elements**

   Ex. 2.448 g sample of which 1.771 g is Fe and 0.677 g is O.

2. **From Percentage Composition**

   Ex. 43.64 % P and 56.36 % O.

3. **From Combustion Data**

   Given masses of combustion products

   Ex. The combustion of a 5.217 g sample of a compound of C, H, and O in pure oxygen gave 7.406 g CO_2 and 4.512 g of H_2O.

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.
    - Multiply by smallest number to make subscripts in step 3 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.

- The smallest is 3.722×10^{-3} mole

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

	Mole ratio	Integer ratio
• C = $\dfrac{3.722\times10^{-3}\ \text{mol C}}{3.722\times10^{-3}\ \text{mol C}} =$	1.000	= 1
• H = $\dfrac{1.860\times10^{-2}\ \text{mol H}}{3.722\times10^{-3}\ \text{mol C}} =$	4.997	= 5
• N = $\dfrac{3.723\times10^{-3}\ \text{mol N}}{3.722\times10^{-3}\ \text{mol C}} =$	1.000	= 1

Empirical formula = CH_5N

1. Empirical Formula from Mass Data

Ex 2:One of the compounds of iron and oxygen, “black iron oxide,” occurs naturally in the mineral magnetite. 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.

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.

$$\frac{0.03171\text{ mol Fe}}{0.03171\text{ mol Fe}} = 1.000\text{ Fe}$$

$$= Fe_{1.00}O_{1.33}$$

$$\frac{0.0423\text{ mol O}}{0.03171\text{ mol Fe}} = 1.33\text{ O}$$

3-Multiply by smallest number to make subscripts in step 2 integers

$$Fe_{(1.00\times3)}O_{(1.33\times3)} = Fe_3O_{3.99}$$

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.

Step 1: Assume 100 g of compound.

- 43.64 g P
- 56.36 g O

1 mol P = 30.97 g

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

$$\frac{1.409\ \mathrm{mol\ P}}{1.409\ \mathrm{mol\ P}} = 1.000$$

$$\frac{3.523\ \mathrm{mol\ O}}{1.409\ \mathrm{mol\ P}} = 2.500$$

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

Here **n = 2**

P: $1.00 \times 2 = 2$

O: $2.500 \times 2 = 5$

Empirical formula = P_2O_5

3. Empirical Formulas from Combustion Analysis:

Combustion Analysis

- Compounds containing carbon, hydrogen, & oxygen, can be burned completely in pure oxygen gas
  - Only carbon dioxide & water are produced

Ex. Combustion of ethanol (C_2H_5OH)

$$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

Apparatus for determining the empirical formula of ethanol. The absorbers are substances that can retain water and carbon dioxide, respectively.

Combustion of ethanol

3. Empirical Formulas from Combustion Analysis:

- Carbon dioxide & water separated & weighed separately
  - All C ends up as CO_2
  - All H ends up as H_2O
  - Mass of **C** can be derived from amount of $\mathbf{CO_2}$
    - mass CO_2 → mol CO_2 → mol C → mass C
  - Mass of **H** can be derived from amount of $\mathbf{H_2O}$
    - mass H_2O → mol H_2O → mol H → mass H
  - Mass of oxygen is obtained by difference

    mass O = mass sample – (mass C + mass H)

Ex.The combustion of a 5.217 g sample of a compound of C, H, and O in pure oxygen gave 7.406 g CO_2 and 4.512 g of H_2O. Calculate the empirical formula of the compound.

	C	H	O	CO_2
Molar mass (g/mol)	12.011	1.008	15.999	44.01

1. Calculate mass of C from mass of CO_2.

mass CO_2 → mole CO_2 → mole C → mass C

$$7.406\ \cancel{g\ CO_2}\left(\frac{1\ \cancel{mol\ CO_2}}{44.01\ \cancel{g\ CO_2}}\right)\left(\frac{1\ \cancel{mol\ C}}{1\ \cancel{mol\ CO_2}}\right)\left(\frac{12.011\ g\ C}{1\ \cancel{mol\ C}}\right)$$

= 2.021 g C

2. Calculate mass of H from mass of H_2O.

mass H_2O → mol H_2O → mol H → mass H

$$4.512\ \cancel{\text{g H}_2\text{O}}\left(\frac{1\ \cancel{\text{mol H}_2\text{O}}}{18.015\ \cancel{\text{g H}_2\text{O}}}\right)\left(\frac{2\ \cancel{\text{mol H}}}{1\ \cancel{\text{mol H}_2\text{O}}}\right)\left(\frac{1.008\ \text{g H}}{1\ \cancel{\text{mol H}}}\right)$$

= 0.5049 g H

3. Calculate mass of O from difference.

Mass O= total mass-(C mass + H mass)

= 5.217 g– (2.021 g C + 0.5049 g H) **= 2.691 g O**

Or we can use the following rule:

$mass\ of\ element\ in\ sample = \left(\frac{mass\ of\ product\ contain\ this\ element}{it\ molar\ mass}\right)$ x (#of element atoms in product) x (atomic mass of element)

∴ mass of C in CO_2: $\frac{7.406}{44.01}$ x 1 x 12.01= 2.02 mass of C

mass of H in H_2O: $\frac{4.512}{18}$ x 2 x 1.008 = 0.504 mass of H

	C	H	O
MM	12.011	1.008	15.999
g	2.021	0.5049	2.691

4. Calculate mol of each element

$$\text{mol C} = \frac{\text{g C}}{\text{MM C}} = \frac{2.021\ \text{g}}{12.011\ \text{g/mol}} = 0.1683\ \text{mol C}$$

$$\text{mol H} = \frac{\text{g H}}{\text{MM H}} = \frac{0.5049\ \text{g}}{1.008\ \text{g/mol}} = 0.5009\ \text{mol H}$$

$$\text{mol O} = \frac{\text{g O}}{\text{MM O}} = \frac{2.691\ \text{g}}{15.999\ \text{g/mol}} = 0.1682\ \text{mol O}$$

$$C_{\frac{0.1683}{0.1682}}H_{\frac{0.5009}{0.1682}}O_{\frac{0.1682}{0.1682}}$$

- Preliminary empirical formula
  - $C_{0.1683}H_{0.5009}O_{0.1682} = C_{1.00}H_{2.97}O_{1.00}$

5. Calculate mol ratio of each element

Empirical Formula = CH_3O

- Since all values are close to integers, round to

Determining Molecular Formula

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

$$\textbf{Molecular formula} = \frac{\textit{molar mass of unknown}}{\textit{molar mass of EF}} \textbf{xEF}$$

$$\left(\frac{\textit{molar mass of unknown}}{\textit{molar mass of EF}}\right) = n$$

Ex. molar mass of Glucose is 180.16 g/mol

Empirical formula = CH_2O

Empirical formula molar mass = 30.03 g/mol, find the molecular formula for Glucose .

$$\text{Molecular formula} = \frac{180.16}{30.03} \text{ x } CH_2O = 6 \text{ x } CH_2O$$

Molecular formula is $C_6H_{12}O_6$

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

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

Solution

Molar mass of NH_2 = (1×14.01) + (2×1.008) = 16.017g

$$\textbf{Molecular formula} = \frac{\textit{molar mass of unknown}}{\textit{molar mass of EF}} \text{ x EF}$$

$$= \frac{32}{16.017} \text{ x } NH_2$$

$$= 2 \text{ x } NH_2$$

Molecular formula : N_2H_4

Chemical reactions and chemical equations

A process in which one or more substances is changed into one or more new substances is a ***chemical reaction.***

A ***chemical equation*** uses chemical symbols to show what happens during a chemical reaction.

3 ways of representing the reaction of H_2 with O_2 to form H_2O

Two hydrogen molecules + One oxygen molecule ⟶ Two water molecules

$$2H_2 + O_2 \longrightarrow 2H_2O$$

reactants ⟶ products

How to "Read" Chemical Equations

$$2\ Mg + O_2 \longrightarrow 2\ MgO$$

2 atoms Mg + 1 molecule O_2 makes 2 formula units MgO

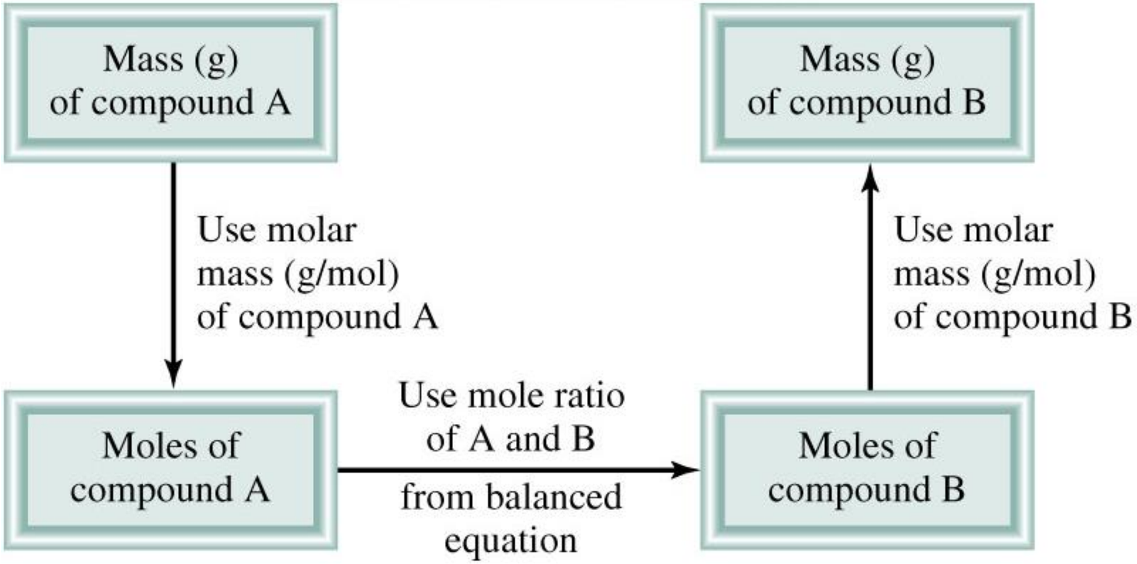
2 moles Mg + 1 mole O_2 makes 2 moles MgO

48.6 grams Mg + 32.0 grams O_2 makes 80.6 g MgO

IS NOT

2 grams Mg + 1 gram O_2 makes 2 g MgO

Stoichiometry Calculations: Amounts of Reactants and Products in chemical reaction



Use the **fabulous four steps**!

1. Write the **balanced chemical equation**.
2. Convert quantities of **known** substances into **moles**.
3. Use **coefficients** in balanced equation to calculate the number of **moles of the sought quantity**.
4. Convert moles of sought quantity into the **desired units**.

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

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

2. Assemble the tools

$96.1\ g\ C_3H_8 \rightarrow$ moles $C_3H_8 \rightarrow$ moles $O_2 \rightarrow g\ O_2$

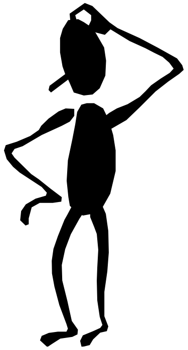
✓ $n_{C_3H_8} = \frac{96.1}{44.1} = 2.18\ \text{mol}\ C_3H_8$

✓ $1\text{mol}\ C_3H_8 \longrightarrow 5\ \text{mol}\ O_2$

$2.18\ \text{mol} \longrightarrow ???\ \text{mol}\ O_2$

✓ $n_{O_2} = \frac{2.18 \times 5}{1} = 10.9\ \text{mol}\ O_2$

✓ $mass_{O_2} = 10.9\ x\ 32 = 348.8\ g$



Ex: Methanol burns in air according to the equation

$$2\ CH_3OH + 3\ O_2 \longrightarrow 2\ CO_2 + 4\ \underset{m=??}{H_2O}$$

If 209 g of methanol are used up in the combustion, what mass of water is produced?

grams CH_3OH ⟶ moles CH_3OH ⟶ moles H_2O ⟶ grams H_2O

- ✓ Balanced equation
- ✓ $n_{CH_3OH} = \frac{209}{32} = 6.53\ mol$ CH_3OH
- ✓ n_{H2O} :

$2\ CH_3OH \longrightarrow 4H_2O$ (mol ratio)

6.53 mol ⟶ ???

- ✓ $n_{H_2O} = \frac{6.53x4}{2} = 13.06$
- ✓ $mass_{H_2O} = 13.06 \text{ x } 18 = 235.08\ g\ H_2O$

Limiting Reactant

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

Excess reactant

- Reactant that has some amount left over at end
- Present in higher # of moles

Four Steps to determine the limiting reagent

1. Balanced reaction: Done.
2. Find the mole of each reactant in the reaction
3. Divide the # of mole of each reactant on it coefficient
4. The one that give the smallest # in step 3 is the limiting reagent

Ex: For the following reaction $2NH_3 + CO_2 \longrightarrow (NH_2)_2CO + H_2O$

If we start with 637.2 g NH_3 and 1142g CO_2

a) which of the two reactants is the limiting reagent ?

1- Balanced reaction √

2- mol $NH_3 = \frac{637.2}{17.03} = 37.16$, and mol $CO_2 = \frac{1142}{44} = 25.9$

3- NH_3 : 37.16/2 =18.7 (Smallest) ∴ **NH_3 is the Limiting reagent**

and CO_2 : 25.9/1= 25.9 (CO_2 is excess)

b) Calculate the mass of product $(NH_2)_2CO$ formed

To find the mass formed of this product, we relate it to the limiting reagent (using mole ratio)

2 mol NH_3 $\longrightarrow$ 1 mol $(NH_2)_2CO$

37.16 mol $\longrightarrow$???? mol $(NH_2)_2CO$

✓ mol $(NH_2)_2CO = \frac{37.16 \text{ x } 1}{2} = 18.71$ mol

✓ mass $(NH_2)_2CO$ = 18.71 x 60.06 g/mol =1124 g (theoretical yield)

c) How many excess reagent (gram)is left at the end of reaction ?

The CO_2 excess left (left over)=(initial mass of CO_2 – reacted mass of CO_2)

➢ **First will find the Reacted mass of CO2 :**

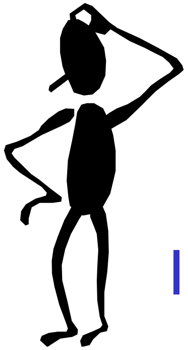
1 mol CO_2 $\longrightarrow$ 2mol NH_3

???? mol CO_2 $\longleftarrow$ 37.16 mol NH_3

✓ **mol CO_2 =37.16/2 =18.71**

✓ **reacted mass of CO_2 = 18.71 x 44= 823.4 g**

✓ **The mass left over of CO_2= initial mass - reacted mass= 1142-823.4= 319 g**



Do You Understand **Limiting Reactants**?

In a reaction, 124 g of Al are reacted with 601 g of Fe_2O_3.

$$2\,Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2\,Fe$$

Calculate the mass of Al_2O_3 formed in grams.

Also Limiting reagent can be determine based on the following statement
“ the limiting reagent will yield the smaller amount of the product”

1. Balanced reaction: √

2. Moles of “given” reactants.

Moles of Al = 124 g / 26.9815 g/mol = 4.60 mol
Moles of Fe_2O_3 = 601 g / 159.6882 g/mol = 3.76 mol

3. Moles of “desired” product, Al_2O_3.

$$2\,Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2\,Fe$$

$$\begin{array}{l}\text{Moles of } Al_2O_3\\ \text{based on Al}\end{array} = \frac{4.60 \text{ mol Al}}{1} \times \frac{1 \text{ mol } Al_2O_3}{2 \text{ mol Al}} = 2.30 \text{ mol } Al_2O_3$$

$$\begin{array}{l}\text{Moles of } Al_2O_3\\ \text{based on } Fe_2O_3\end{array} = \frac{3.76 \text{ mol } Fe_2O_3}{1} \times \frac{1 \text{ mol } Al_2O_3}{1 \text{ mol } Fe_2O_3} = 3.76 \text{ mole } Al_2O_3$$

Keep the smaller answer! Al is the limiting reactant.

4. Grams of Al_2O_3.

Grams of Al_2O_3 = 2.30 mol X 101.9612 g/mol = **235 g**

Reaction Yield

Theoretical Yield is the amount of product that would result if all the limiting reagent reacted.(calculated)

Actual Yield is the amount of product actually obtained from a reaction(experimentally).

-How much is obtained in mass units or in moles

- Actual yield usually is less than theoretical yield

Percent yield Relates the actual yield to the theoretical yield, It is calculated as:

$$\textbf{\% Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

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 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?

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

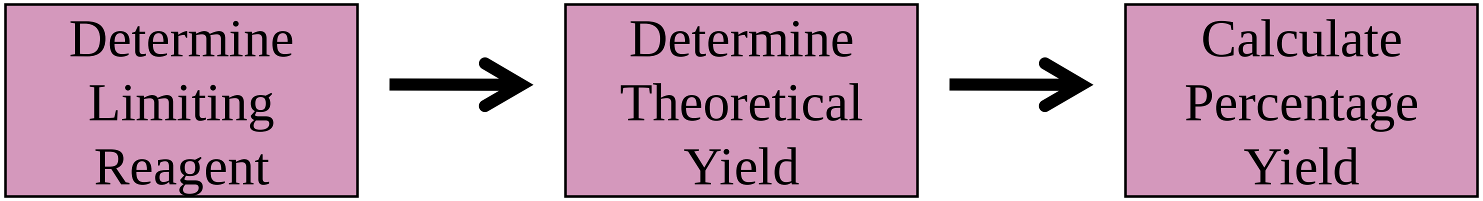
$$\%\ \text{yield} = \frac{58.3\ \text{g Cu}}{72.2\ \text{g Cu}} \times 100\% \mathbf{= 80.7\%}$$

Ex A chemist set up a synthesis of solid phosphorus trichloride 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

$$2\mathrm{P}(s) + 3\mathrm{Cl}_2(g) \longrightarrow 2\mathrm{PCl}_3(s)$$



Determine Limiting Reagent → Determine Theoretical Yield → Calculate Percentage Yield

Solution:

$$2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(s)$$

1. Determine Limiting Reactant

mol of P= 12/30.97= 0.39/2=0.19

mol of Cl_2= 35/70.9= 0.49/3=0.16 (smallest) Cl_2 is limiting reagent

2. Determine Theoretical Yield (mass of product PCl_3)

3 Cl_2: 2 PCl_3

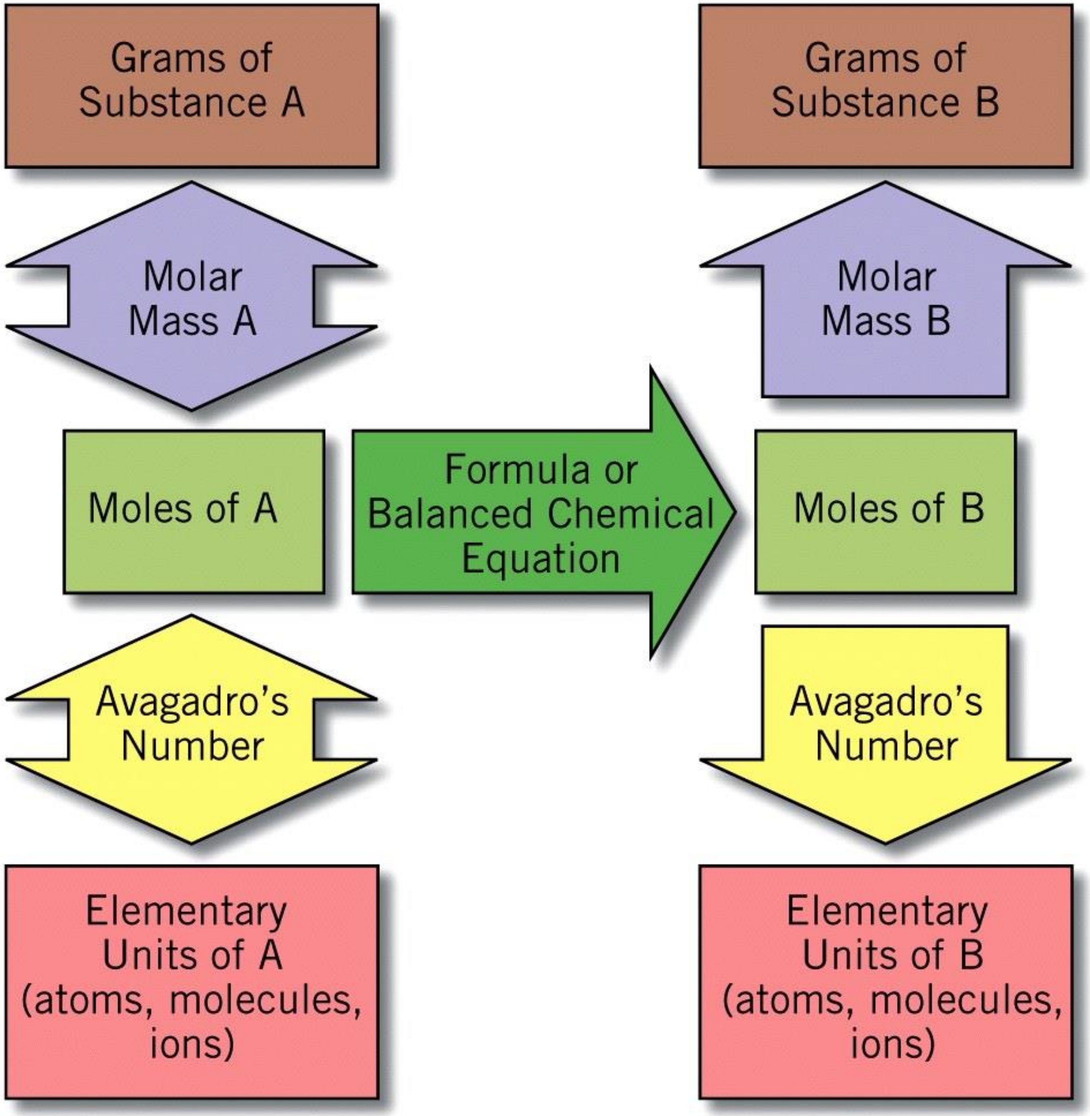
- ✓ mol PCl_3 =(0.49x2)/3= 0.33 mol PCl_3
- ✓ Mass PCl_3 = 0.33 x 137.32 = 44.9 g PCl_3 (theoretical yield)

3. Determine Percentage Yield

- Actual yield = 42.4 g

$$\boldsymbol{percentage\ yield = \left(\frac{42.4\ g\ PCl3}{44.9\ g\ PCl3}\right)} \text{ x100=94.43\%}$$

Stoichiometry Summary



Grams of Substance A

Molar Mass A

Moles of A

Avagadro's Number

Elementary Units of A (atoms, molecules, ions)

Formula or Balanced Chemical Equation

Grams of Substance B

Molar Mass B

Moles of B

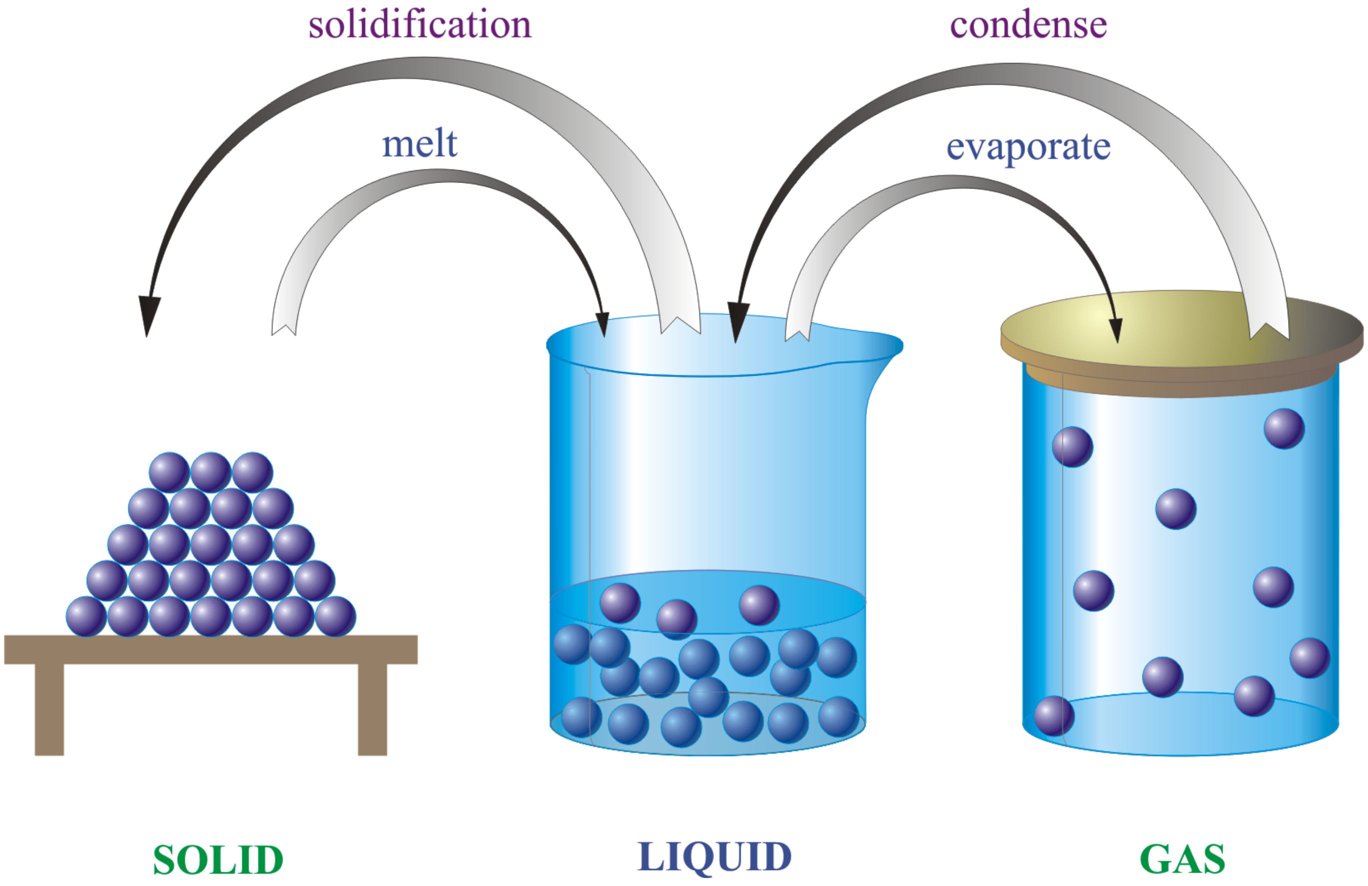
Avagadro's Number

Elementary Units of B (atoms, molecules, ions)

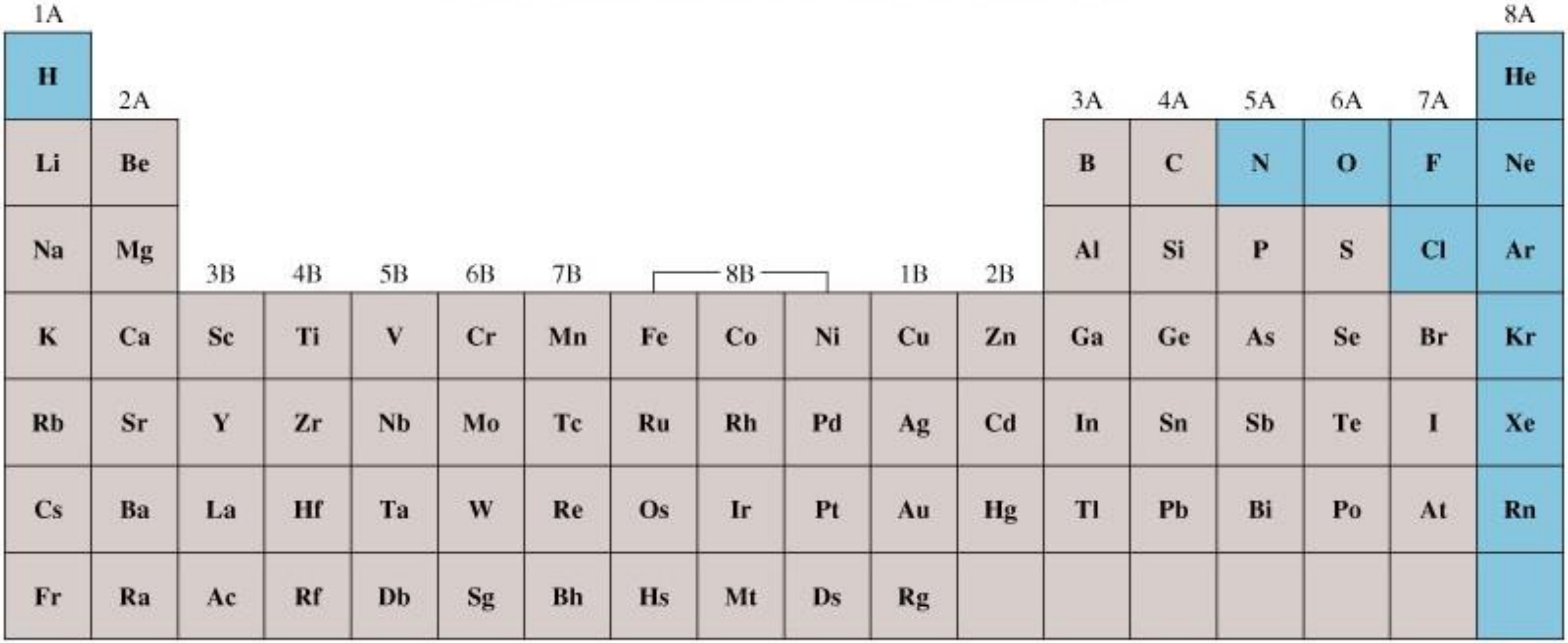
Gases

Chapter 5

States of matter



Elements that exist as gases at 25^{0}C and 1 atmosphere



1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

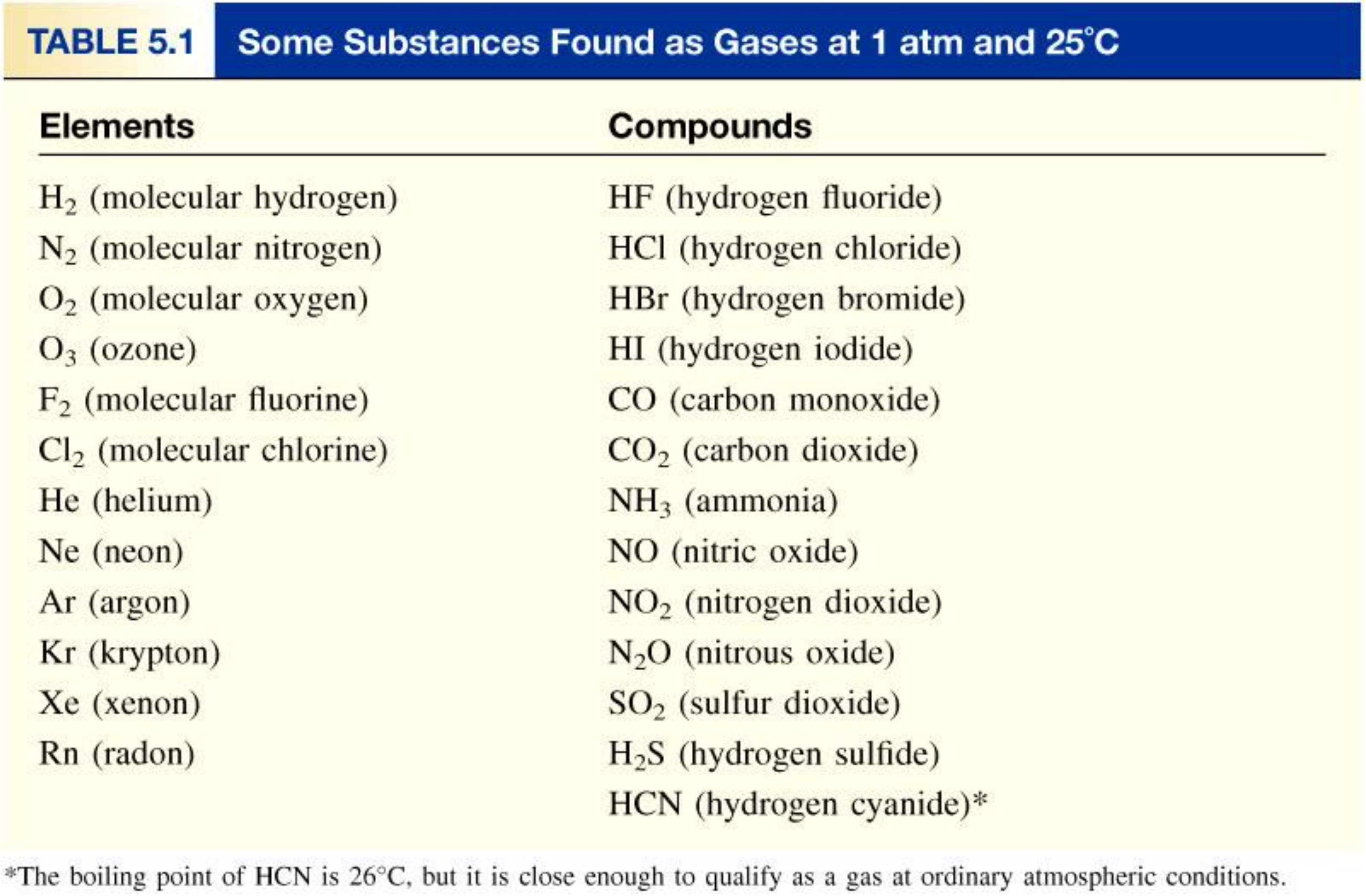


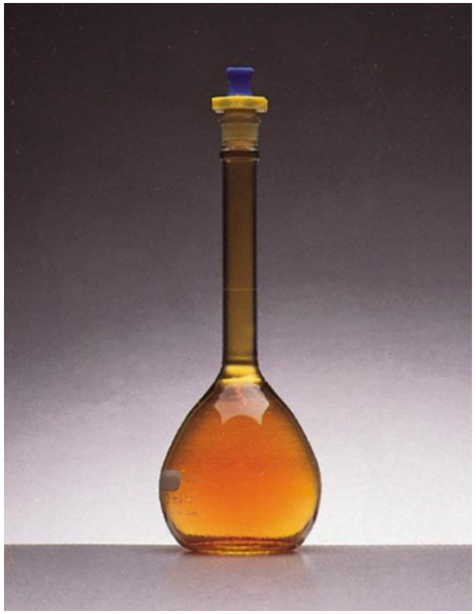
TABLE 5.1 Some Substances Found as Gases at 1 atm and 25°C

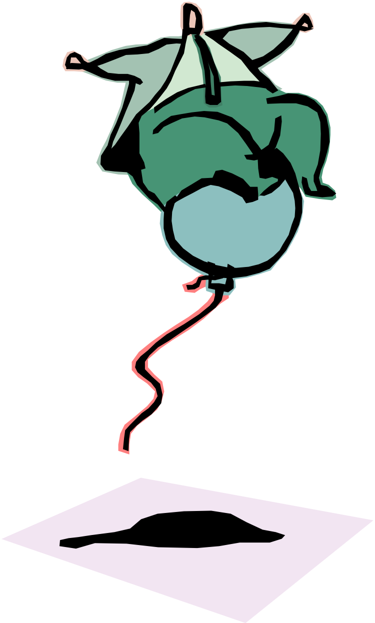
Elements	Compounds
H_2 (molecular hydrogen)	HF (hydrogen fluoride)
N_2 (molecular nitrogen)	HCl (hydrogen chloride)
O_2 (molecular oxygen)	HBr (hydrogen bromide)
O_3 (ozone)	HI (hydrogen iodide)
F_2 (molecular fluorine)	CO (carbon monoxide)
Cl_2 (molecular chlorine)	CO_2 (carbon dioxide)
He (helium)	NH_3 (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO_2 (nitrogen dioxide)
Kr (krypton)	N_2O (nitrous oxide)
Xe (xenon)	SO_2 (sulfur dioxide)
Rn (radon)	H_2S (hydrogen sulfide)
	HCN (hydrogen cyanide)*

*The boiling point of HCN is 26°C, but it is close enough to qualify as a gas at ordinary atmospheric conditions.

Physical Characteristics of Gases

- Gases take the volume and shape of their containers.
- Gases are the most compressible state of matter.
- Gases will mix evenly and completely when confined to the same container.
- Gases have much lower densities than liquids and solids.





Four Physical Properties of Gases

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

Pressure, Its Measurement and Units

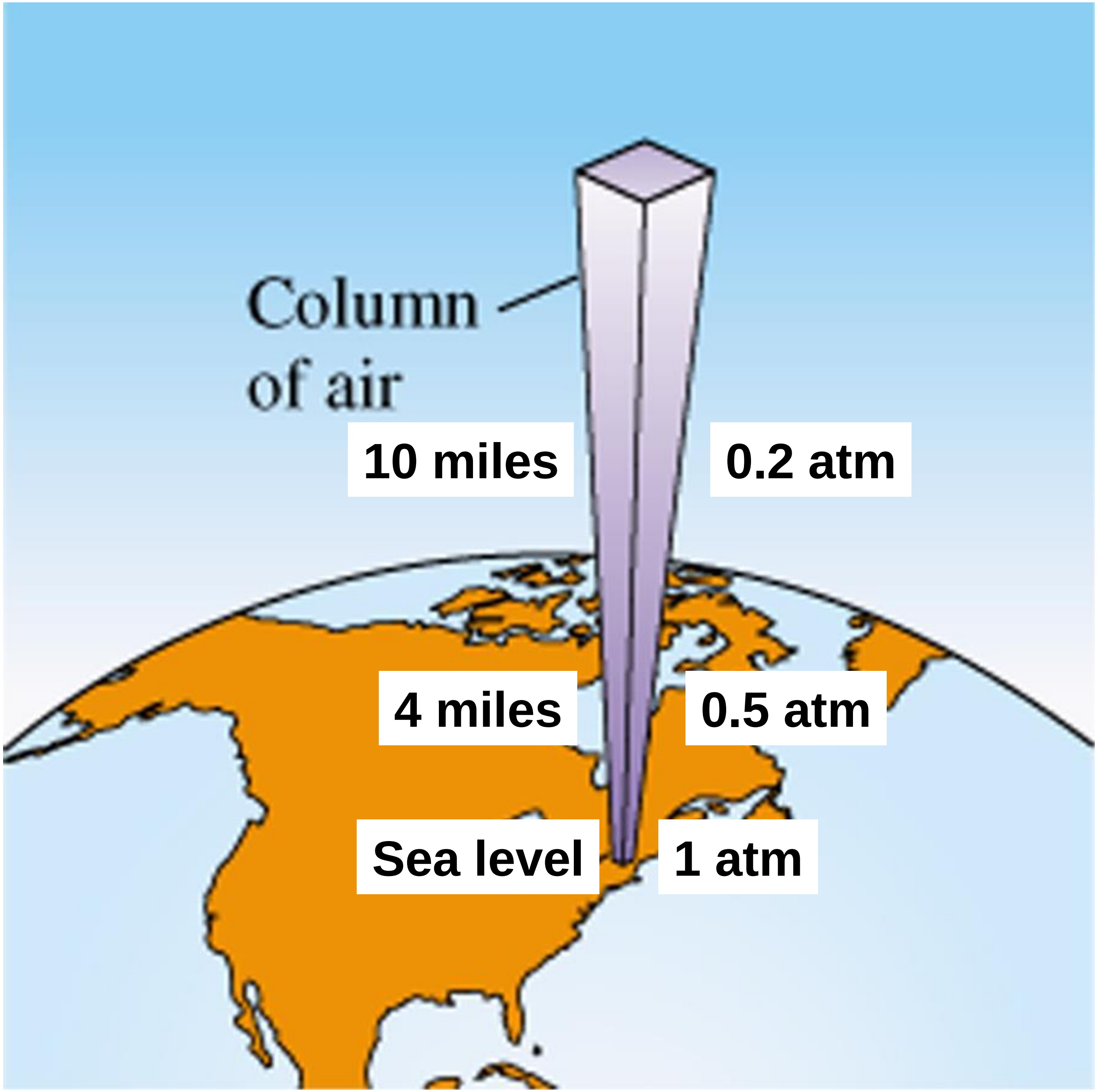
- Gases exert pressure on any surface with which they come in contact

$$\text{Pressure} = \frac{Force}{area} = \frac{\text{N}}{\text{m}^2} = \frac{1\text{Kg.m.s}^{-2}}{\text{m}^2}$$

- SI unit of pressure is pascal= pa

1 pascal (Pa) = 1 N/m^2

Atmospheric pressure : Force exerted by atmospheric column of air, per unit area


Column of air
10 miles
0.2 atm
4 miles
0.5 atm
Sea level
1 atm

Barometer: instrument for measuring atmospheric pressure

The standard atmospheric pressure(1 atm):

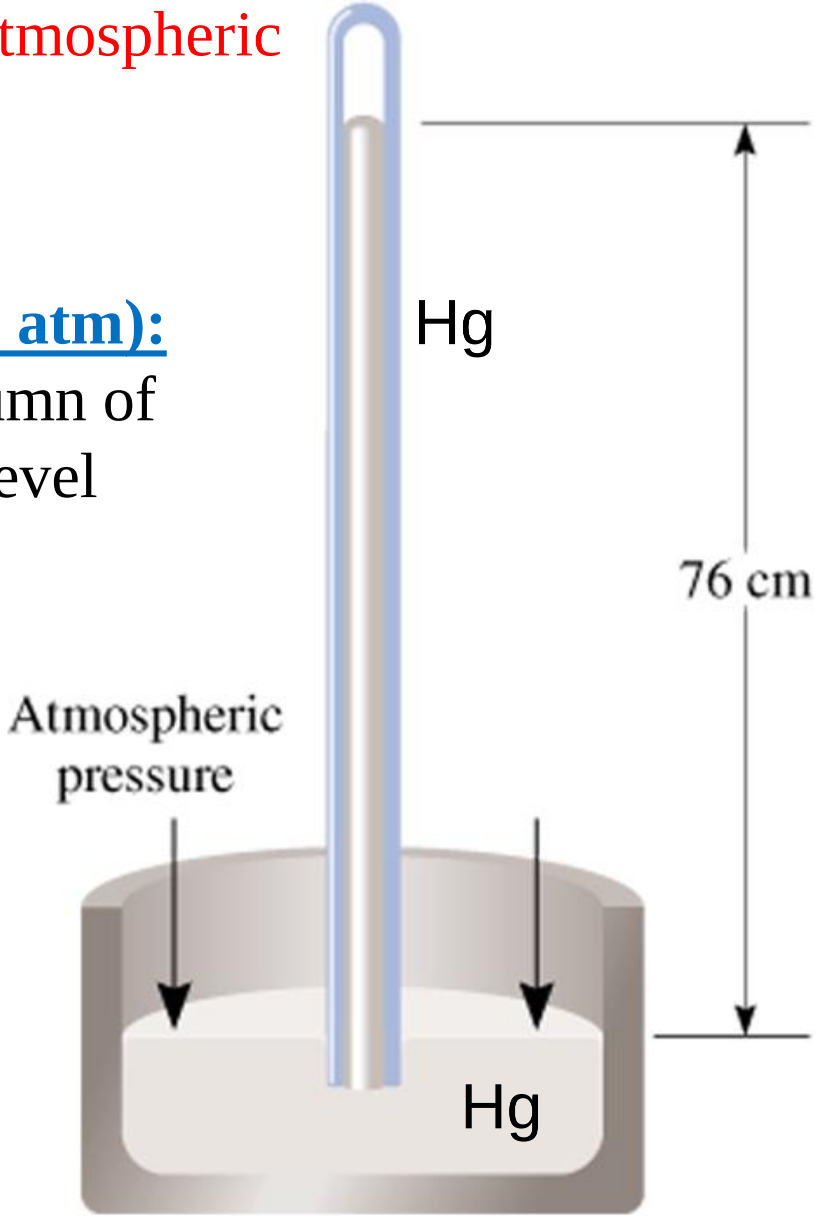
Equal to the pressure that support a column of Hg exactly 760mm(76 cm) high at sea level

1 atm = 760 mmHg = 760 torr

1 torr=1 mmHg

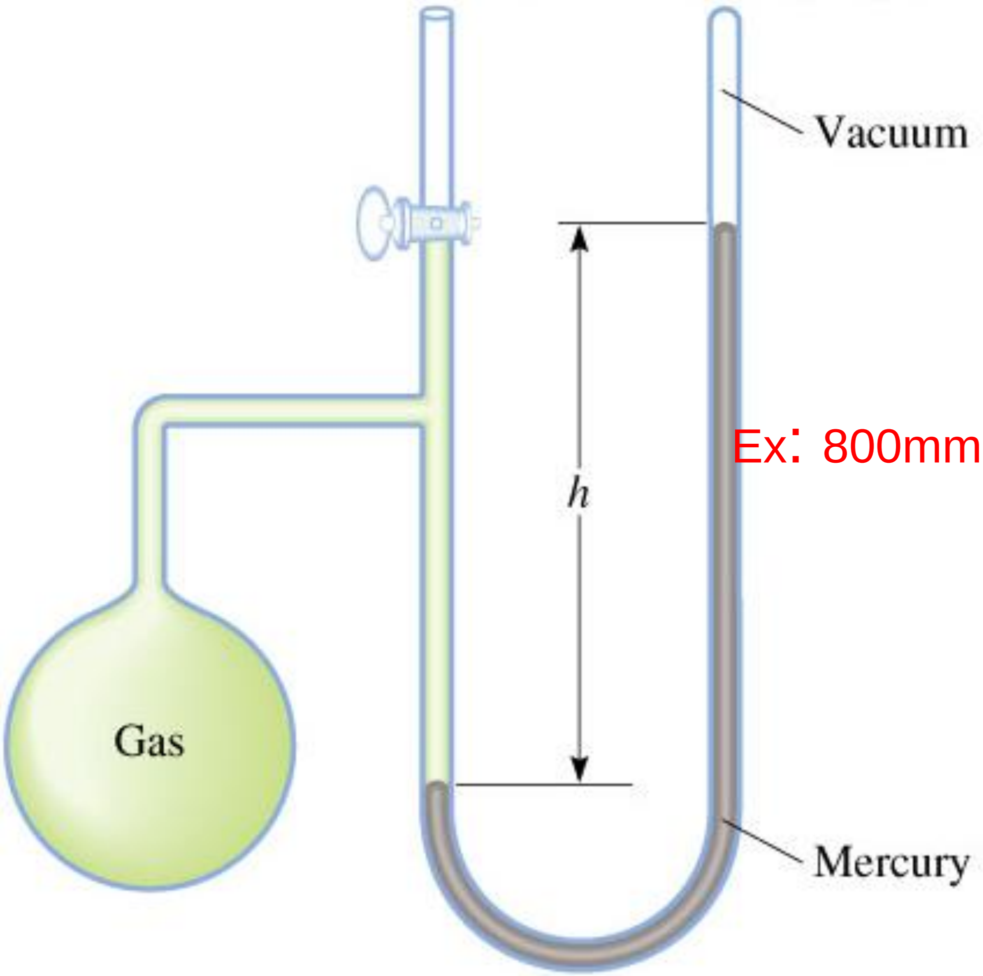
1 atm = 101,325 Pa=101Kpa

$1atm \equiv$ 1.013 Bar



Barometer

Manometers Used to Measure Gas Pressures



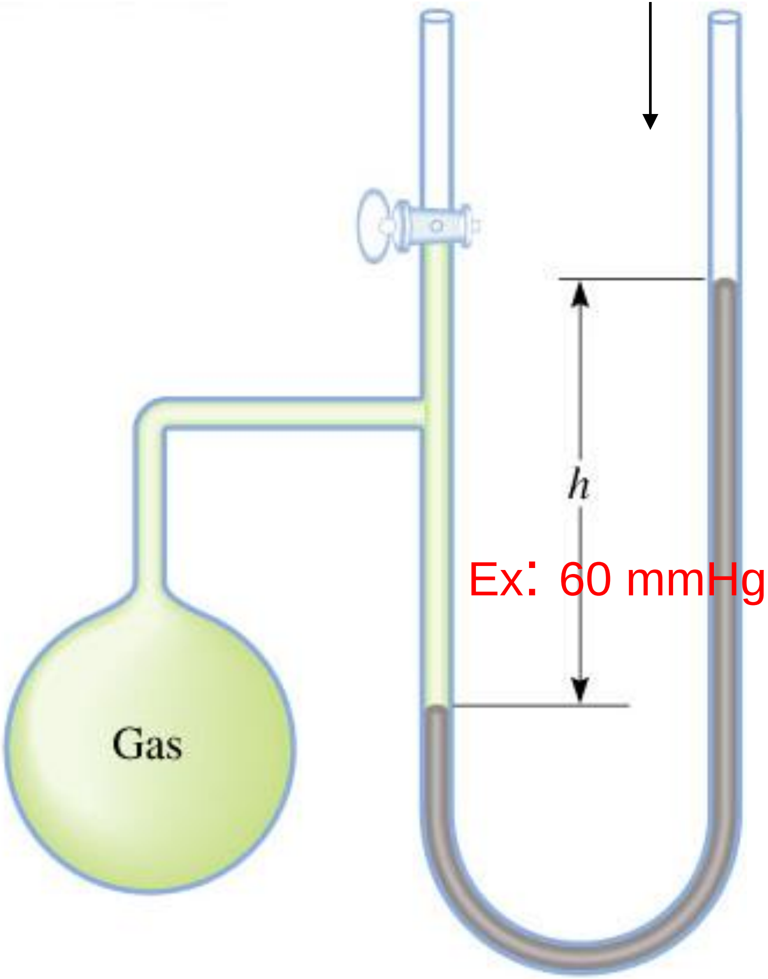
Ex: 800mmHg

$P_{gas} = P_h$ =800 mmHg

(a)

Closed tube manometer

atm.pressure=760mmH



Ex: 60 mmHg

$P_{gas} = P_h + P_{atm}$

$P_{gas} = 60 + 760 = 820\ mmHg$

(b)

open tube manometer

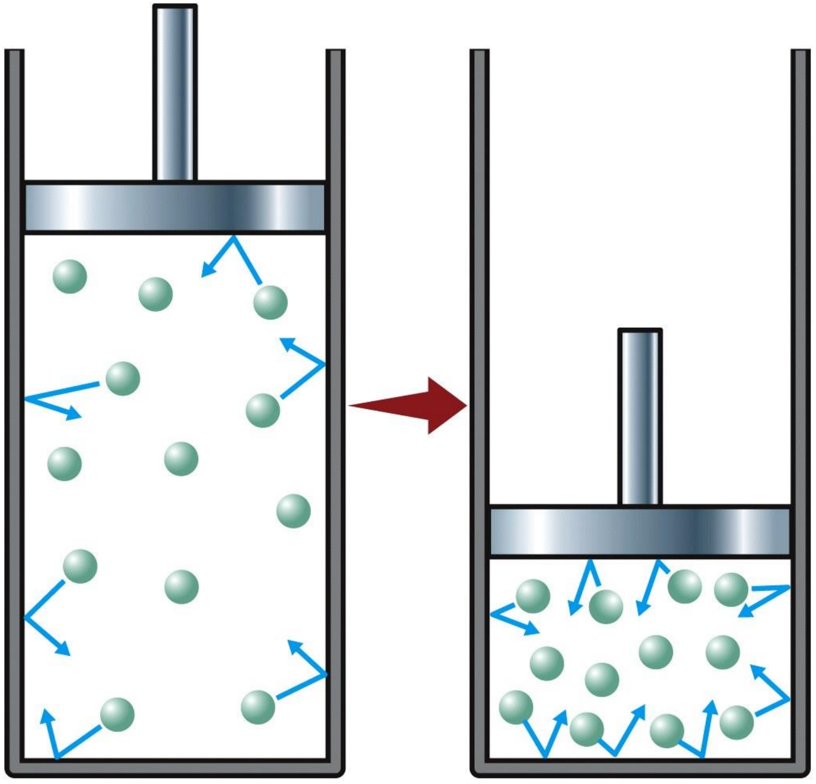
Gas laws

1) **Boyle's Law**: Studied relationship between ***P*** and ***V*** ***(at constant n & T)***

The pressure of a fixed amount of gas at a constant temperature is inversely proportional to the volume of the gas"

As ***V*** ↓, ***P*** ↑ $(V \alpha \frac{1}{P})$

$P_1V_1 = P_2V_2 \quad Boyle's\ law$



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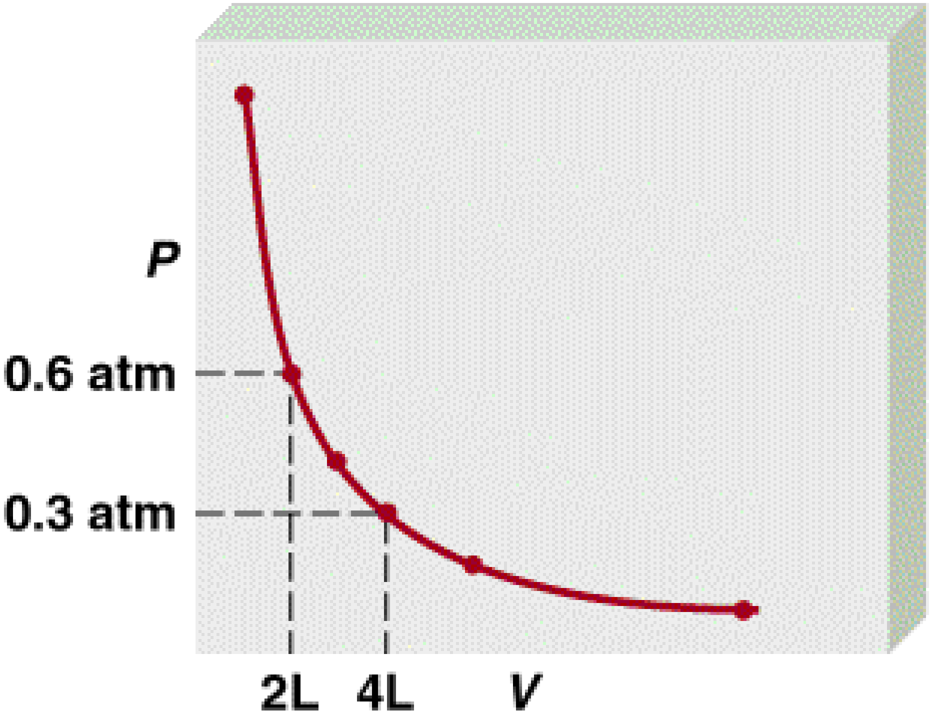
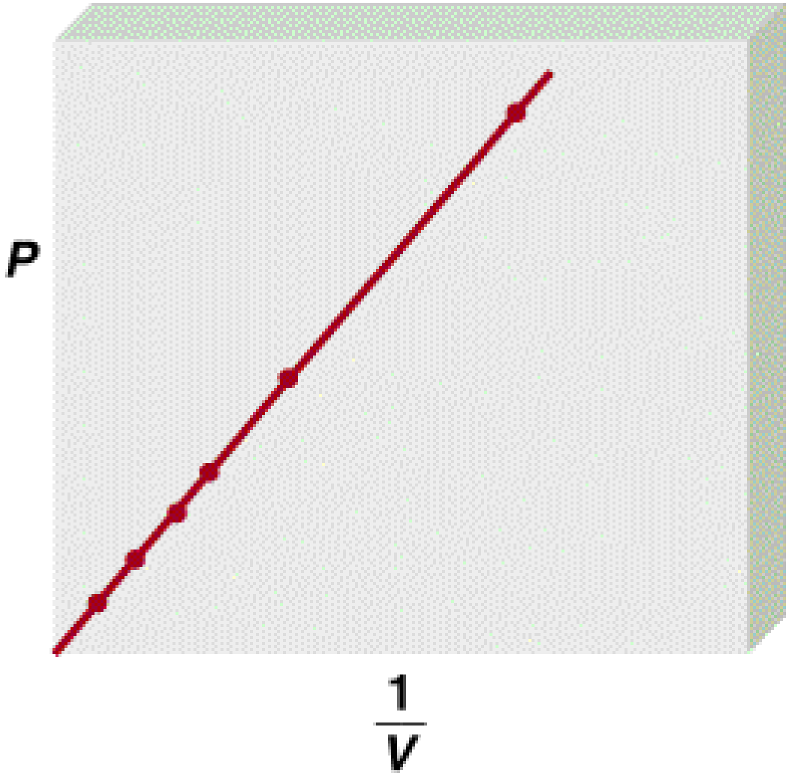


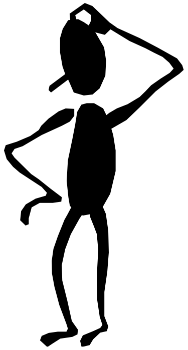


P α $1/V$

P = constant.1/V

P=k.1/V

Constant temperature
Constant amount of gas



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?

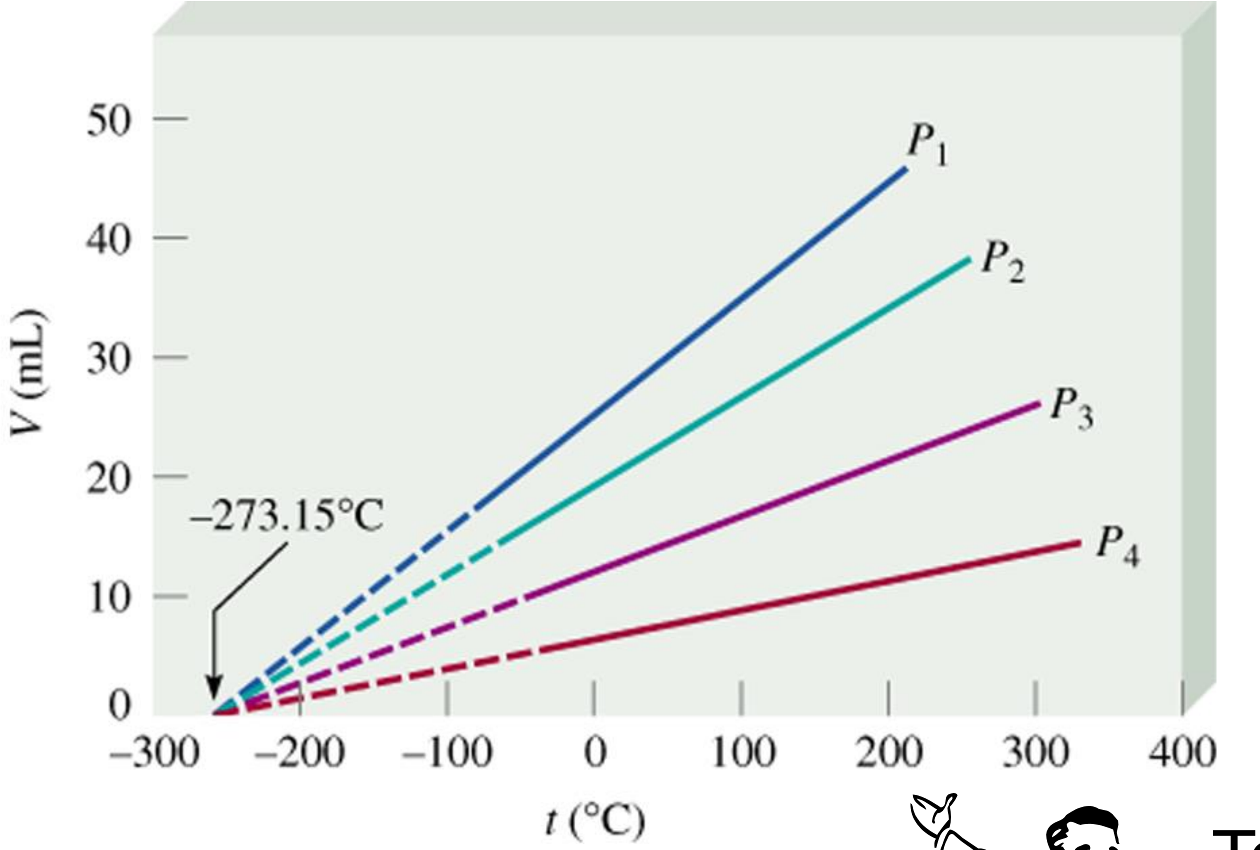
$$P_1 \text{ x } V_1 = P_2 \text{ x } V_2$$

$P_1 = 726 \text{ mmHg}$ $P_2 = ?$

$V_1 = 946 \text{ mL}$ $V_2 = 154 \text{ mL}$

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

2) Charles's and Gay-Lussac's Law: Studied relationship between *T* and *V* (at constant P & n).



Charles' & Gay-Lussac's Law

$V \alpha T$

$V = \text{constant x } T$

$V_1/T_1 = V_2/T_2$ Charles's Law

Temperature **must** b in Kelvin

T (K) = t (^{0}C) + 273.15

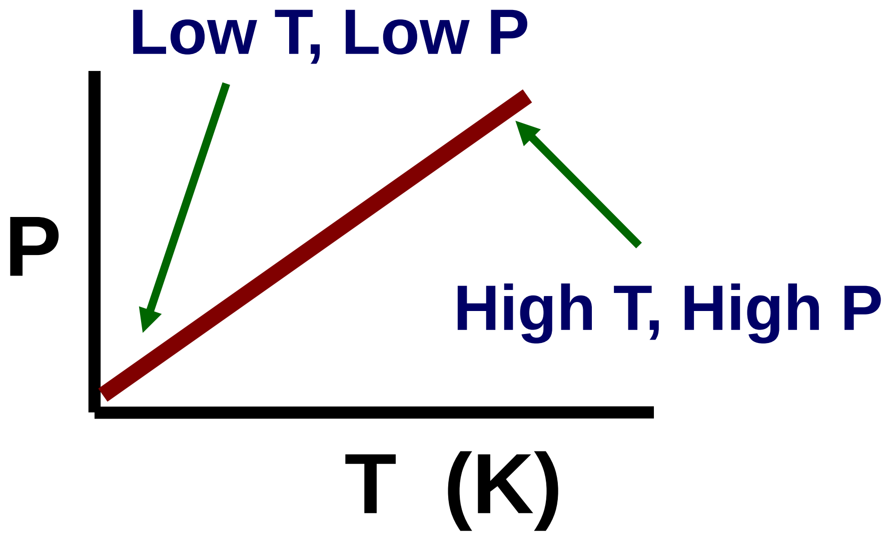
- They also Worked on relationship between pressure and temperature(at constant V & n)
- ***P*** ↑ as ***T*** ↑
- This is why we don't heat canned foods on a campfire without opening them!
- Showed that gas pressure is directly proportional to absolute temperature

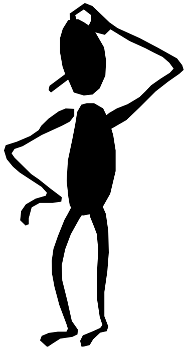
$$P \propto T$$

$$P = k_3 T$$

$$\frac{P}{T} = k_3$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$





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 L

V_2 = 1.54 L

T_1 = 398.15 K

T_2 = ?

T_1 = 125 (^{0}C) + 273.15 (K) = 398.15 K

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

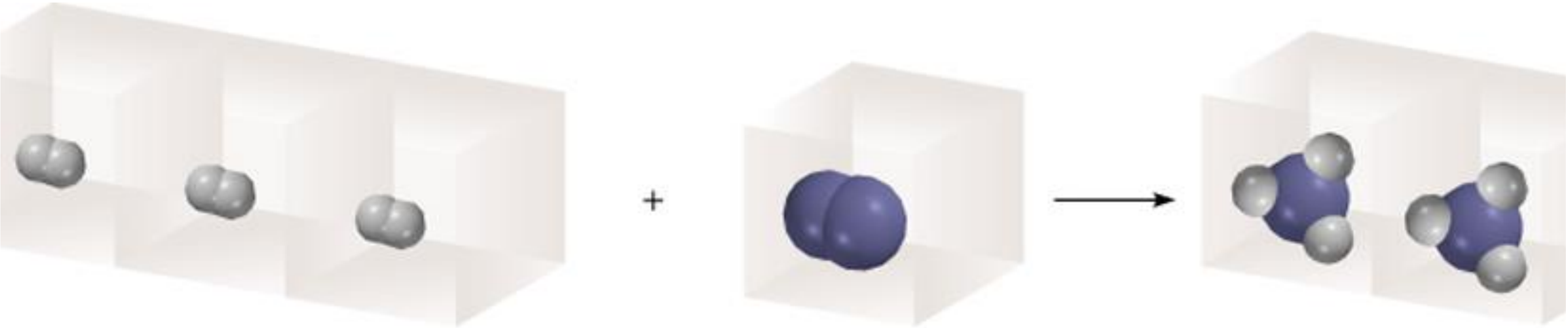
3) ***Avogadro's Law***: Studied relationship between ***n*** and ***V*** (at constant P & T).

$V \propto$ number of moles (n)

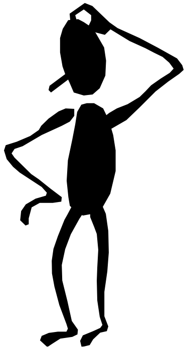
V = constant x n

$V_1 / n_1 = V_2 / n_2$ Avogadro's Law

Constant temperature
Constant pressure



$3H_2\ (g)$	+	$N_2\ (g)$	$\longrightarrow$	$2NH_3\ (g)$
3 molecules	+	1 molecule	$\longrightarrow$	2 molecules
3 moles	+	1 mole	$\longrightarrow$	2 moles
3 volumes	+	1 volume	$\longrightarrow$	2 volumes



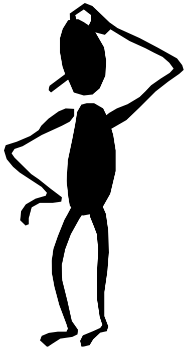
Ammonia burns in oxygen to form nitric oxide (NO) and water vapor. How many volumes of NO are obtained from one volume of ammonia at the same temperature and pressure?

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

$$1 \text{ mole } NH_3 \longrightarrow 1 \text{ mole } NO$$

At constant *T* and *P*

$$1 \text{ volume } NH_3 \longrightarrow 1 \text{ volume } NO$$



Ex. A certain lightbulb containing argon at 1.20 atm and 18 ^{0}C is heated to 85 ^{0}C at constant volume. What is the final pressure of argon in the lightbulb (in atm)?

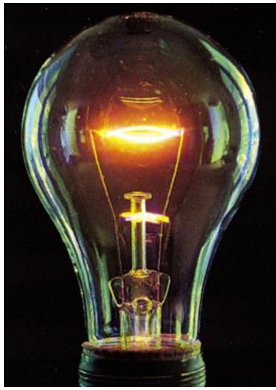
n, and *V* **are constant**

P_1 = 1.20 atm P_2 = ?

T_1 = 291 K T_2 = 358 K

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = P_1 \times \frac{T_2}{T_1} = 1.20 \text{ atm} \times \frac{358 \cancel{\text{K}}}{291 \cancel{\text{K}}} = 1.48 \text{ atm}$$



4)Ideal Gas law

Boyle's law: $\mathrm{V}\ \alpha\ \frac{1}{P}$ (at constant n and T)

Charles' law: $V\ \alpha\ T$ (at constant n and P)

Avogadro's law: $\mathrm{V}\ \alpha\ n$ (at constant P and T)

$$V\ \alpha\ \frac{nT}{P}$$

$$V = \text{constant x} \frac{nT}{P} = R\,\frac{nT}{P}$$

R is the **gas constant**

$$\boxed{PV = nRT}$$

Ideal Gas Law

PV = nRT

- Equation of state of a gas**:**
- If we know 3 of these variables, then we can calculate 4th
- Can define ***state*** of the gas by defining 3 of these values

Ideal Gas

- Hypothetical gas that obeys Ideal Gas Law relationship over all ranges of ***T***, ***V***, ***n*** and ***P***
- As T↑ and P↓, real gases ⇒ ideal gases

What is the value of *R*?

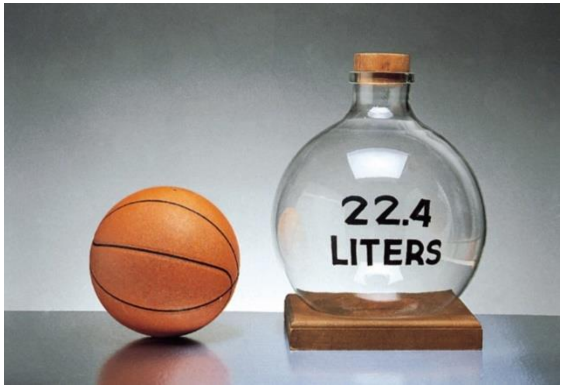
- The conditions 0 ^{0}C and 1 atm are called **standard temperature and pressure (STP).**

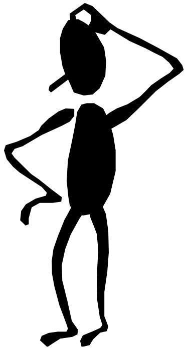
  STP= 1 atm and 273.15 K (0.0°C)
- Experiments show that at STP, 1 mole of an ideal gas occupies 22.414 L (standard molar volume)

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{(1\ \mathrm{atm})(22.414\mathrm{L})}{(1\ \mathrm{mol})(273.15\ \mathrm{K})}$$

$$R = 0.082057\ \mathrm{L} \bullet \mathrm{atm} / (\mathrm{mol} \bullet \mathrm{K})$$





What is the volume (in liters) occupied by 49.8 g of HCl at STP?

$T = 0\ ^{0}\text{C} = 273.15\ \text{K}$

$P = 1\ atm$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$n = 49.8\ \text{g} \times \frac{1\ \text{mol HCl}}{36.45\ \text{g HCl}} = 1.37\ \text{mol}$$

$$V = \frac{1.37\ \cancel{\text{mol}} \times 0.0821\ \frac{\text{L}\bullet\cancel{\text{atm}}}{\cancel{\text{mol}}\bullet\cancel{\text{K}}} \times 273.15\ \cancel{\text{K}}}{1\ \cancel{\text{atm}}}$$

$$V = 30.6\ \text{L}$$

Or volume of gas at STP = n x22.4L

- Ex: The label on a cylinder of an inert gas became illegible, so a student allowed some of the gas 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? Which of the periodic table inert gases was it?
- What do I know?
  - ***V***, ***mass***, ***T*** and ***P***

$$n = \frac{PV}{RT}$$

- $$V = 300mL \times \frac{1L}{1000mL} = 0.300L$$
- $Mass = 1.45\ g$
- Convert T from **°*C*** to ***K***.
- $T = 27.0°\mathrm{C} + 273.15\ \mathrm{K} = 300.2\ K$
- Convert ***P*** from ***torr*** to ***atm***

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

- Use ***V***, ***P***, and ***T*** to calculate ***n***

$$n = \frac{PV}{RT} = \frac{0.901atm \times 0.300L}{0.082057(atm \cdot L / mol \cdot K) \cdot 300.2K} = 0.01098\ mole$$

- Now use the **mass** of the sample and the moles of the gas (***n***) to calculate the molecular mass (***MM***)

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

- Gas = Xe (At. Mass = 131.29 *g/mol*)

- Ideal gas equation PV= nRT is useful for problems do not involve change in P,V, T and n
- If we have change in the conditions, we can use the modified form of the combined ideal gas equation:

$$\frac{P_1V_1}{n_1T_1} = R \quad (before\ change)$$

$$\frac{P_2V_2}{n_2T_2} = R \quad (after\ change)$$

$$\therefore \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

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

if $n_1 = n_2$

Combined Gas Law

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

Used for calculating effects of *changing conditions*

- T in Kelvin
- P and V any units, as long as units cancel

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

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

V_2 = 890 mL

* STP: Standard Temperature and Pressure

Standard Temperature = 273.15K and Standard Pressure = 1 atm

Using Combined Gas Law

- Ex: 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?
  - First, number of moles is constant even though actual number is not given
- You are given ***V***, ***P*** and ***T*** for initial state of system as well as ***T*** and ***V*** for final state of system and must find P_{final}
- This is a clear case for combined gas law

- List what you know and what you don’t know
- Convert all Temperatures to Kelvin
- Then solve for unknown—here P_2

P_1 = 745 torr

V_1 = 950 m^3

T_1 = 25.0 °C + 273.15
= 298.15 K

P_2 = ?

V_2 = 1150 m^3

T_2 = 60.0 °C + 273.15
= 333.15 K

$$P_2 = \frac{P_1V_1T_2}{T_1V_2} = \frac{745\,torr \times 950\,m^3 \times 333.15\,K}{298.15\,K \times 1150\,m^3}$$

P_2 = 688 torr

Combined Gas Law

- 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?

  - What do we know?
  - ***P*** and ***n*** are constant
- So Combined Gas Law simplifies to $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

V_1 = 1.60 L

V_2 = ?

T_1 = 20.0 °C + 273.15
= 293.15 K

T_2 = 37.0 °C + 273.15
= 310.15 K

- List what you know and what you don't know
- Convert all Temperatures to Kelvin
- Then solve for unknown—here V_2

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

$V_2 = 1.69\ L$

Determining Density of Gas

The number of moles of the gas, n, is given by

$$n = \frac{m}{\mathcal{M}}$$

where m is the mass of the gas in grams and $\mathcal{M}$ is its molar mass. Therefore

$$\frac{m}{\mathcal{M}V} = \frac{P}{RT}$$

Because density, d, is mass per unit volume, we can write

$$\boxed{d = \frac{m}{V} = \frac{P\mathcal{M}}{RT}} \longrightarrow \boxed{\mathcal{M} = \frac{dRT}{P}}$$

d is the density of the gas in g/L

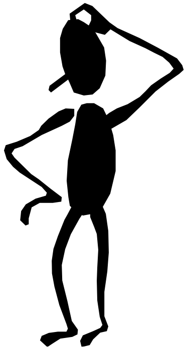
$$d = \frac{\text{atm}.g/mol}{\frac{L.atm}{K.mol}.K}$$

Ex: Calculate the density of carbon dioxide (CO_2) in grams per liter (g/L) at 0.990 atm and 55 ^{o}C.

Solution we convert temperature to kelvins (T = 273 + 55 = 328 K) and use 44.01 g for the molar mass of CO_2:

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT}$$

$$= \frac{(0.990\ \text{atm})(44.01\ \text{g/mol})}{(0.0821\ \text{L} \cdot \text{atm/K} \cdot \text{mol})(328\ \text{K})} = \boxed{1.62\ \text{g/L}}$$



A 2.10-L vessel contains 4.65 g of a gas at 1.00 atm and 27.0 ^{0}C. What is the molar mass of the gas?

$$\mathcal{M} = \frac{dRT}{P}$$

$$d = \frac{m}{V} = \frac{4.65\text{ g}}{2.10\text{ L}} = 2.21\,\frac{\text{g}}{\text{L}}$$

$$\mathcal{M} = \frac{2.21\,\frac{\text{g}}{\cancel{\text{L}}} \text{ x } 0.0821\,\frac{\cancel{\text{L}}\bullet\cancel{\text{atm}}}{\text{mol}\bullet\cancel{\text{K}}} \text{ x } 300.15\,\cancel{\text{K}}}{1\,\cancel{\text{atm}}}$$

$$\mathcal{M} = 54.6\text{ g/mol}$$

- **Ex**:A gaseous compound of phosphorus and fluorine 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.
- Know
  - Density
  - Temperature
  - Pressure

- ***d* =** 5.60 *g/L* $\therefore$ 1 *L* weighs 5.60 *g*
- So assume you have 1 *L* of gas
- ***V*** = 1.000 *L*
- ***Mass*** = 5.60 *g*
- Convert T from ***°C*** to ***K***
- ***T* =** 23.0**°*C*** + 273.15 ***K*** **=** 296.2 ***K***
- Convert ***P*** from ***torr*** to ***atm***

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

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

$$0.04058\ mole$$

- Use ***n*** and ***mass*** to calculate ***MM***

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

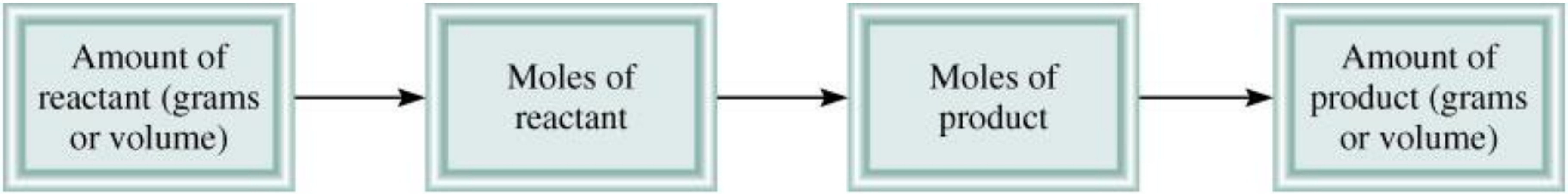
- Now to find molecular formula given ***empirical formula*** and ***MM***
- First find mass of empirical formula unit
- 1 **P** = 1 × 31*g/mol* = 31*g/mol*
- 2 **F** = 2 × 19 *g/mol* = 38 *g/mol*

- Mass of PF_2 = 69 g/mol

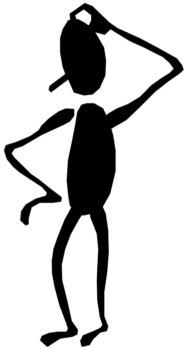
$$MF = \frac{molecular\ \ mass}{empirical\ \ mass} = \frac{138\,g\ /\ mol}{69\,g\ /\ mol} = 2$$

$\therefore$ the correct molecular formula is P_2F_4

Gas Stoichiometry



Amount of reactant (grams or volume) → Moles of reactant → Moles of product → Amount of product (grams or volume)



What is the volume of CO_2 produced at 37 ^{0}C and 1.00 atm when 5.60 g of glucose are used up in the reaction:

$$C_6H_{12}O_6\ (s) + 6O_2\ (g) \longrightarrow 6CO_2\ (g) + 6H_2O\ (l)$$

$$\text{g } C_6H_{12}O_6 \longrightarrow \text{mol } C_6H_{12}O_6 \longrightarrow \text{mol } CO_2 \longrightarrow V\ CO_2$$

$$5.60\ \cancel{\text{g } C_6H_{12}O_6} \times \frac{1\ \cancel{\text{mol } C_6H_{12}O_6}}{180\ \cancel{\text{g } C_6H_{12}O_6}} \times \frac{6 \text{ mol } CO_2}{1\ \cancel{\text{mol } C_6H_{12}O_6}} = 0.187 \text{ mol } CO_2$$

$$V = \frac{nRT}{P} = \frac{0.187\ \cancel{\text{mol}} \times 0.0821\ \dfrac{\text{L}\bullet\cancel{\text{atm}}}{\cancel{\text{mol}}\bullet\cancel{\text{K}}} \times 310.15\ \cancel{\text{K}}}{1.00\ \cancel{\text{atm}}} = 4.76 \text{ L}$$

- **Ex**: In one lab, the gas collecting apparatus used a 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:

$$Na_2CO_{3(s)} + 2\ HCl_{(aq)} \rightarrow 2\ NaCl_{(aq)} + CO_{2(g)} + H_2O_{(\ell)}$$

- What do I know?
  - ***T***, ***P***, ***V*** and ***MM*** of Na_2CO_3
- What do I need to find?
  - grams Na_2CO_3
- How do I find this?
  - Use Ideal Gas Law to calculate moles CO_2
  - Convert moles CO_2 to moles Na_2CO_3
  - Convert moles Na_2CO_3 to grams Na_2CO_3

1. Use Ideal Gas Law to calculate moles CO_2
   a. First convert *mL* to *L*

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

   b. Convert torr to atm

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

   c. Convert °*C to K*

$$\boldsymbol{T} = 23.0°C + 273.15\ K = 296.2\ K$$

1. Use Ideal Gas Law to calculate moles CO_2

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

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

2. Convert moles CO_2 to moles Na_2CO_3

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

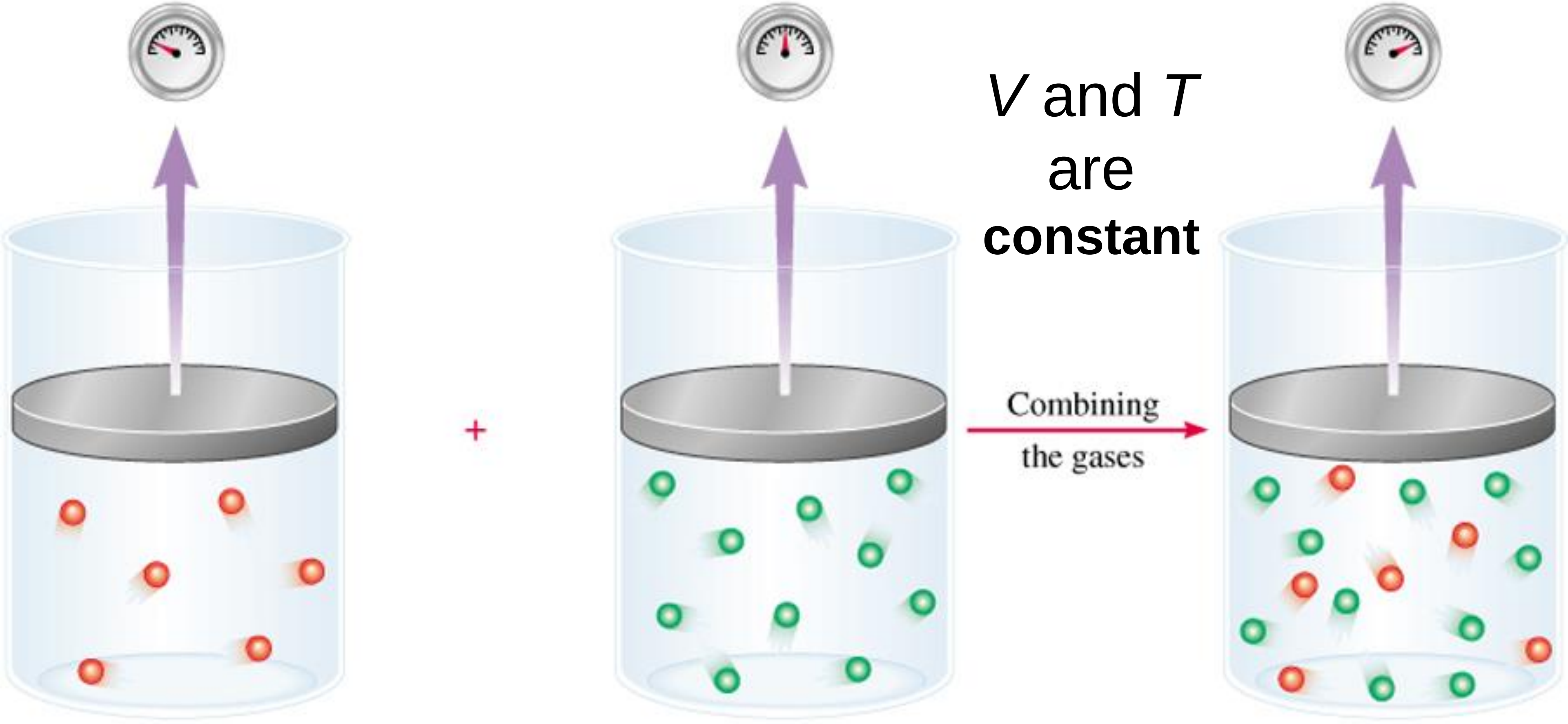
$$= 9.989 \text{ x } 10^{-3}\ mol\ \mathrm{Na_2CO_3}$$

3. Convert moles Na_2CO_3 to grams Na_2CO_3

$$9.989\times10^{-3}\,mol\ Na_2CO_3\times\frac{106\,g\ Na_2CO_3}{1\,mol\ Na_2CO_3}$$

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

Dalton's Law of Partial Pressures



V and *T*
are
constant

P_1 P_2 $P_{\text{total}} = P_1 + P_2$

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
- $\boldsymbol{P_{total} = P_1 + P_2 + \cdots}$
- Where $\boldsymbol{P_1, P_2,}$ = **partial pressures**

Dalton’s Law of Partial Pressures

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

$$P_1 = \frac{n_1 RT}{V} \qquad P_2 = \frac{n_2 RT}{V}$$

- So Total Pressure is

$$P_{total} = P_1 + P_2 + \cdots$$

$$= \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \cdots$$

Dalton’s Law of Partial Pressures

- Rearranging

$$P_{total} = (n_1 + n_2 + \cdots)\left(\frac{RT}{V}\right)$$

- Or

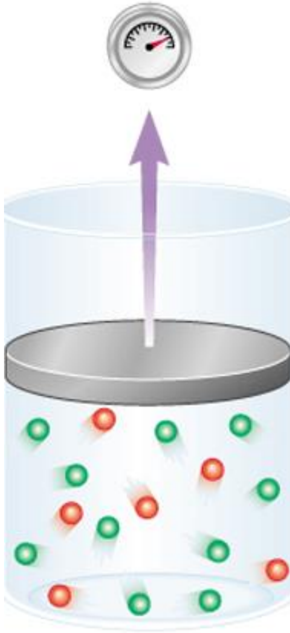
$$\boxed{P_{total} = n_{total}\left(\frac{RT}{V}\right)}$$

- Where $n_{total} = n_1 + n_2 + \cdots$

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

To relate the partial presser of component to the total pressure

:Consider a case in which two gases, A and B, are in a container of volume V.



$$P_A = \frac{n_A RT}{V}$$

n_A is the number of moles of A

$$P_B = \frac{n_B RT}{V}$$

n_B is the number of moles of B

$$P_T = P_A + P_B$$

$$\frac{P_A}{P_T} = (n_A RT/V)/(n_T RT/V)$$

$$= \frac{n_A}{n_T} = X_A$$

$$\therefore \frac{P_A}{P_T} = X_A$$

$$X_A = \frac{n_A}{n_A + n_B}$$

$$X_B = \frac{n_B}{n_A + n_B}$$

$X_A + X_B = 1$

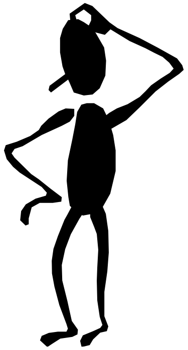
In binary solution

$$P_A = X_A P_T$$

$$P_B = X_B P_T$$

mole fraction $\boldsymbol{(X_i)} =$ $\dfrac{n_i}{n_T}$

$$\boxed{P_i = X_i P_T}$$



A sample of natural gas contains 8.24 moles of CH_4, 0.421 moles of C_2H_6, and 0.116 moles of C_3H_8. If the total pressure of the gases is 1.37 atm, what is the partial pressure of propane (C_3H_8)?

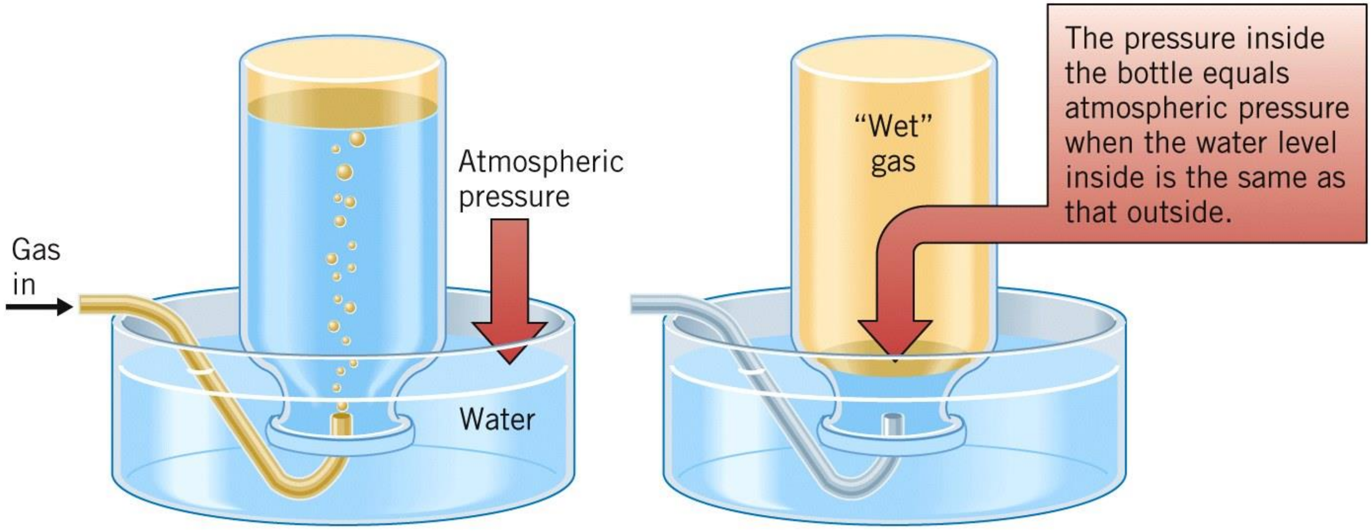
$P_i = X_i P_\mathrm{T}$ $\qquad$ $P_\mathrm{T} = 1.37\ \mathrm{atm}$

$$X_\mathrm{propane} = \frac{0.116}{8.24 + 0.421 + 0.116} = 0.0132$$

$$P_\mathrm{propane} = 0.0132 \text{ x } 1.37\ \mathrm{atm} = 0.0181\ \mathrm{atm}$$

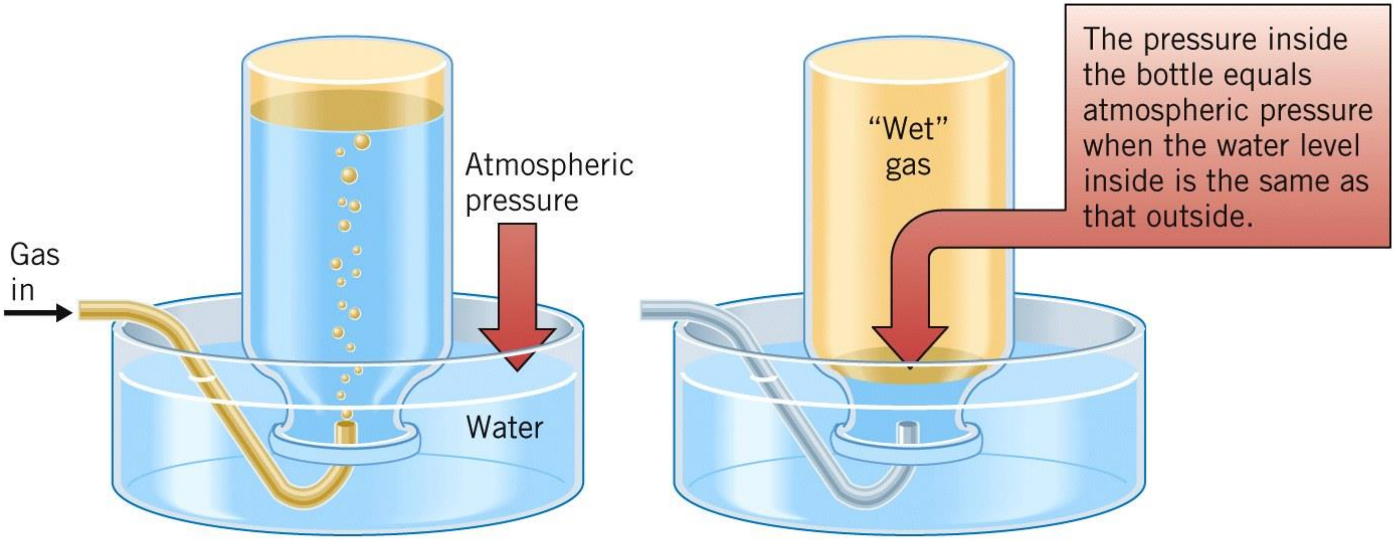
Collecting Gases over Water

- Application of Dalton’s Law of Partial Pressures
- Gases that don’t react with water can be trapped over water
- Whenever gas is collected by displacement of water, mixture of gases results
  - Gas in bottle is mixture of water vapor and gas being collected

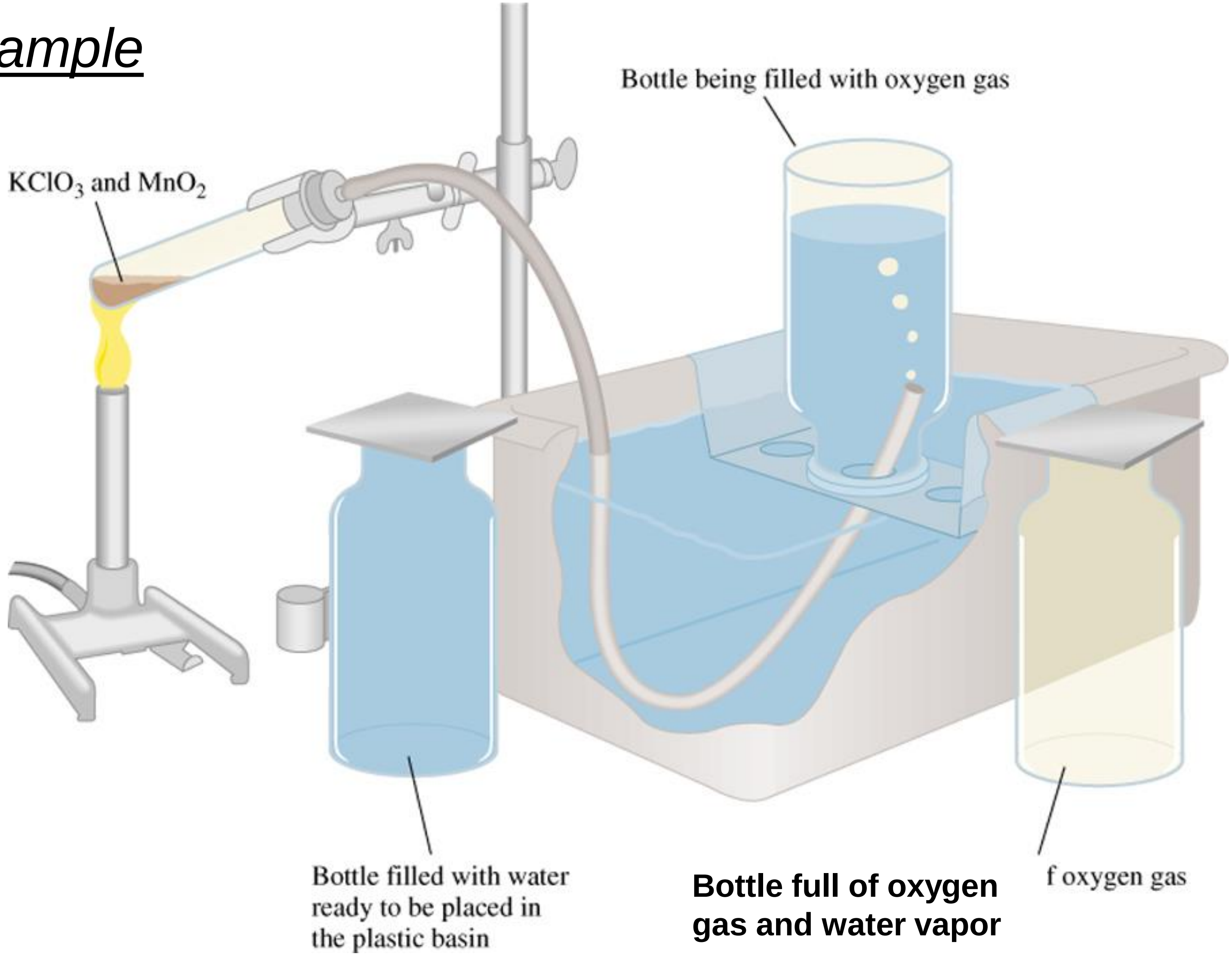


Collecting Gases over Water

- 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
- When rate of escape = rate of return
  - Number of water molecules in vapor state remains constant
- Gas saturated with water vapor = "Wet" gas



Example

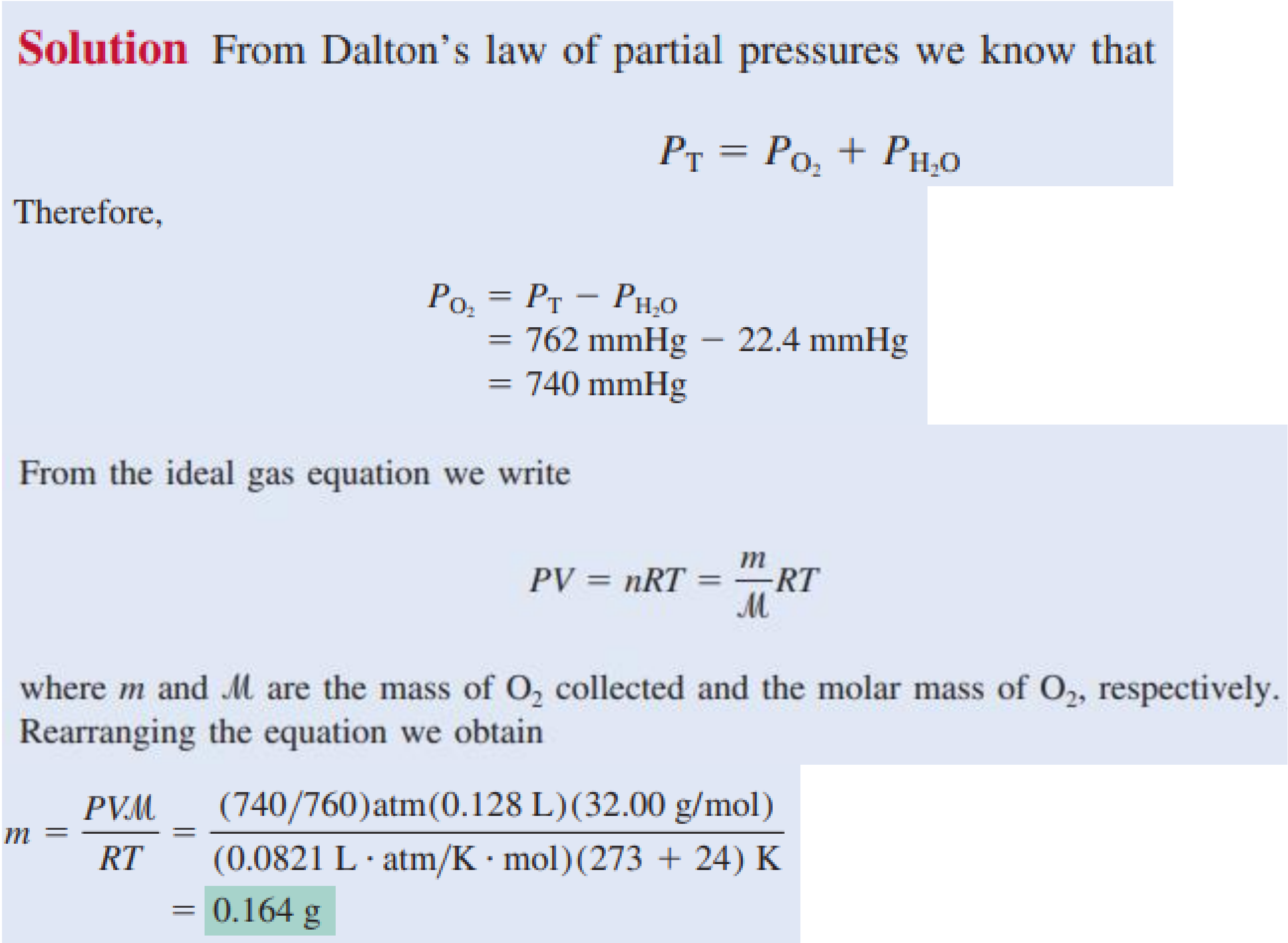


Bottle full of oxygen gas and water vapor

$$2\mathrm{KClO_3}\ (s) \longrightarrow 2\mathrm{KCl}\ (s) + 3\mathrm{O_2}\ (g)$$

$$P_\mathrm{T} = P_{\mathrm{O_2}} + P_{\mathrm{H_2O}}$$

Ex Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in the previous. The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of the water vapor at 24°C is 22.4 mmHg.



Solution From Dalton's law of partial pressures we know that

$$P_T = P_{O_2} + P_{H_2O}$$

Therefore,

$$\begin{aligned} P_{O_2} &= P_T - P_{H_2O} \\ &= 762\ \text{mmHg} - 22.4\ \text{mmHg} \\ &= 740\ \text{mmHg} \end{aligned}$$

From the ideal gas equation we write

$$PV = nRT = \frac{m}{\mathcal{M}}RT$$

where m and $\mathcal{M}$ are the mass of O_2 collected and the molar mass of O_2, respectively. Rearranging the equation we obtain

$$\begin{aligned} m = \frac{PV\mathcal{M}}{RT} &= \frac{(740/760)\text{atm}(0.128\ \text{L})(32.00\ \text{g/mol})}{(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(273+24)\ \text{K}} \\ &= 0.164\ \text{g} \end{aligned}$$

Kinetic Molecular Theory of Gases:

Attempts to explain properties of **ideal gases**.

1. A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be *points*; that is, they possess mass but have negligible volume. $V_{gas} \sim 0$
2. Particles are in constant motion
   - Collisions of particles with walls of container are cause of pressure exerted by gas
   - number collisions $\propto P_{gas}$
3. Gas molecules exert neither attractive nor repulsive forces on one another.
4. The average kinetic energy (KE_{avg})of the molecules is proportional to the temperature of the gas in kelvins.

$$KE_{avg} \propto T_K$$

$$\overline{\mathrm{KE}} = \tfrac{1}{2}m\overline{u^2} = CT$$

m is the mass of the molecule and ***u*** is its speed.

$\overline{u^2}$ is called mean square speed = the average of the square of the speeds of all the molecules.

$$\overline{\text{KE}} = \tfrac{1}{2}m\overline{u^2} = CT$$

The absolute temperature of a gas is a measure of the average kinetic energy of the molecules $\text{KE}_{\text{ave}} \propto T$

$$\text{KE}_{\text{ave}} = \frac{3}{2}RT$$

- As increase T, ↑ KE_{ave},
  - ↑ number collisions with walls, thereby increasing P

➢ One way to estimate molecular speed is to calculate the ***root-mean-square (rms) speed*** $\boldsymbol{(u_{rms})}$**,**

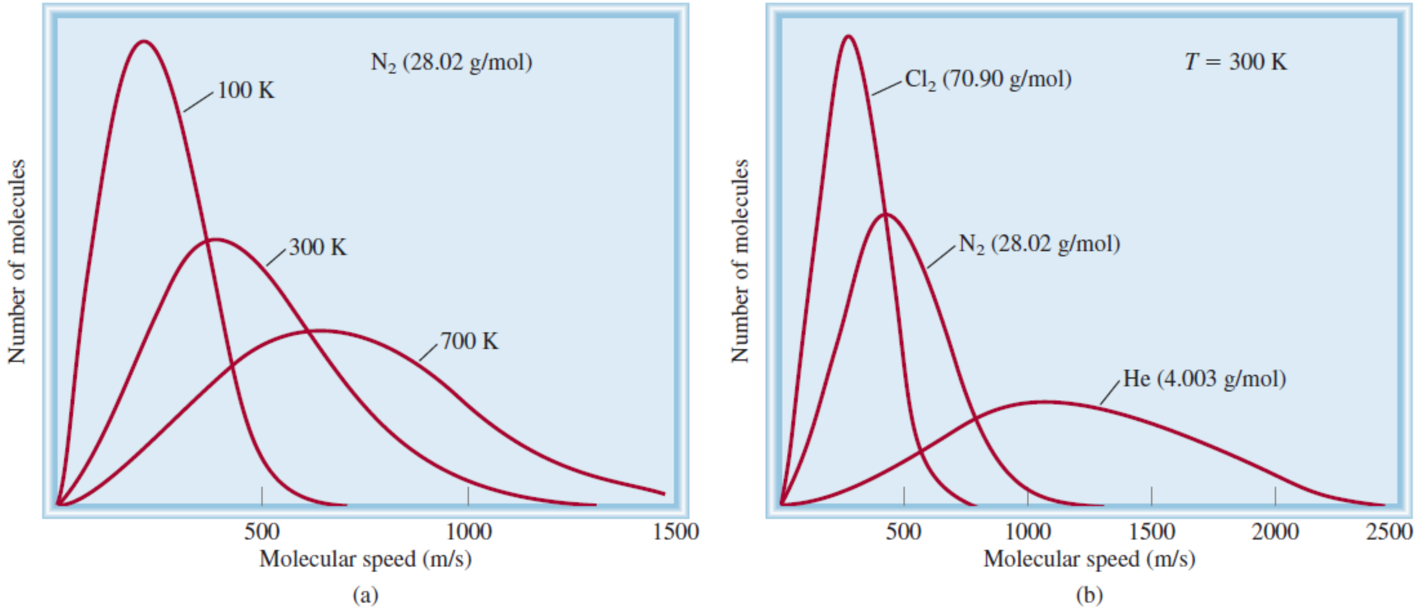
$$\sqrt{\overline{u^2}} = u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

Molar mass of gas

As molar mass of gas increase *rms* value decrease

Maxwell distribution of molecular speed

$$\sqrt{\overline{u^2}} = u_{\mathrm{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

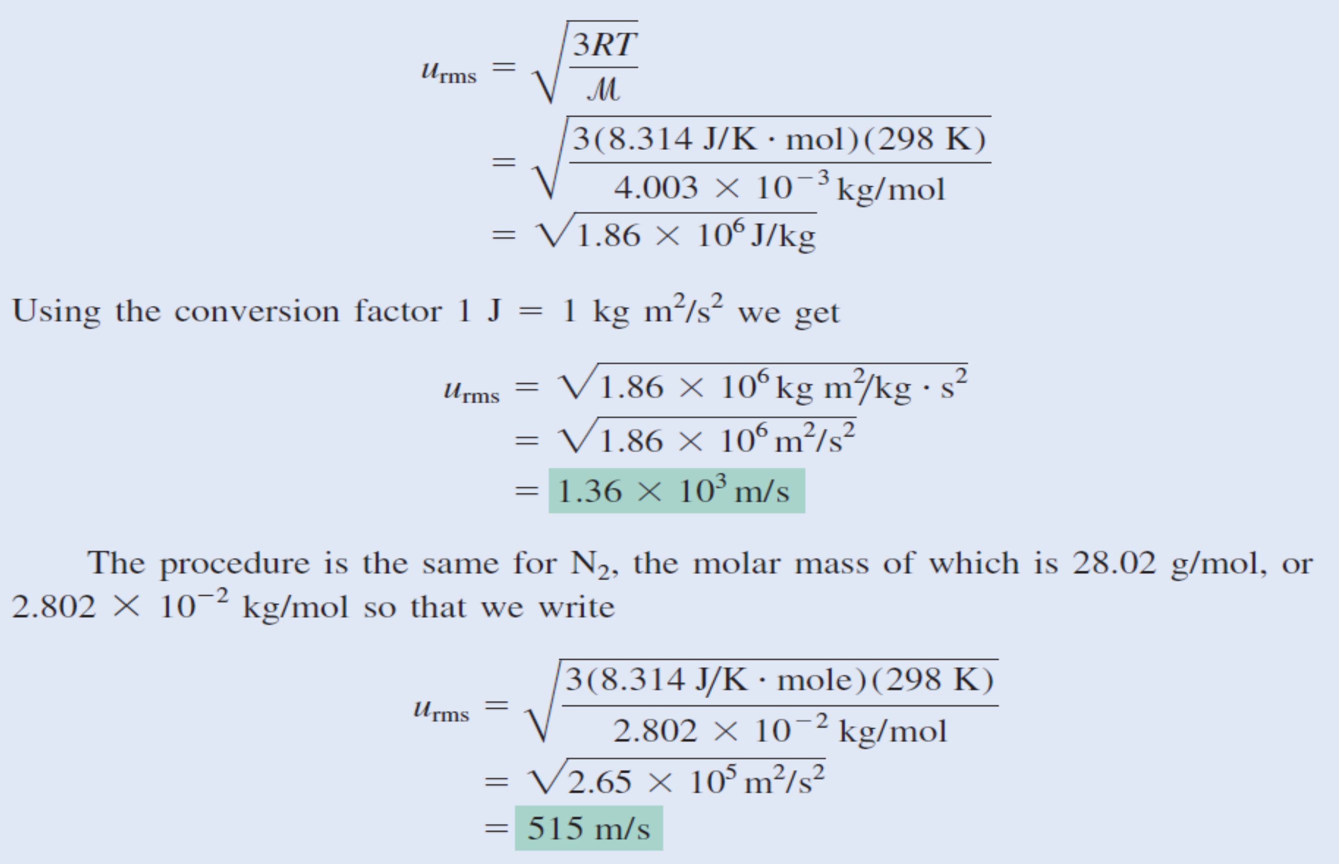


(a) The distribution of speeds for nitrogen gas at three different temperatures. At the higher temperatures, more molecules are moving at faster speeds. (b) The distribution of speeds for three gases at 300 K. At a given temperature, the lighter molecules are moving faster, on the average.

Ex: Calculate the root-mean-square speeds $\boldsymbol{u}_{\mathbf{rms}}$ of helium atoms and nitrogen molecules in m/s at 25°C.

Solution To calculate $\boldsymbol{u}_{\mathbf{rms}}$, the units of R should be 8.314 J/K.mol and, because 1 J = 1 kg m^2/s^2, the molar mass must be in **kg**/mol.

The molar mass of He is 4.003 g/mol = 4.003 x 10^{-3} kg/mol.



$$
\begin{aligned}
u_{\text{rms}} &= \sqrt{\frac{3RT}{\mathcal{M}}} \\
&= \sqrt{\frac{3(8.314\ \text{J/K}\cdot\text{mol})(298\ \text{K})}{4.003 \times 10^{-3}\ \text{kg/mol}}} \\
&= \sqrt{1.86 \times 10^{6}\ \text{J/kg}}
\end{aligned}
$$

Using the conversion factor 1 J = 1 kg m^2/s^2 we get

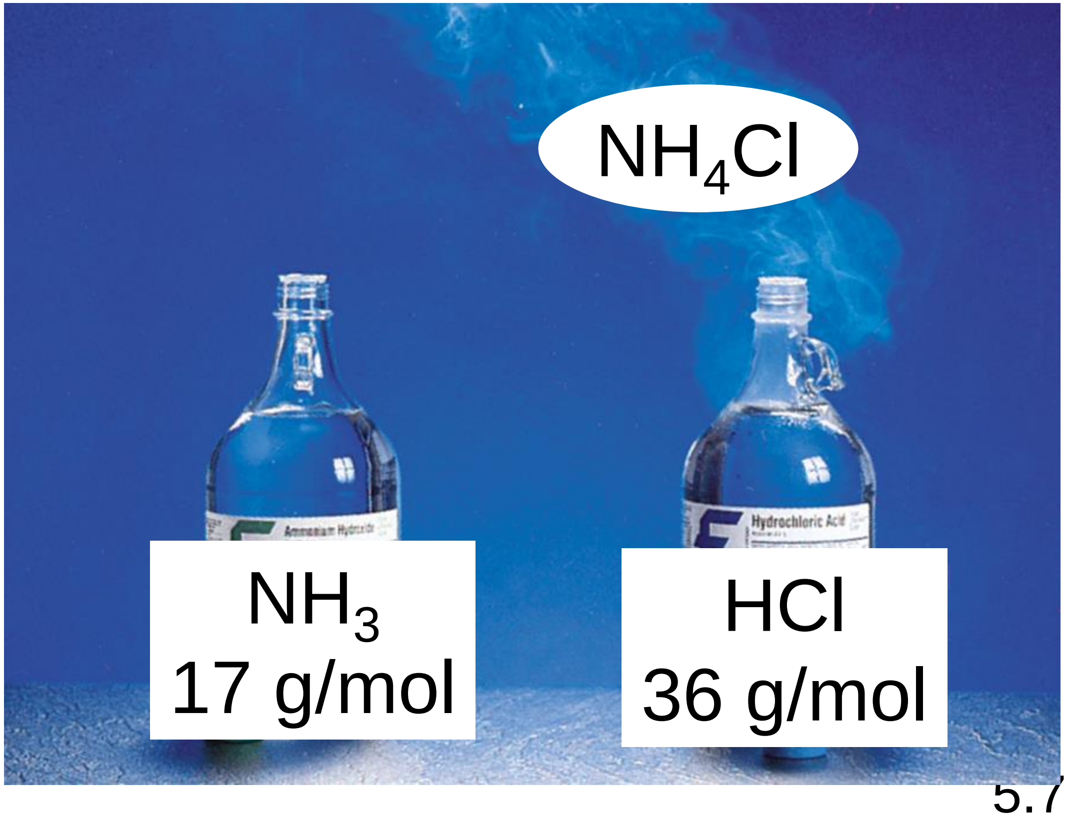
$$
\begin{aligned}
u_{\text{rms}} &= \sqrt{1.86 \times 10^{6}\ \text{kg m}^2/\text{kg}\cdot\text{s}^2} \\
&= \sqrt{1.86 \times 10^{6}\ \text{m}^2/\text{s}^2} \\
&= 1.36 \times 10^{3}\ \text{m/s}
\end{aligned}
$$

The procedure is the same for N_2, the molar mass of which is 28.02 g/mol, or 2.802×10^{-2} kg/mol so that we write

$$
\begin{aligned}
u_{\text{rms}} &= \sqrt{\frac{3(8.314\ \text{J/K}\cdot\text{mole})(298\ \text{K})}{2.802 \times 10^{-2}\ \text{kg/mol}}} \\
&= \sqrt{2.65 \times 10^{5}\ \text{m}^2/\text{s}^2} \\
&= 515\ \text{m/s}
\end{aligned}
$$

Gas diffusion is the gradual mixing of molecules of one gas with molecules of another by based on their kinetic properties.

Ex. Perfume in room



- Graham’s law of diffusion

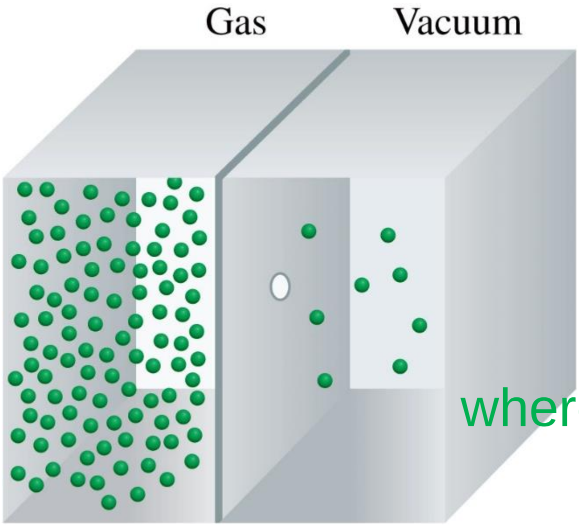
$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

where r_1 and r_2 are the diffusion rates of gases 1 and 2, and μ_1 and μ_2 are their molar masses, respectively

Result: Rate of effusion is inversely proportional to molecular mass of gas

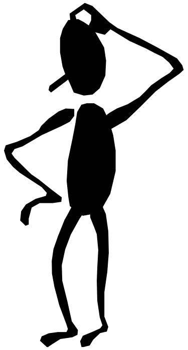
- Heavier gases effuse more slowly
- Lighter gases effuse more rapidly

Gas effusion is the is the process by which gas under pressure escapes from one compartment of a container to another by passing through a small opening.



$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

where t_1 and t_2 are the times for effusion for gases 1 and 2, respectively.



Nickel forms a gaseous compound of the formula $Ni(CO)_x$ What is the value of *x* given that under the same conditions methane (CH_4) effuses 3.3 times faster than the compound?

$r_1 = 3.3 \text{ x } r_2$

$\mathcal{M}_1 = 16 \text{ g/mol}$

$$\mathcal{M}_2 = \left(\frac{r_1}{r_2}\right)^2 \text{ x } \mathcal{M}_1 = (3.3)^2 \text{ x } 16 = 174.2$$

$58.7 + x \cdot 28 = 174.2$ $\quad x = 4.1 \sim 4$

Ex. Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6)

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

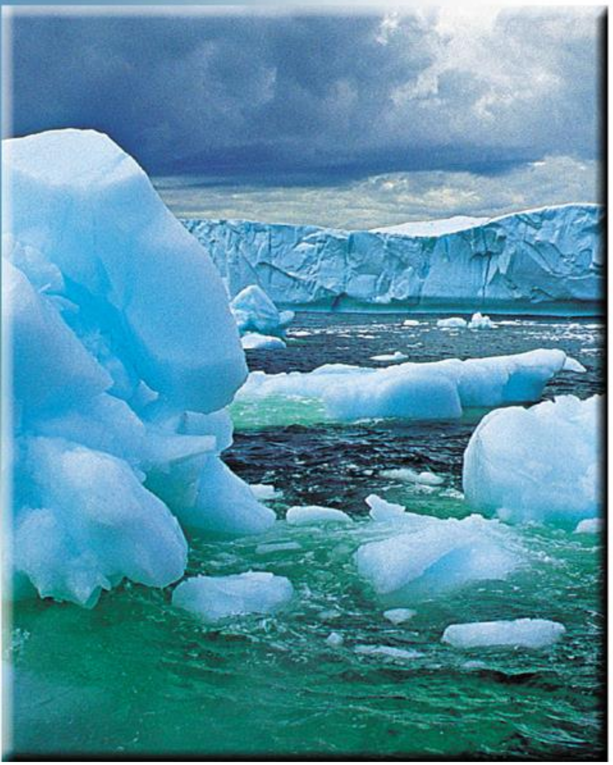
$$\frac{\text{Effusion Rate }(H_2)}{\text{Effusion Rate }(UF_6)} = \sqrt{\frac{M_{UF_6}}{M_{H_2}}} = \sqrt{\frac{352.02}{2.016}} = 13.2$$

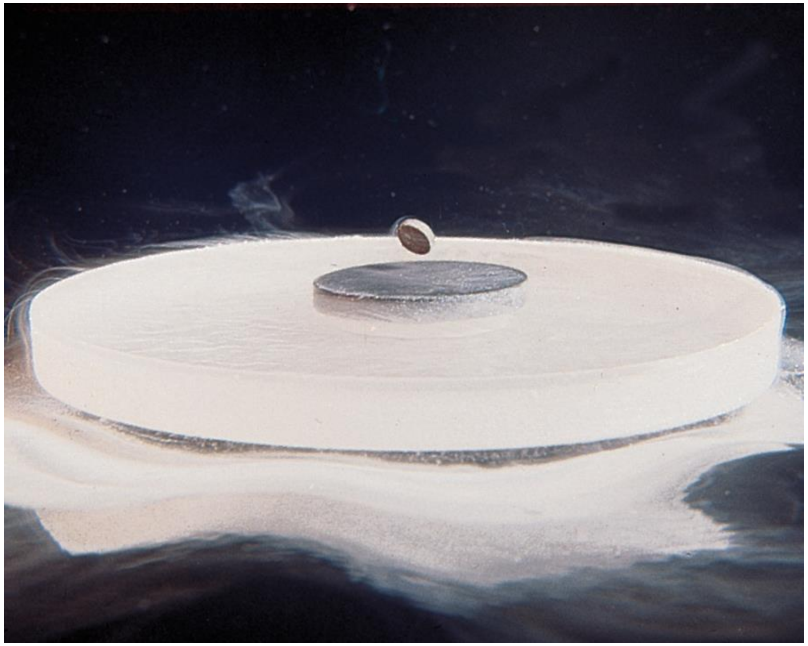
- Thus the very light H_2 molecules effuse ~13 times as fast as the massive UF_6 molecules.

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





Intermolecular Forces and Liquids and Solids

Chapter 11

A ***phase*** is a homogeneous part of the system in contact with other parts of the system but separated from them by a well-defined boundary.

2 Phases

Solid phase - ice

Liquid phase - water

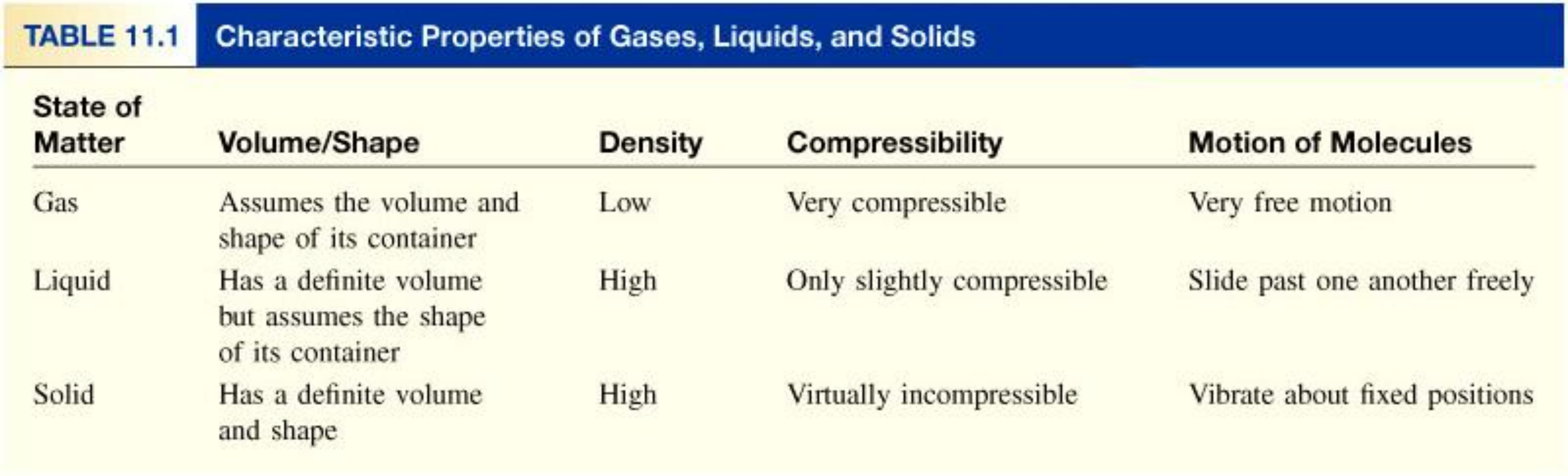


TABLE 11.1 Characteristic Properties of Gases, Liquids, and Solids

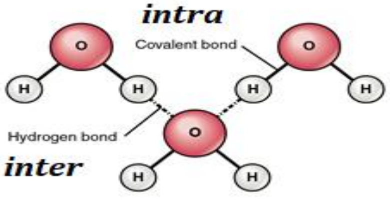
State of Matter	Volume/Shape	Density	Compressibility	Motion of Molecules
Gas	Assumes the volume and shape of its container	Low	Very compressible	Very free motion
Liquid	Has a definite volume but assumes the shape of its container	High	Only slightly compressible	Slide past one another freely
Solid	Has a definite volume and shape	High	Virtually incompressible	Vibrate about fixed positions

Intermolecular Forces

Intermolecular forces are attractive forces **between** molecules.

Intramolecular forces hold atoms together in a molecule.

Intermolecular vs Intramolecular



- 41 kJ to vaporize 1 mole of water (Intermolecular)
- 930 kJ to break all O-H bonds in 1 mole of water (Intramolecular)

Generally, **inter**molecular forces are much weaker than **intra**molecular forces.

“Measure” of intermolecular force

boiling point

melting point

ΔH_{vap}

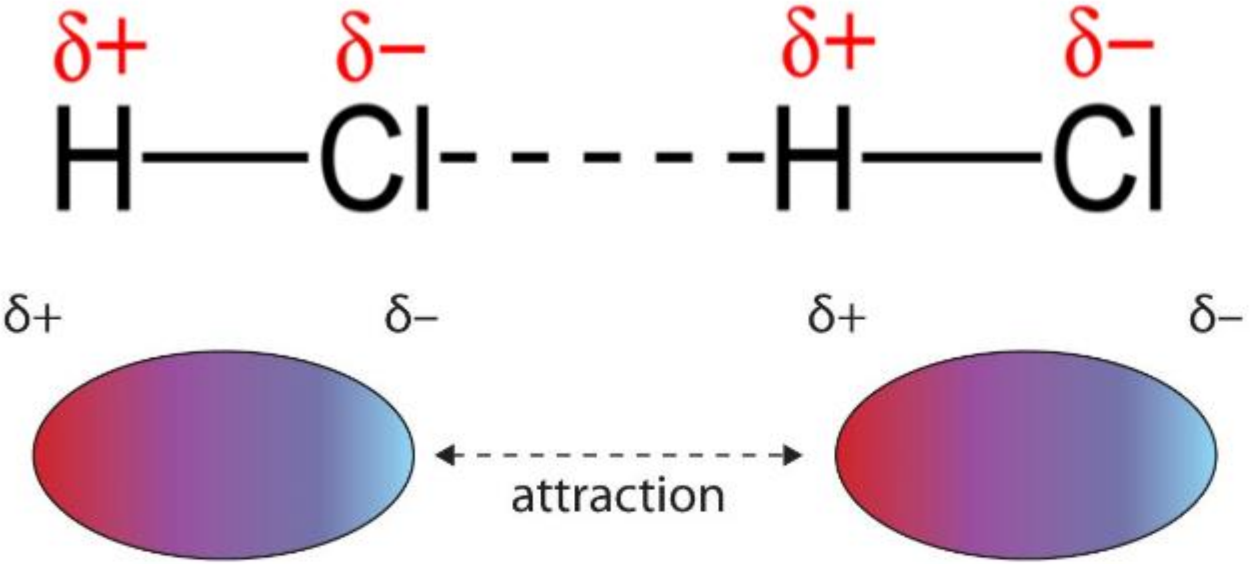
ΔH_{fus}

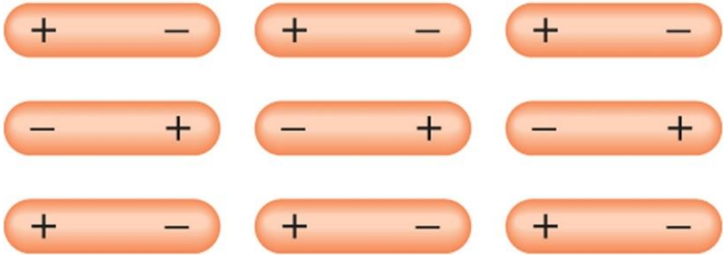
ΔH_{sub}

Intermolecular Forces

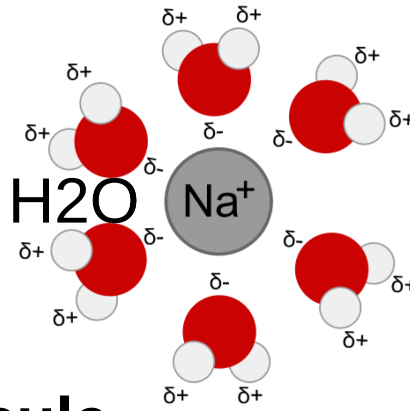
1- Dipole-Dipole Forces

Attractive forces between **polar molecules**





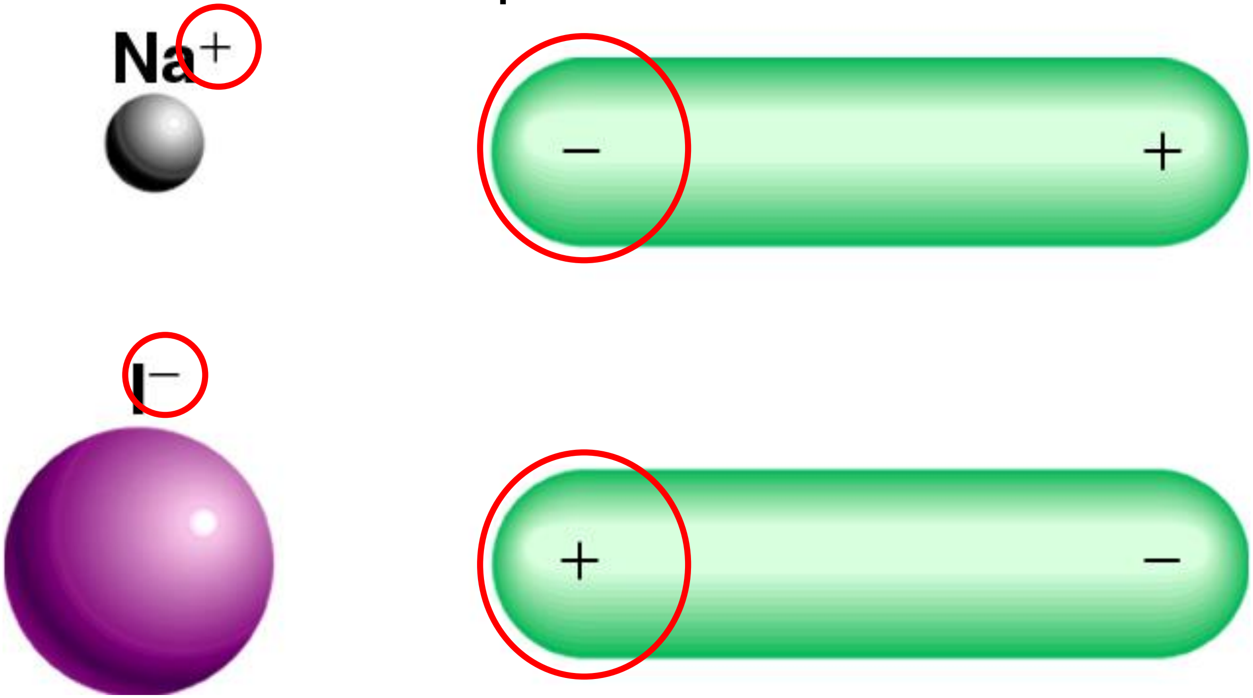
Intermolecular Forces



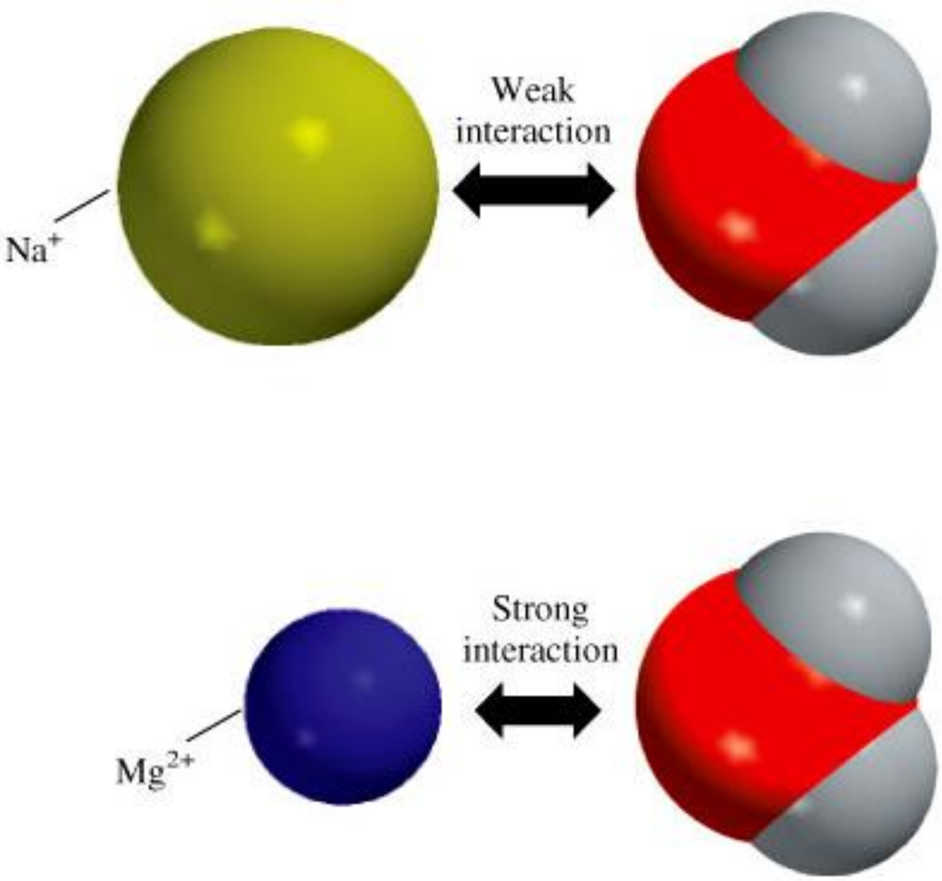
2- Ion-Dipole Forces

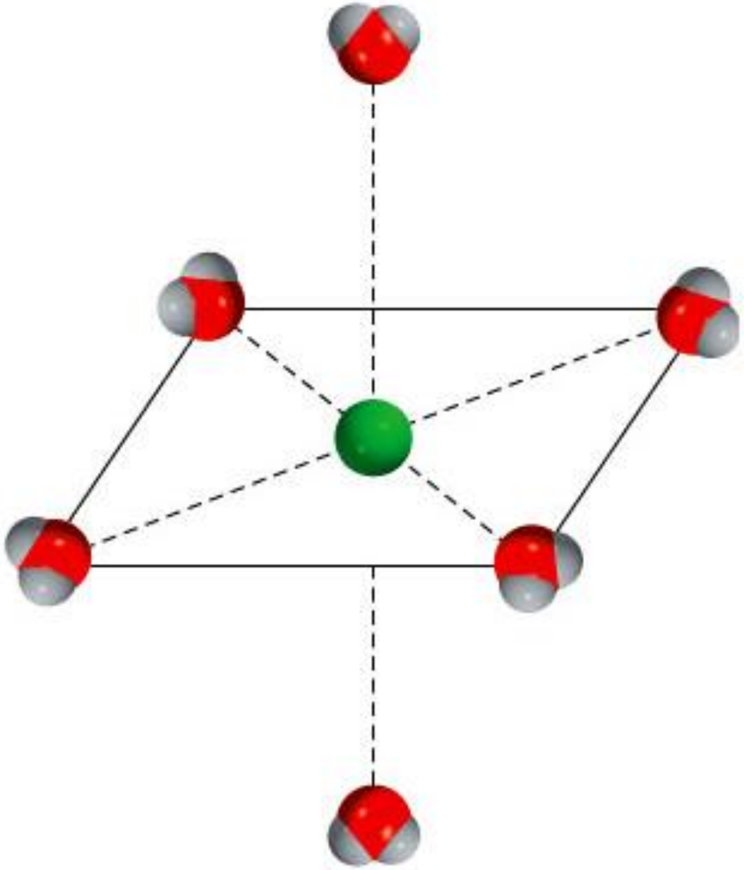
Attractive forces between an **ion** and a **polar molecule**

Ion-Dipole Interaction



Small ion
interact strongly compared to the bigger one

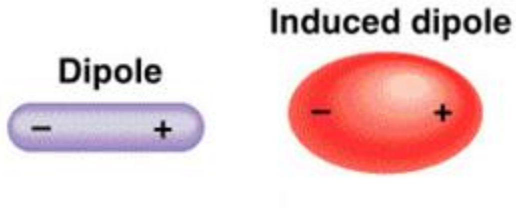




3- Induced –Dipole

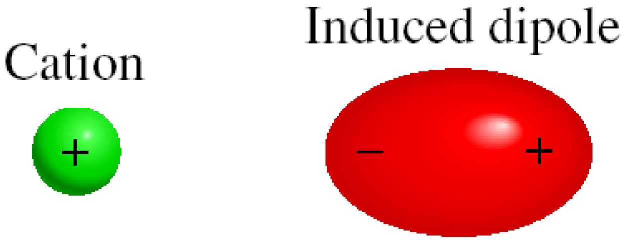
1) Dipole –induced dipole (Temporary)

Polar molecule –nonpolar molecule (ex: HF with H_2)

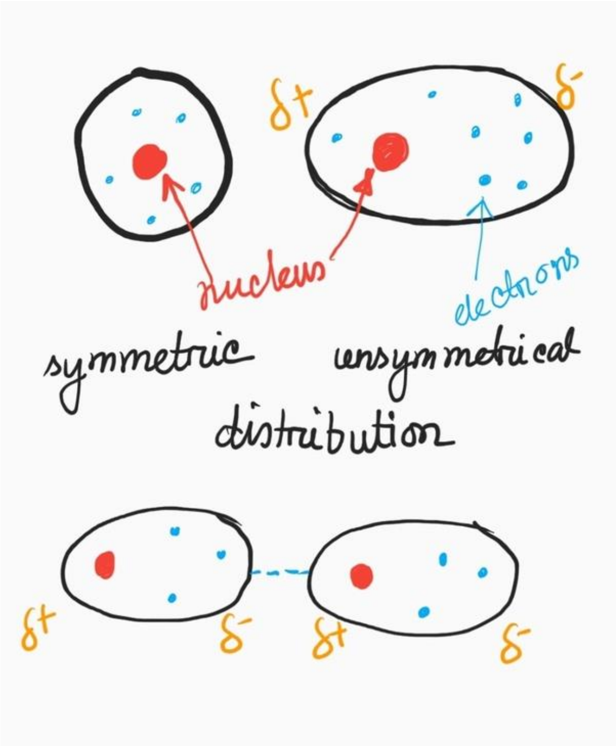


2) Ion- induced Dipole

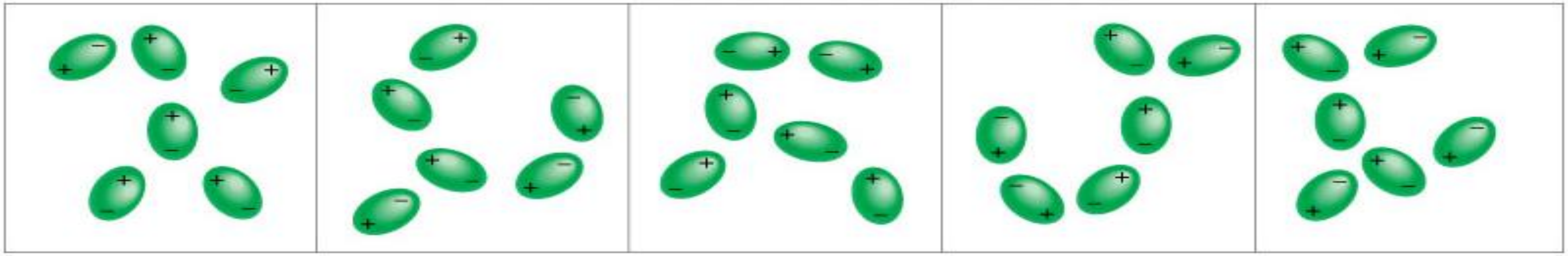
Ion-non polar molecule (ex: Fe^{+2} with O_2)



4- Dispersion force (London force or Van der Waals force)



- Between non polar molecules as a Result of forming instantaneous dipole
- The weakest force
- Present in all other previous forces
- At low temp. this force is strong Enough Ne atoms or He atoms together (causing the gas to condense)
- Dispersion force increase as Mm increase
- Boiling point increase as Dispersion force increase



Induced Dipoles Interacting With Each Other

Intermolecular Forces

Dispersion Forces Continued

Polarizability is the ease with which the electron distribution in the atom or molecule can be distorted.

Polarizability increases with:

- greater number of electrons

Dispersion forces usually increase with molar mass.

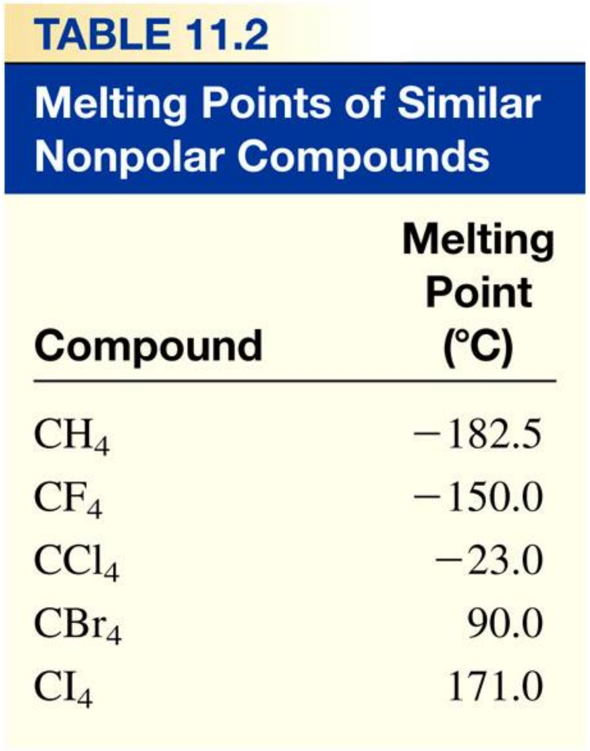
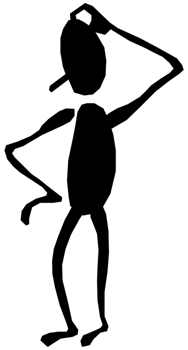


TABLE 11.2

Melting Points of Similar Nonpolar Compounds

Compound	Melting Point (°C)
CH_4	−182.5
CF_4	−150.0
CCl_4	−23.0
CBr_4	90.0
CI_4	171.0



What type(s) of intermolecular forces exist between each of the following molecules?

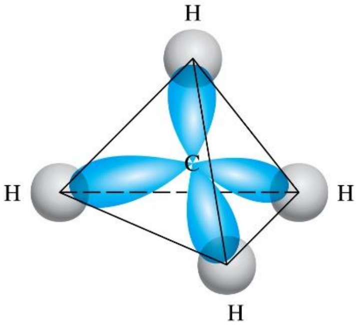
$+\delta\ \mathrm{H} \longrightarrow \mathrm{Br}\,\delta -$

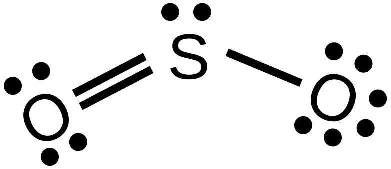
HBr

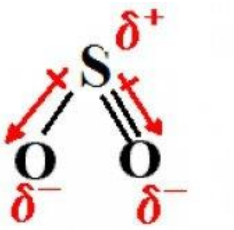
HBr is a polar molecule: dipole-dipole forces. There are also dispersion forces between HBr molecules.

CH_4

CH_4 is nonpolar: dispersion forces.







SO_2

SO_2 is a polar molecule: dipole-dipole forces. There are also dispersion forces between SO_2 molecules.

Example 12.1

What type(s) of intermolecular forces exist between the following pairs?

(a) HBr and H_2S

(b) Cl_2 and CBr_4

(c) I_2 and NO_3^-

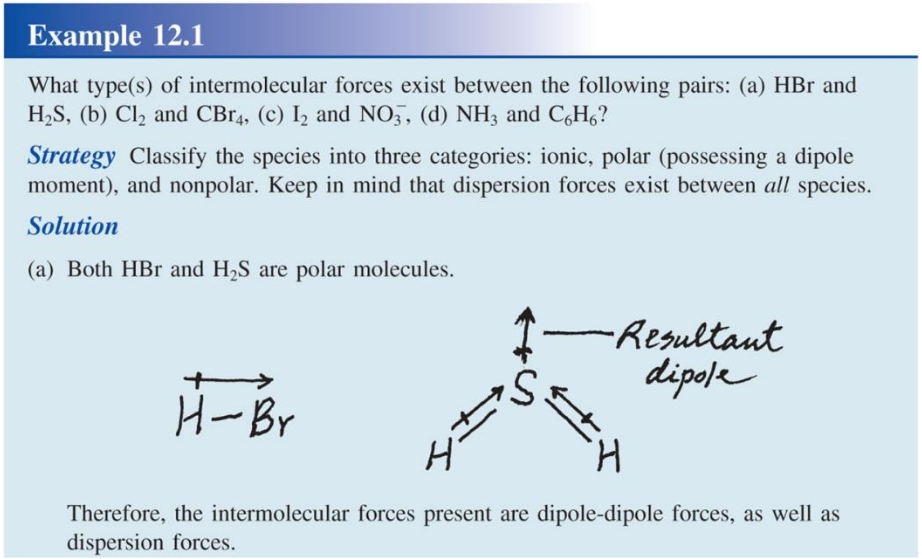
(a) NH_3 and C_6H_6

12.1

Strategy Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

Solution

(a) Both HBr and H_2S are polar molecules. Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.



Example 12.1

What type(s) of intermolecular forces exist between the following pairs: (a) HBr and H_2S, (b) Cl_2 and CBr_4, (c) I_2 and NO_3^-, (d) NH_3 and C_6H_6?

Strategy Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

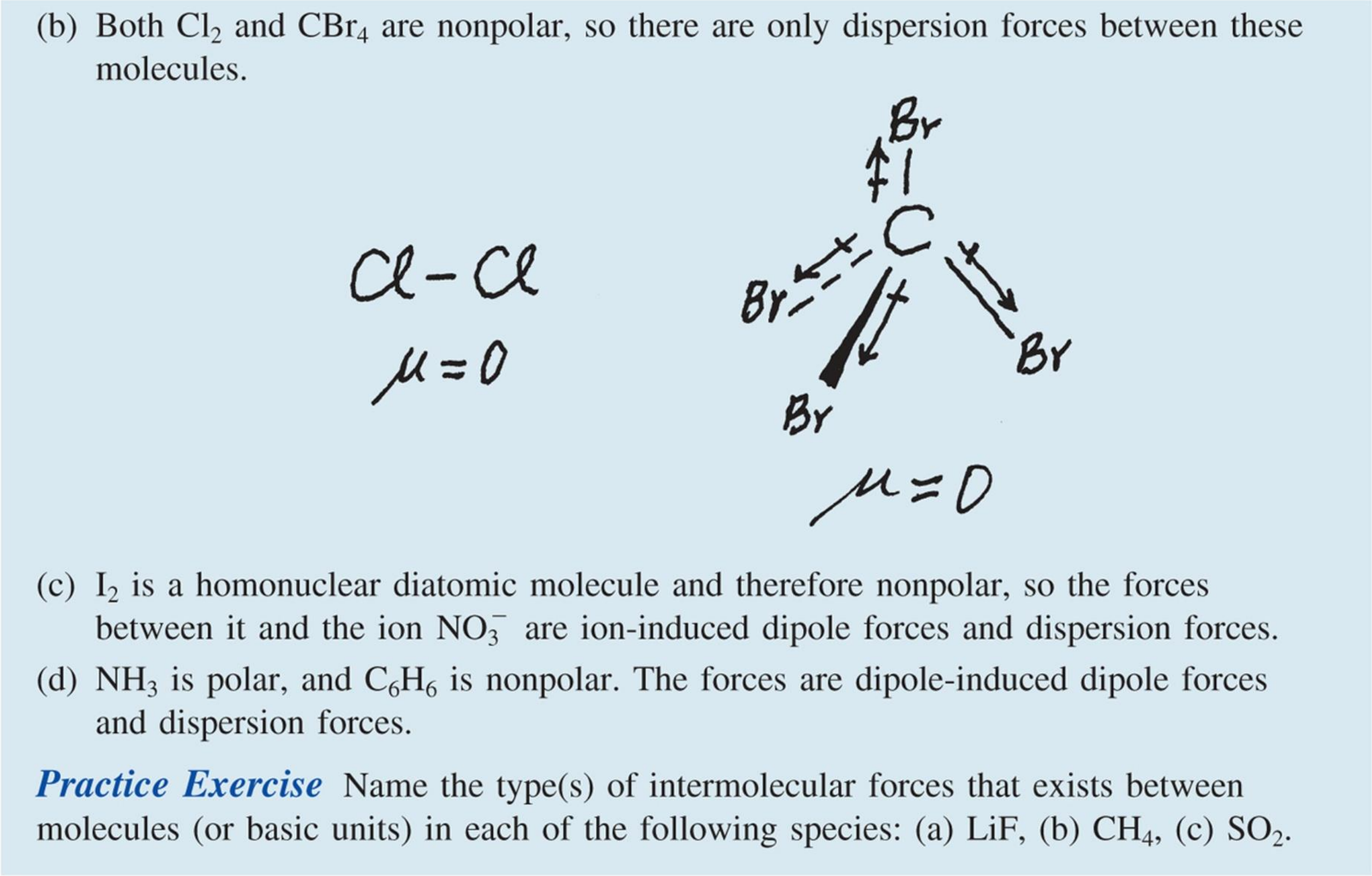
Solution

(a) Both HBr and H_2S are polar molecules.

Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.

12.1

(b) Both Cl_2 and CBr_4 are nonpolar, so there are only dispersion forces between these molecules.



(b) Both Cl_2 and CBr_4 are nonpolar, so there are only dispersion forces between these molecules.

(c) I_2 is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion NO_3^- are ion-induced dipole forces and dispersion forces.

(d) NH_3 is polar, and C_6H_6 is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

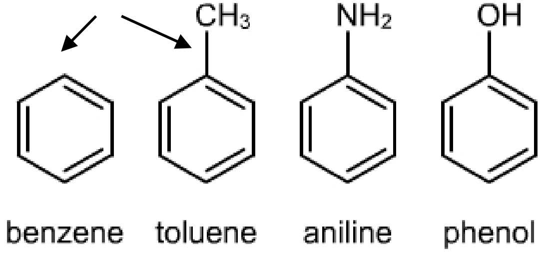
Practice Exercise Name the type(s) of intermolecular forces that exists between molecules (or basic units) in each of the following species: (a) LiF, (b) CH_4, (c) SO_2.

(c) I_2 is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion NO_3^- are ion-induced dipole forces and dispersion forces.

(d) NH_3 is polar, and C_6H_6 is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

- Hydrocarbons are non polar (ex: C6H6)
- Hydrocarbons that have other atoms (like O, N,…) can be polar

Non Polar



Polar Polar

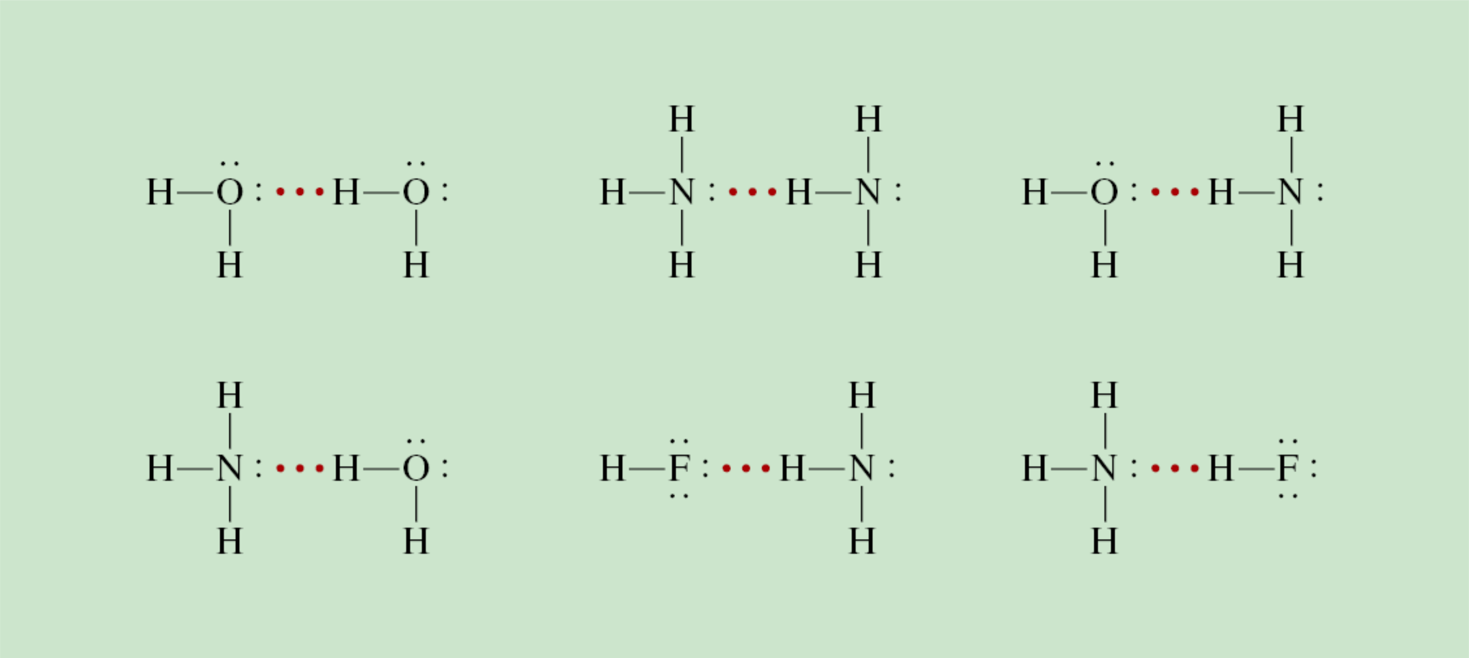
Intermolecular Forces

Hydrogen Bond

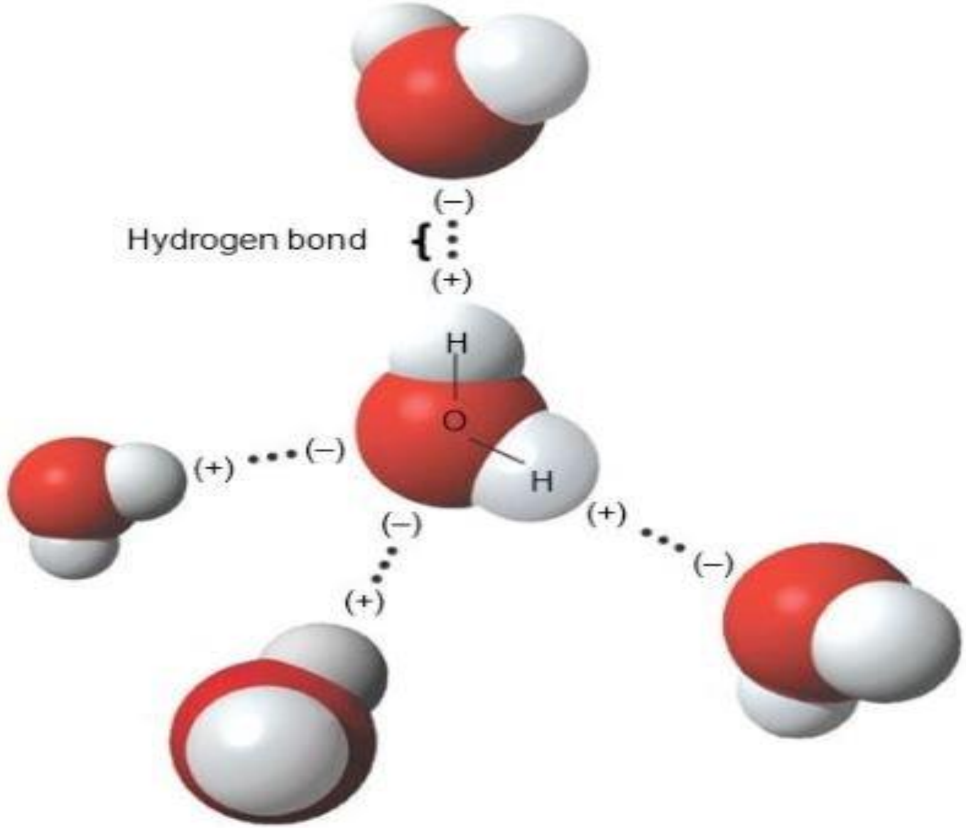
The ***hydrogen bond*** is a special dipole-dipole interaction between the hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom.

$A - H \cdots B$ or $A - H \cdots A$

A & B are N, O, or F



Hydrogen bond between water molecules



Which of the following can form hydrogen bonds with water?

CH_3OCH_3

CH_4

F^-

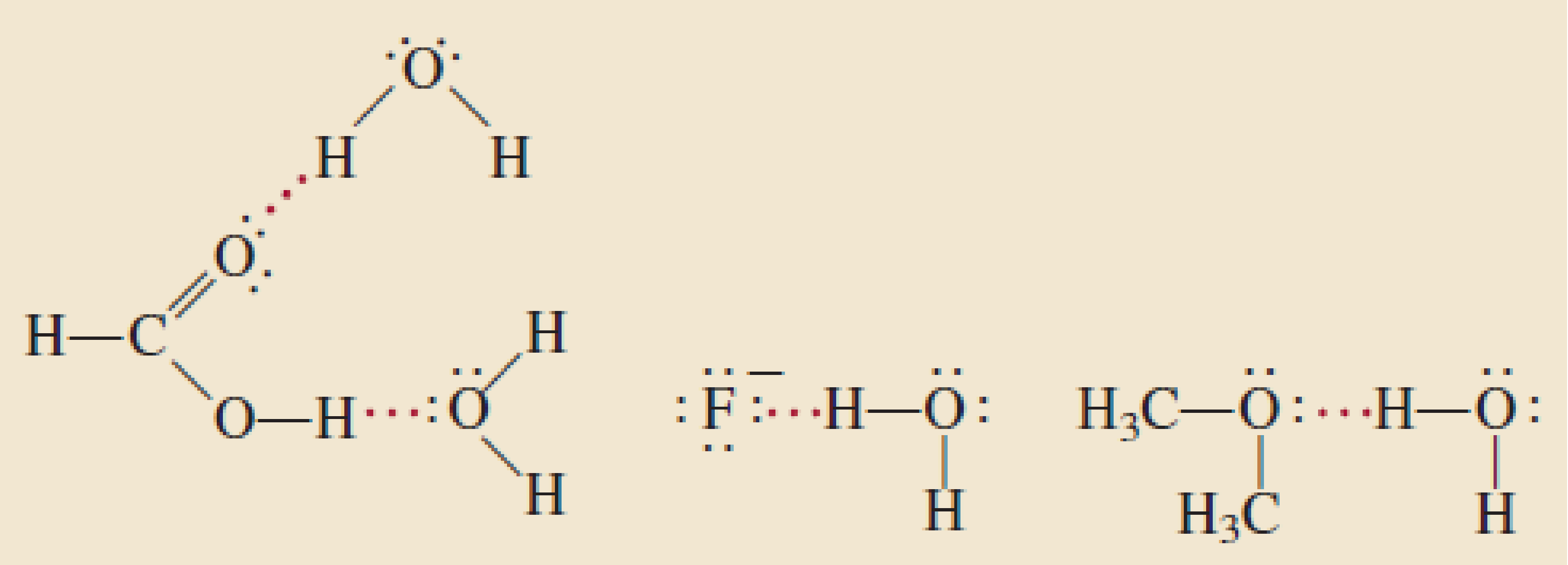
HCOOH

Na^+

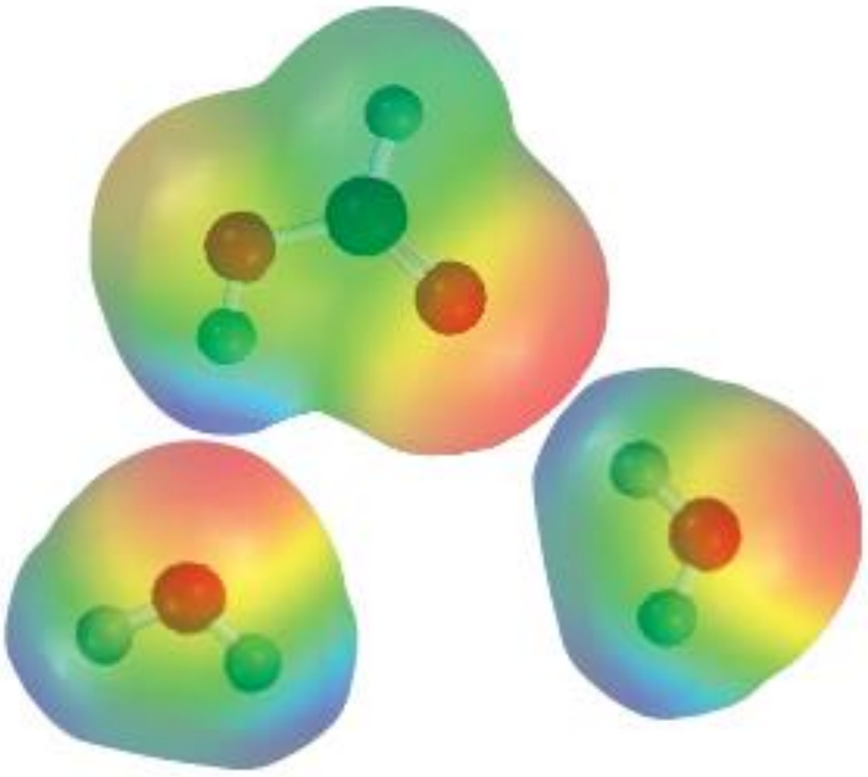
12.2

Strategy A species can form hydrogen bonds with water if it contains one of the three electronegative elements (F, O, or N) or it has a H atom bonded to one of these three elements.

Solution There are no electronegative elements (F, O, or N) in either CH_4 or Na^+. Therefore, only CH_3OCH_3, F^-, and HCOOH can form hydrogen bonds with water.

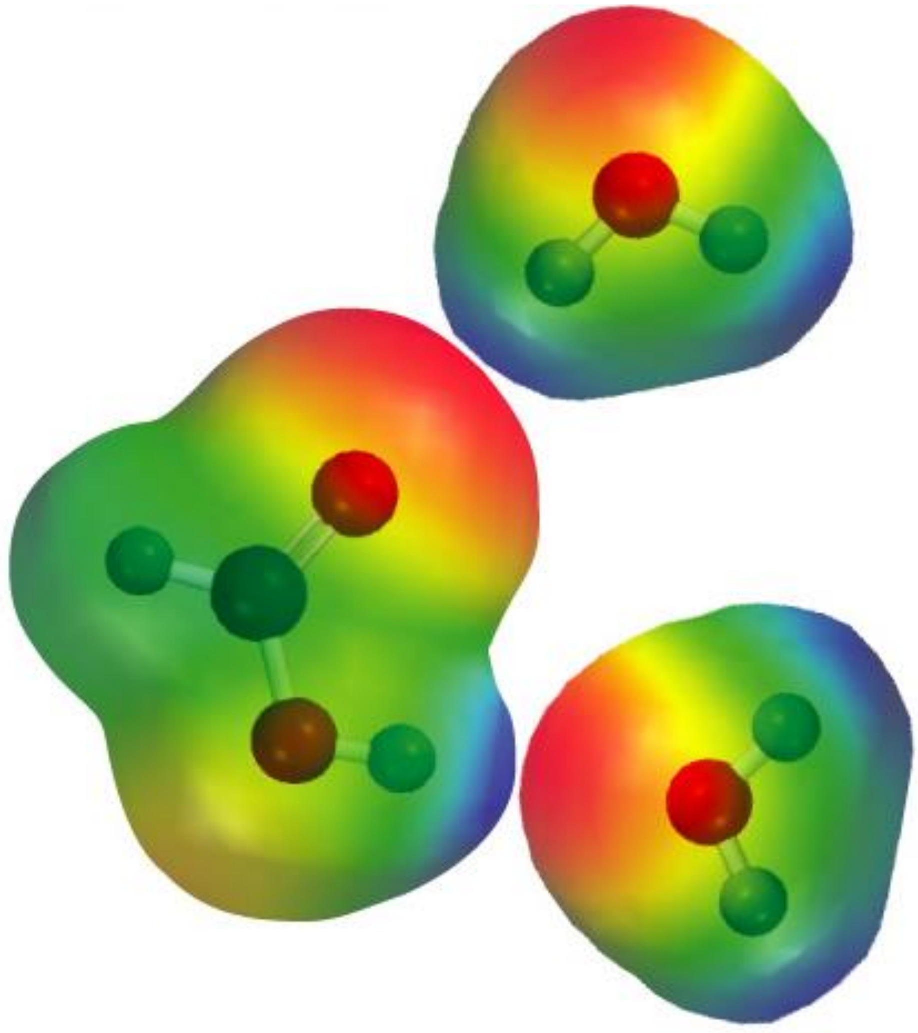


Check Note that HCOOH (formic acid) can form hydrogen bonds with water in two different ways.

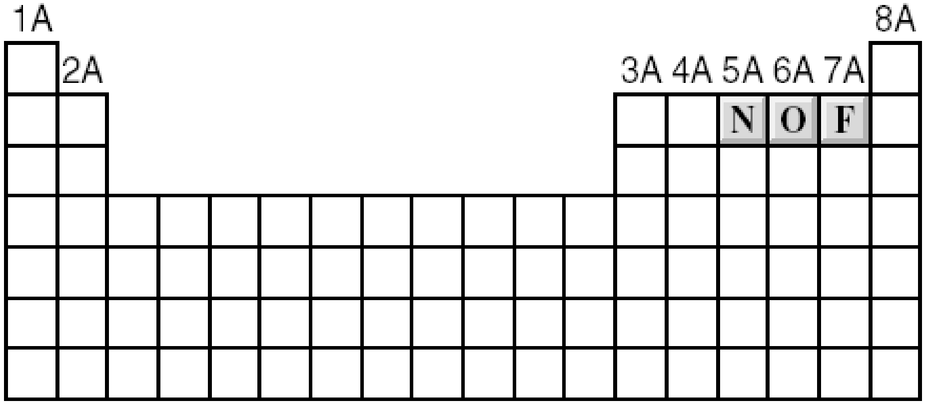


HCOOH forms hydrogen bonds
with two H_2O molecules.

Hydrogen Bond



HCOOH and water



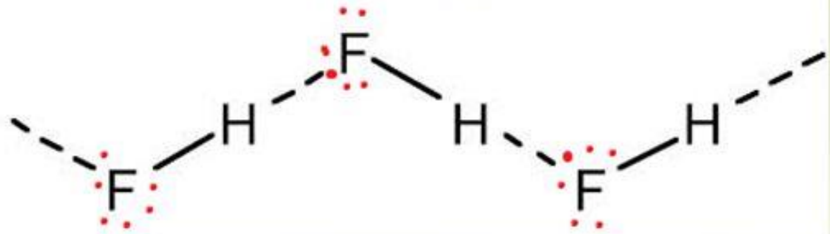
F>O>N   (Electronegativity)

F >O>N (Electronegativity)

- Stronger H-bond existing in substance contain more EN atom, thus will have higher boiling point. However this is not the case when you compare the boiling points of H_2O liquids with NH_3 and HF liquids
- b.p of $H_2O> HF > NH_3$

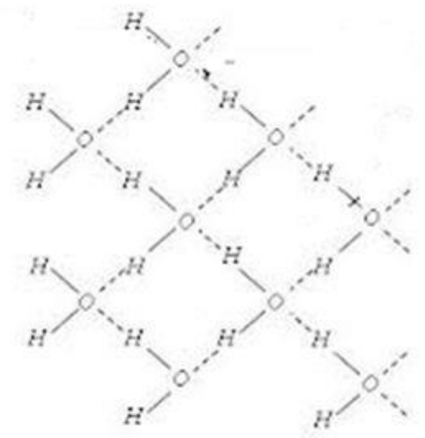
H_2O has a special case compared to other substances, as it form three dimensional structure (due to equality of number of H atoms and lone pairs). While other molecules can form chain or ring but not three dimensional structure (due to non equality of number of H atoms and lone pairs)

Hydrogen bonding in HF

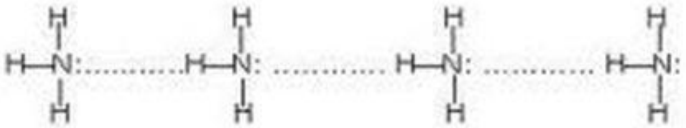


BP 19.0 C

Hydrogen bonding in water



Hydrogen bonding in ammonia



BP -33.0C

BP 100.0C

Lone pair of electrons in oxygen, fluorine or nitrogen is used to attract hydrogen

Strength of intermolecular forces

Ion-ion

Ion-dipole

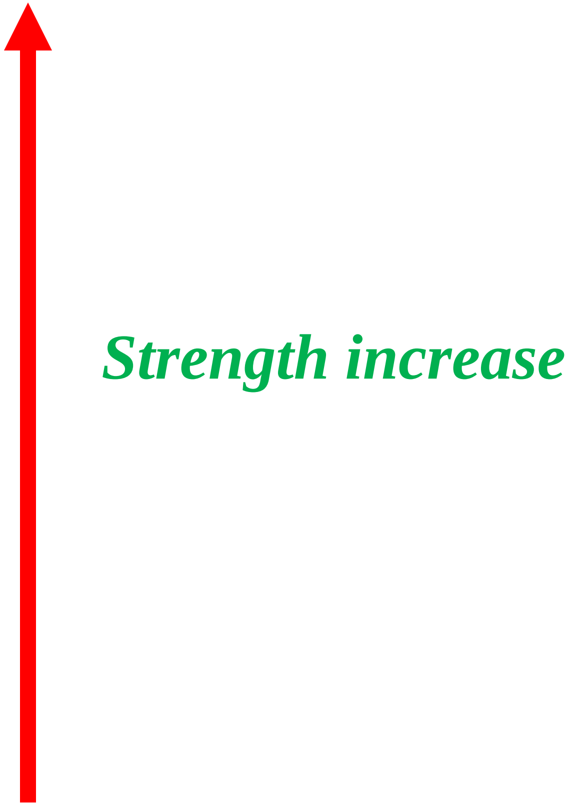
H-bond

Dipole-dipole

Ion-induced dipole

Dipole-induced dipole

London dispersion force



Properties of Liquids(due to intermolecular forces)

1- ***Surface tension*** is the amount of energy required to stretch or increase the surface of a liquid by a unit area.
(or a measure of the elastic force in the surface of a liquid)

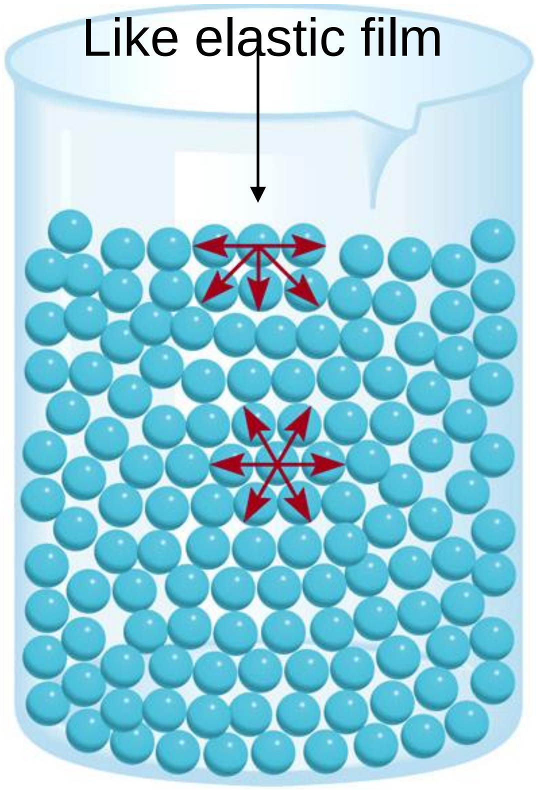
Water has greater surface tension than most liquids(due to strong H-bonds)

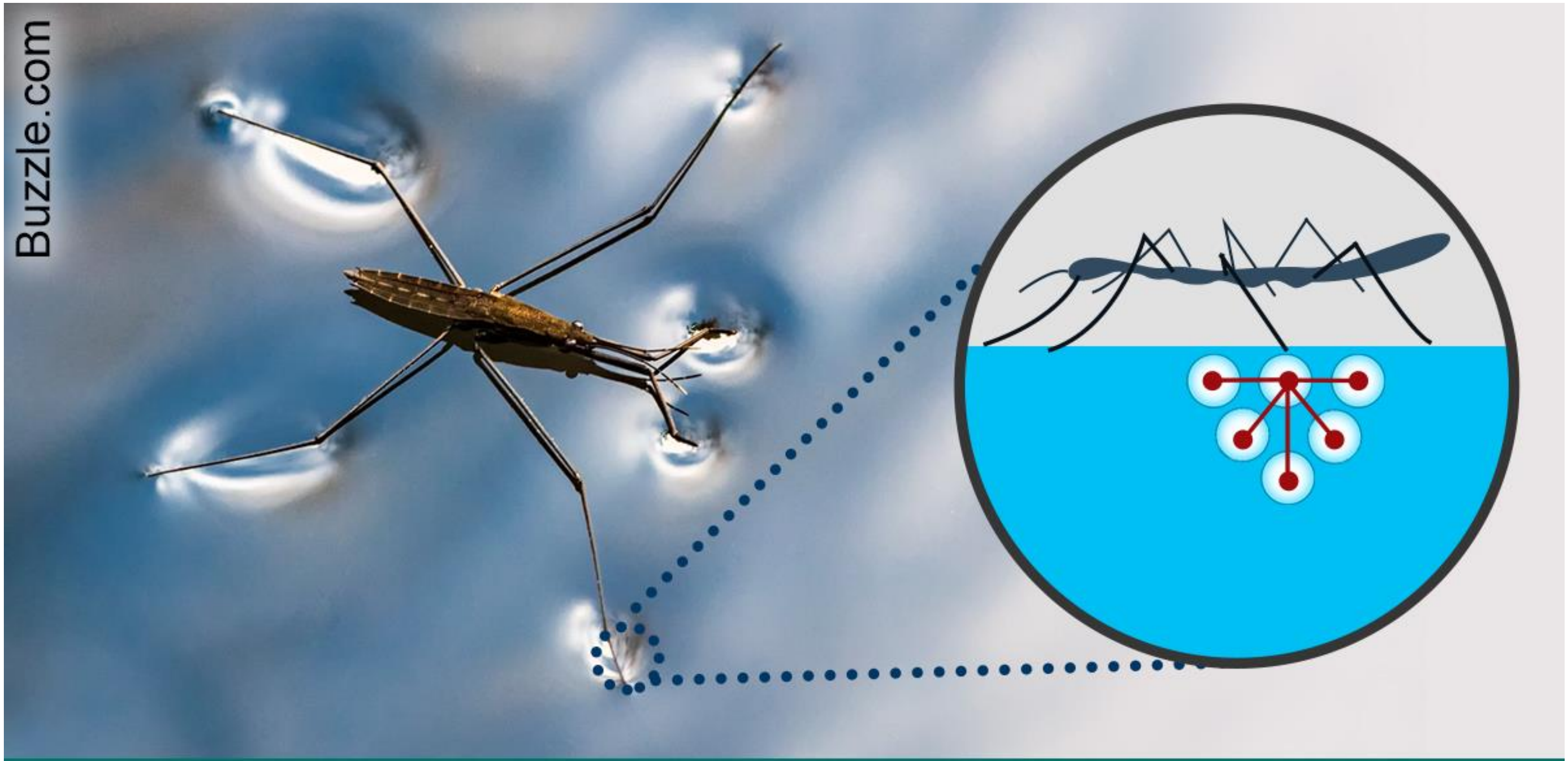
Strong intermolecular forces

↓

High surface tension

Surface tension decrease as Temperature increase





Water striders can walk on water because of the SURFACE TENSION OF WATER.

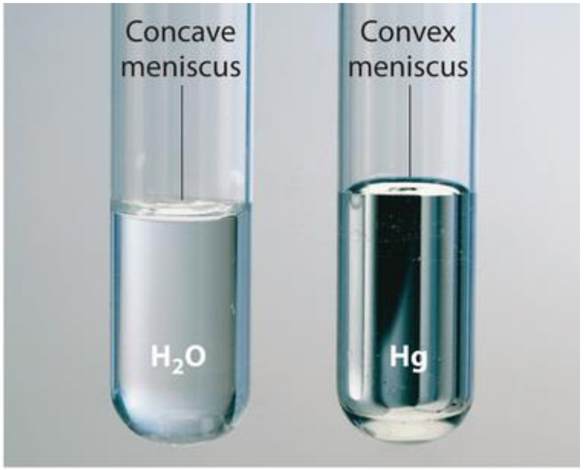
Another example of surface tension: Capillary action

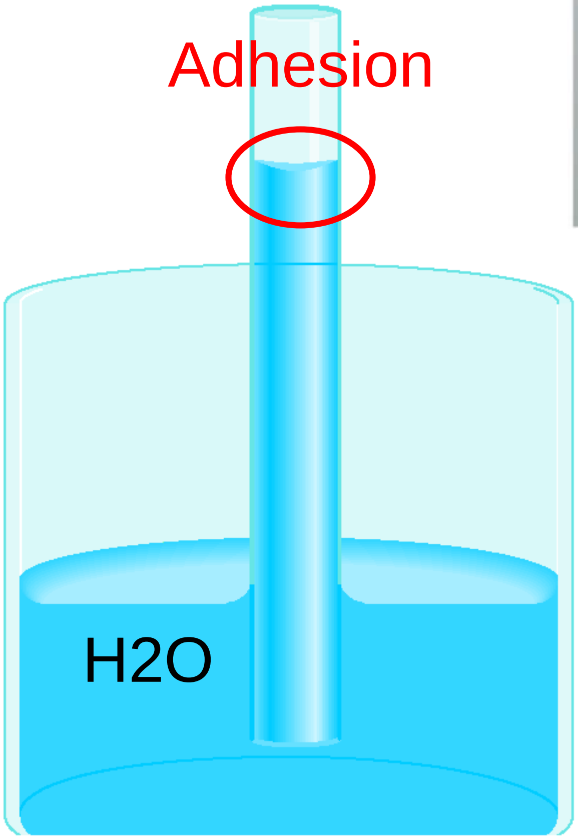
Cohesion is the intermolecular attraction between like molecules (ex:water-water interaction)

Adhesion is an attraction between unlike molecules

(ex:water-silica(glass) interaction)

Capillary action



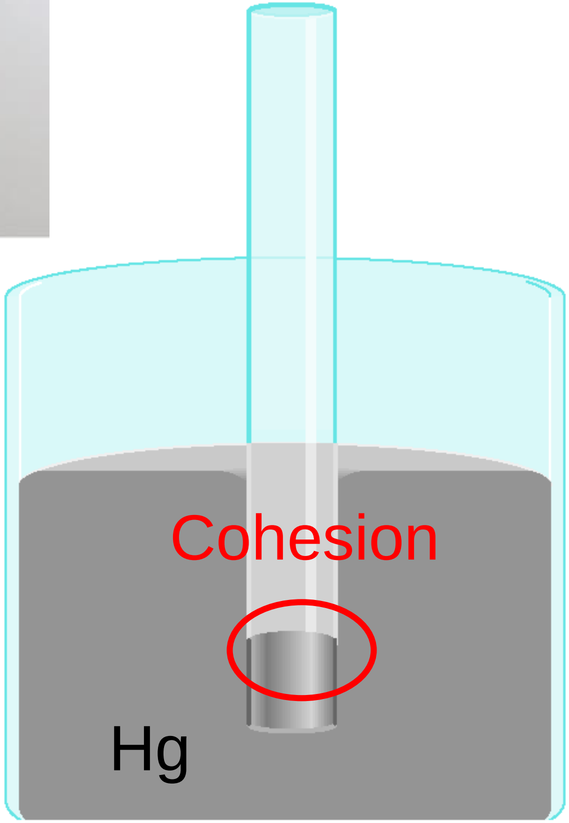


Glass tube

Adhesion

H2O

Adhesion > Cohesion



Glass tube

Cohesion

Hg

Adhesion < Cohesion

Cohesion >Adhesion

Attraction between water-water molecules is greater than water-wax molecules.

water: polar

Wax: non-polar

Figure 11.9 *Water beads on an apple, which has a waxy surface.*

Properties of Liquids

2- *Viscosity* is a measure of a fluid’s resistance to flow (as Temp increase, viscosity decrease)

Strong intermolecular forces

↓

High viscosity

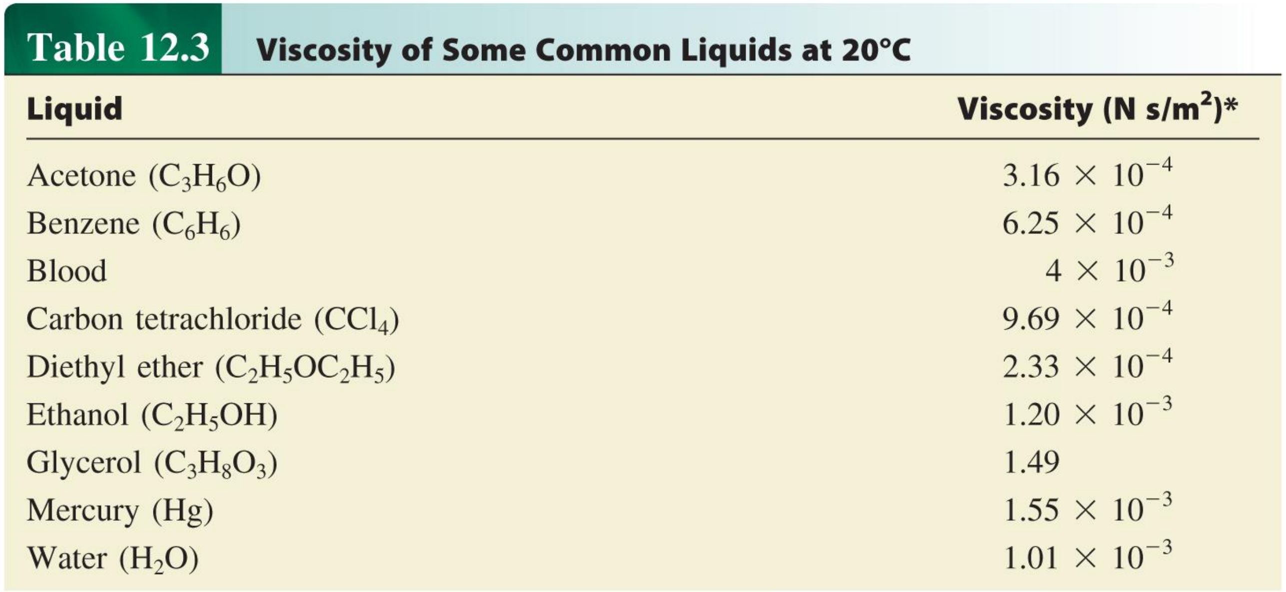
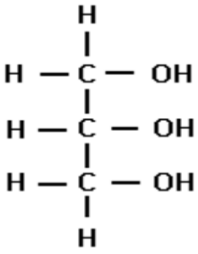


Table 12.3 **Viscosity of Some Common Liquids at 20°C**

Liquid	**Viscosity (N s/m^2)***
Acetone (C_3H_6O)	3.16×10^{-4}
Benzene (C_6H_6)	6.25×10^{-4}
Blood	4×10^{-3}
Carbon tetrachloride (CCl_4)	9.69×10^{-4}
Diethyl ether ($C_2H_5OC_2H_5$)	2.33×10^{-4}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Glycerol ($C_3H_8O_3$)	1.49
Mercury (Hg)	1.55×10^{-3}
Water (H_2O)	1.01×10^{-3}

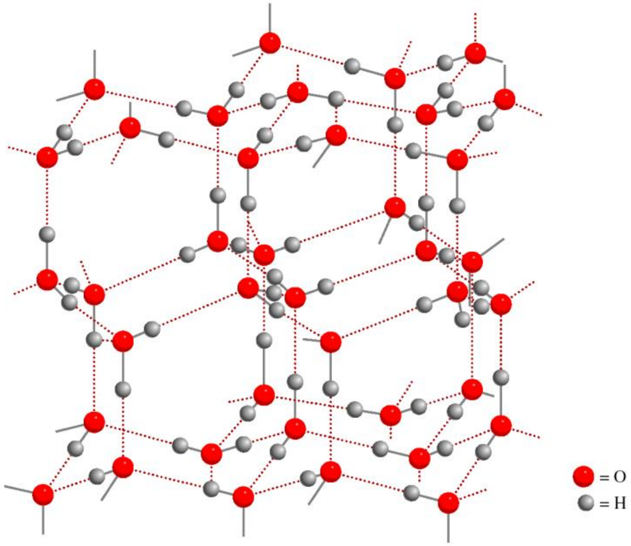
more OH groups, the more H-bonding can occur ←



Glycerol

Water is a Unique Substance

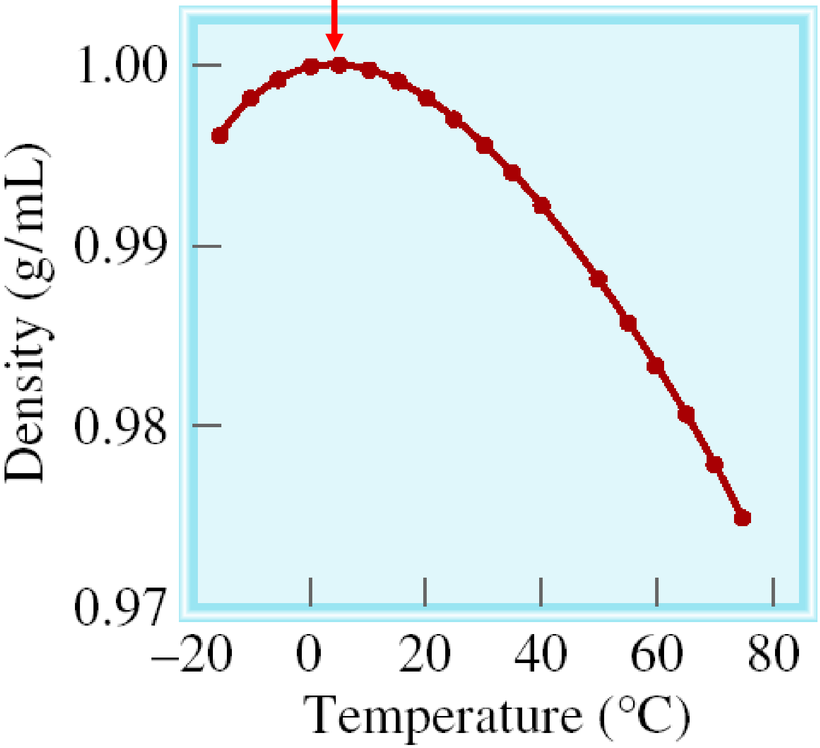
3-D Structure of Water



Ice is less dense than water

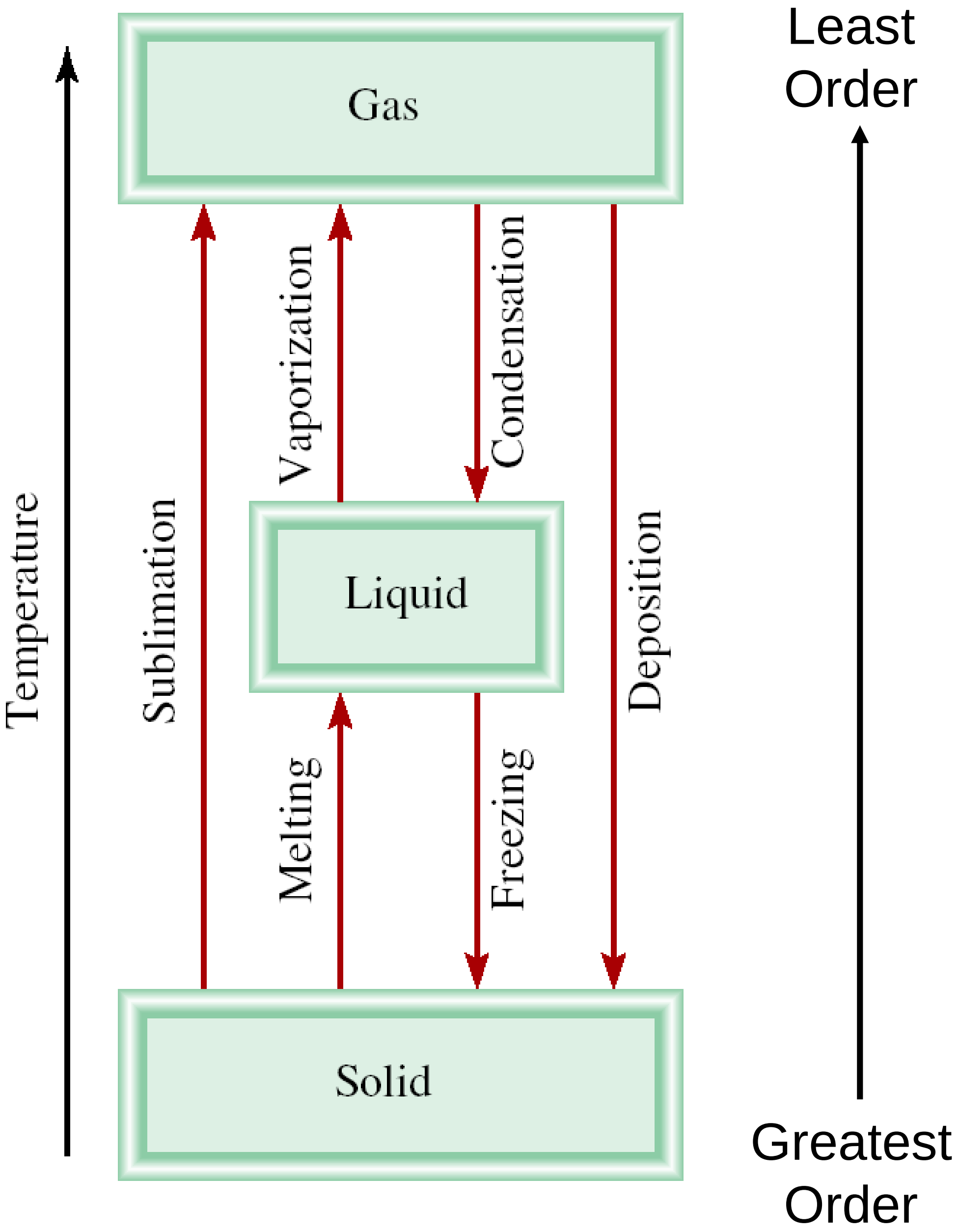
Maximum Density
4^{0}C

Density of Water



Phase Changes

Phase change: Transformation from one phase to another occur when energy (heat) is added or removed from a substance



Least Order

Gas

Liquid

Solid

Temperature

Sublimation

Vaporization

Condensation

Deposition

Melting

Freezing

Greatest Order

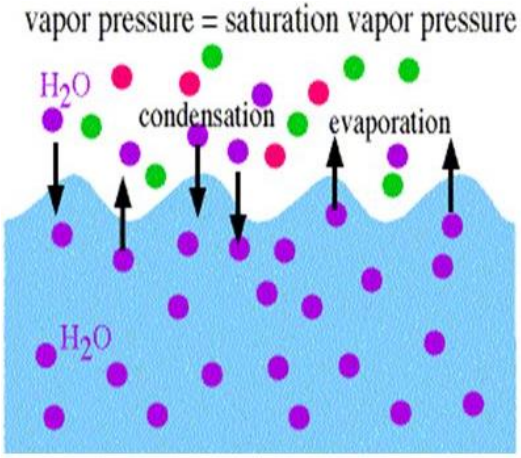
Evaporation or vaporization :the process in which a liquid is transformed into a gas

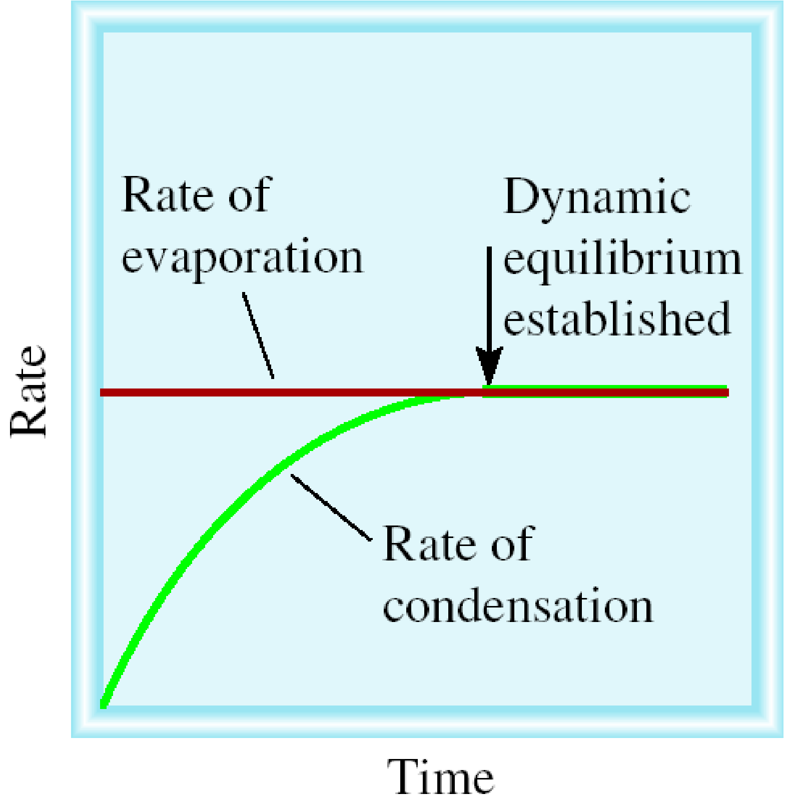
The ***equilibrium vapor pressure*** is the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation

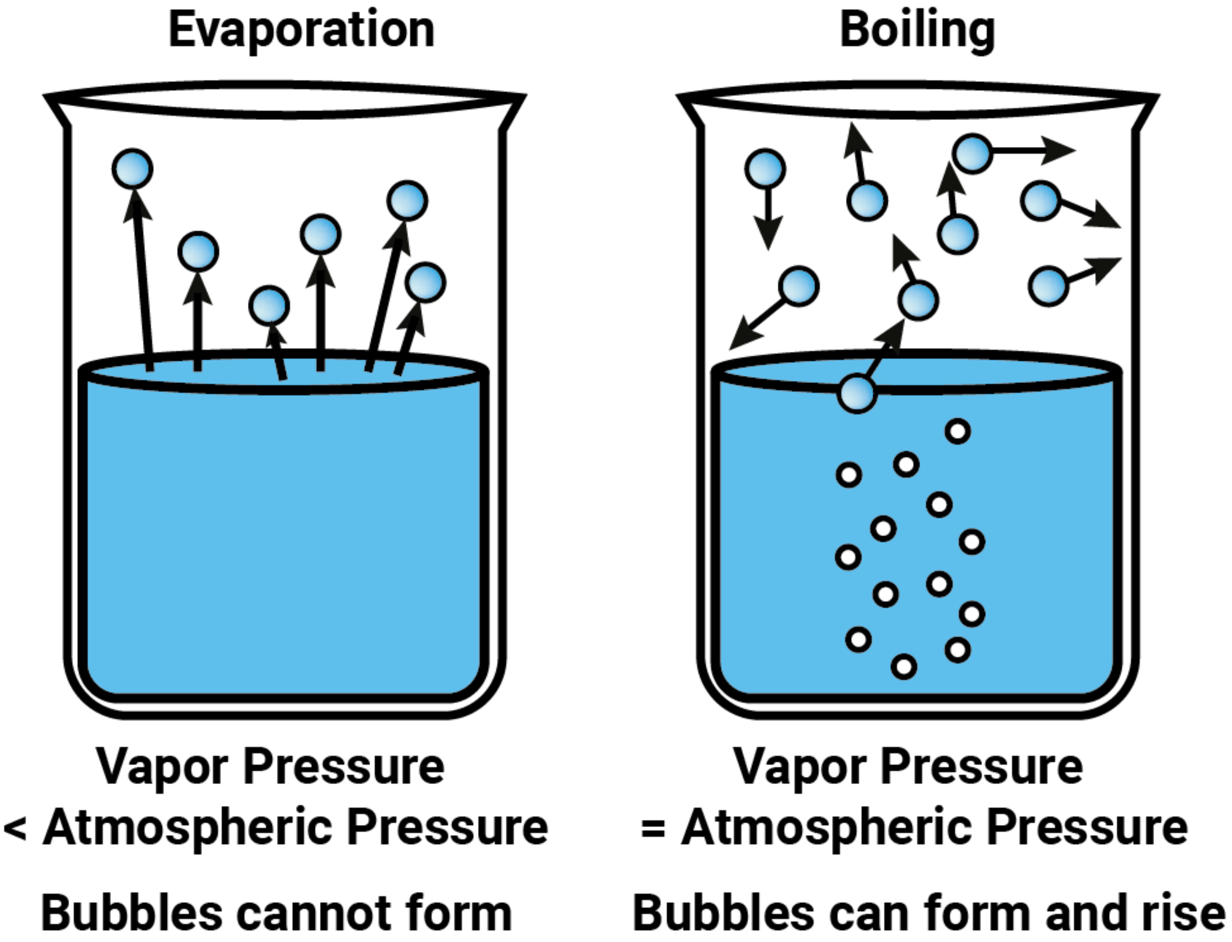
$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

Dynamic Equilibrium

Rate of condensation = Rate of evaporation







Kinetic energy of molecules increase by increasing Temperature

Molar heat of vaporization (ΔH_{vap}) is the energy required to vaporize 1 mole of a liquid at its boiling point.

Clausius-Clapeyron Equation

$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$

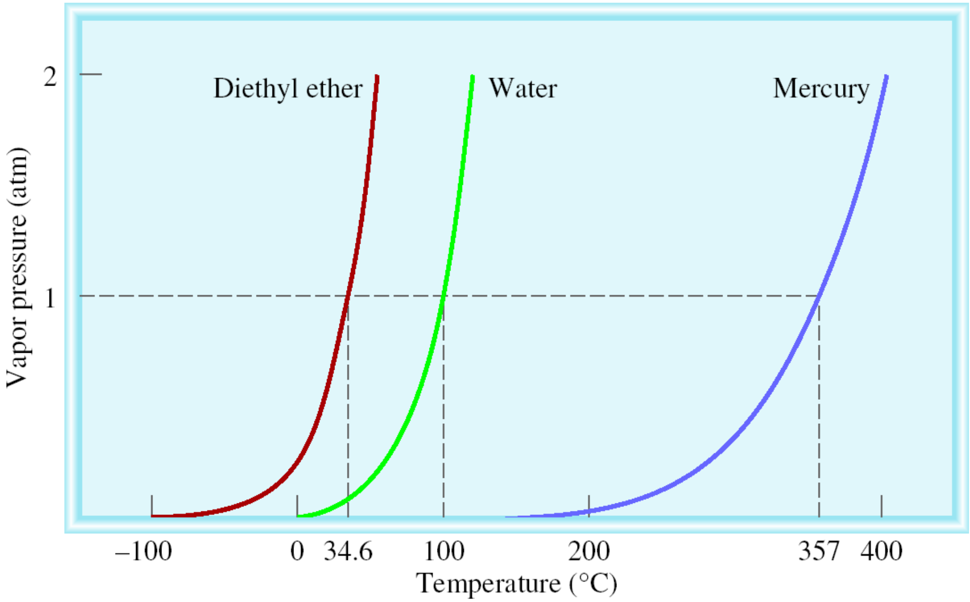
V.P increase as Temp. increase

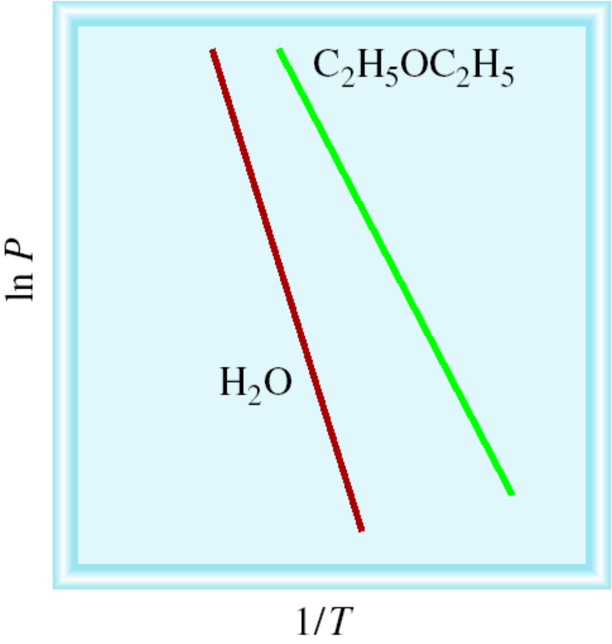
P = (equilibrium) vapor pressure

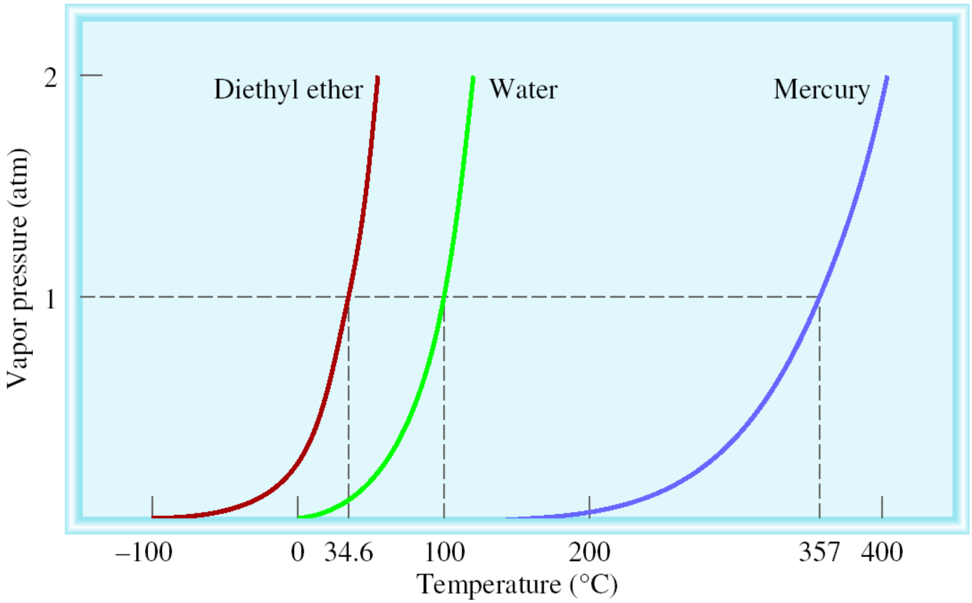
T = temperature (K)

R = gas constant (8.314 J/K•mol)

Vapor Pressure Versus Temperature







The increase in vapor pressure with temperature for three liquids. The normal boiling points of the liquids (at 1 atm) are shown on the horizontal axis.

Alternate Forms of the Clausius-Clapeyron Equation

At two temperatures

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

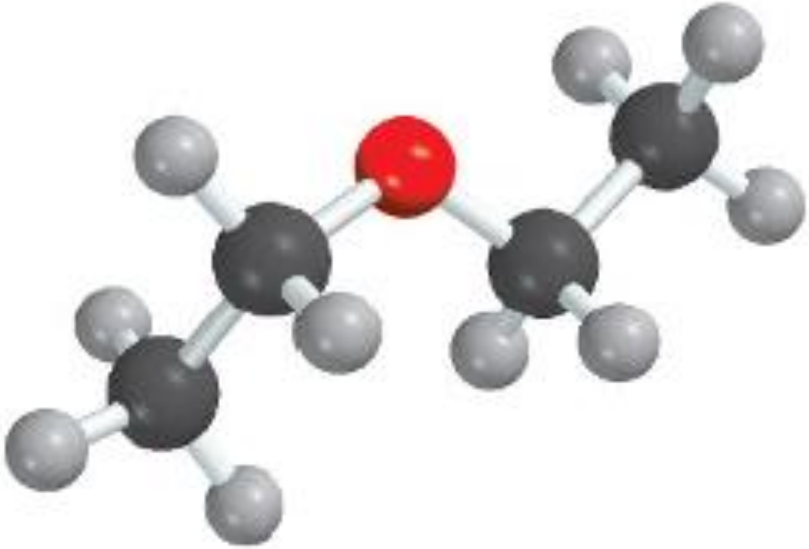
or

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

12.5

Diethyl ether is a volatile, highly flammable organic liquid that is used mainly as a solvent.

The vapor pressure of diethyl ether is 401 mmHg at 18°C. Calculate its vapor pressure at 32°C.



12.5

Strategy We are given the vapor pressure of diethyl ether at one temperature and asked to find the pressure at another temperature. Therefore, we need Equation (12.4).

Solution Table 12.5 tells us that ΔH_{vap} = 26.0 kJ/mol. The data are

$$P_1 = 401 \text{ mmHg} \qquad P_2 = ?$$
$$T_1 = 18°\text{C} = 291 \text{ K} \qquad T_2 = 32°\text{C} = 305 \text{ K}$$

From Equation (12.4) we have

$$\begin{aligned}\ln\frac{401}{P_2} &= \frac{26{,}000 \text{ J/mol}}{8.314 \text{ J/K}\cdot\text{mol}}\left[\frac{291 \text{ K} - 305 \text{ K}}{(291 \text{ K})(305 \text{ K})}\right]\\ &= -0.493\end{aligned}$$

12.5

Taking the antilog of both sides (see Appendix 3), we obtain

$$\frac{401}{P_2} = e^{-0.493} = 0.611$$

Hence

$$P_2 = 656 \text{ mmHg}$$

Check We expect the vapor pressure to be greater at the higher temperature. Therefore, the answer is reasonable.

The ***boiling point*** is the temperature at which the (equilibrium) vapor pressure of a liquid is equal to the external pressure.(as p ↘ , b.p ↘)

The ***normal boiling point*** is the temperature at which a liquid boils when the external pressure is 1 atm.

b.p α ΔH_{vap}

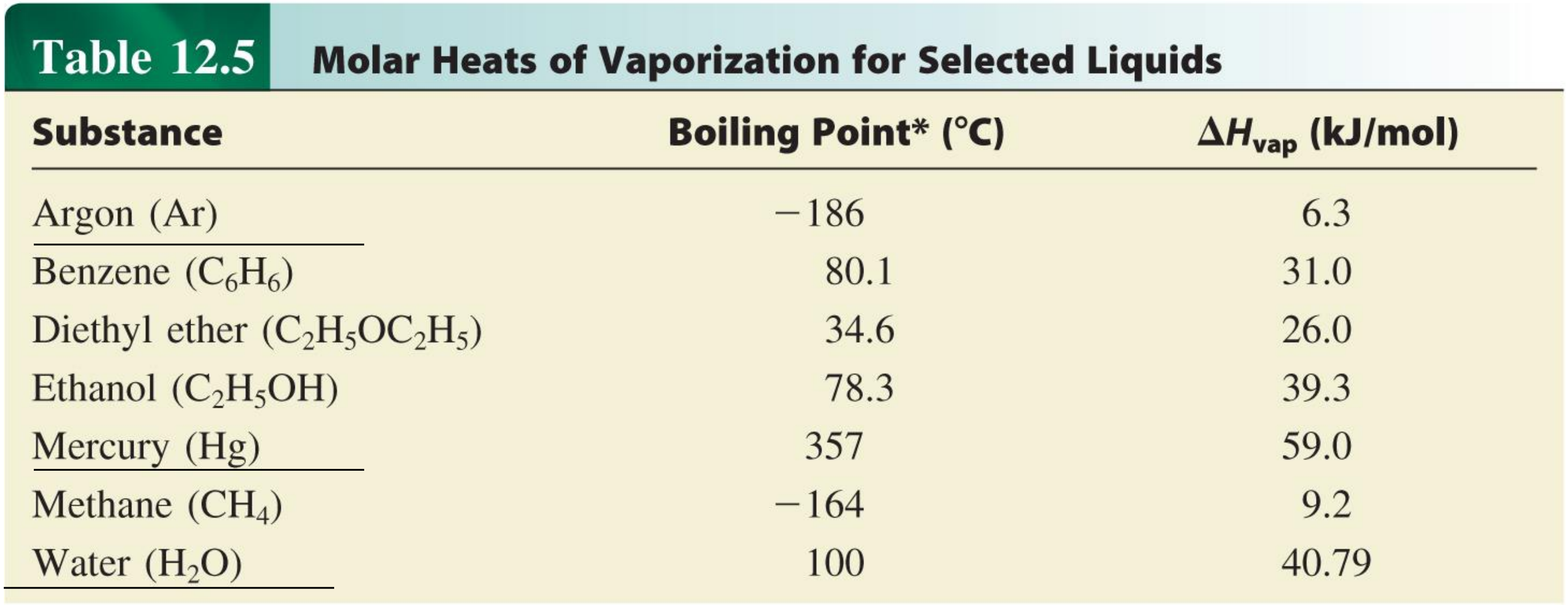


Table 12.5 **Molar Heats of Vaporization for Selected Liquids**

Substance	Boiling Point* (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	80.1	31.0
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Ethanol (C_2H_5OH)	78.3	39.3
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

Condensation ($g \longrightarrow L$) : is the process opposite to evaporation

Gas can be liquefied by two techniques:

1)Cooling : cooling gas will decrease the KE of molecules, then molecules aggregate to form a small drop of liquid

2)Applying pressure to the gas: as compression reduce the average distance between molecules then held together by attraction.

- Two techniques can be combined to liquefied any gas
- every substance has a critical temperature T_c and critical pressure P_c

The ***critical temperature*** (***T_c***) is the temperature above which the gas cannot be made to liquefy, no matter how great the applied pressure.

The ***critical pressure*** (***P_c***) is the minimum pressure that must be applied to bring about liquefaction at the critical temperature.

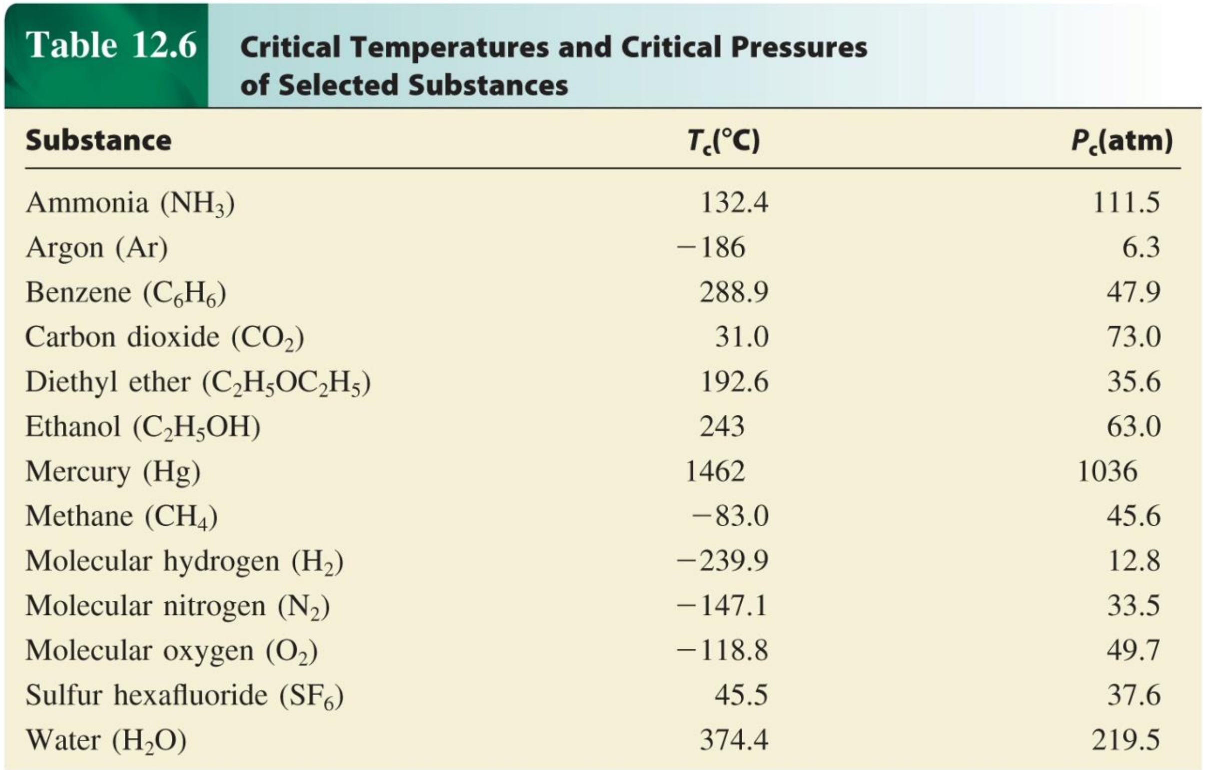
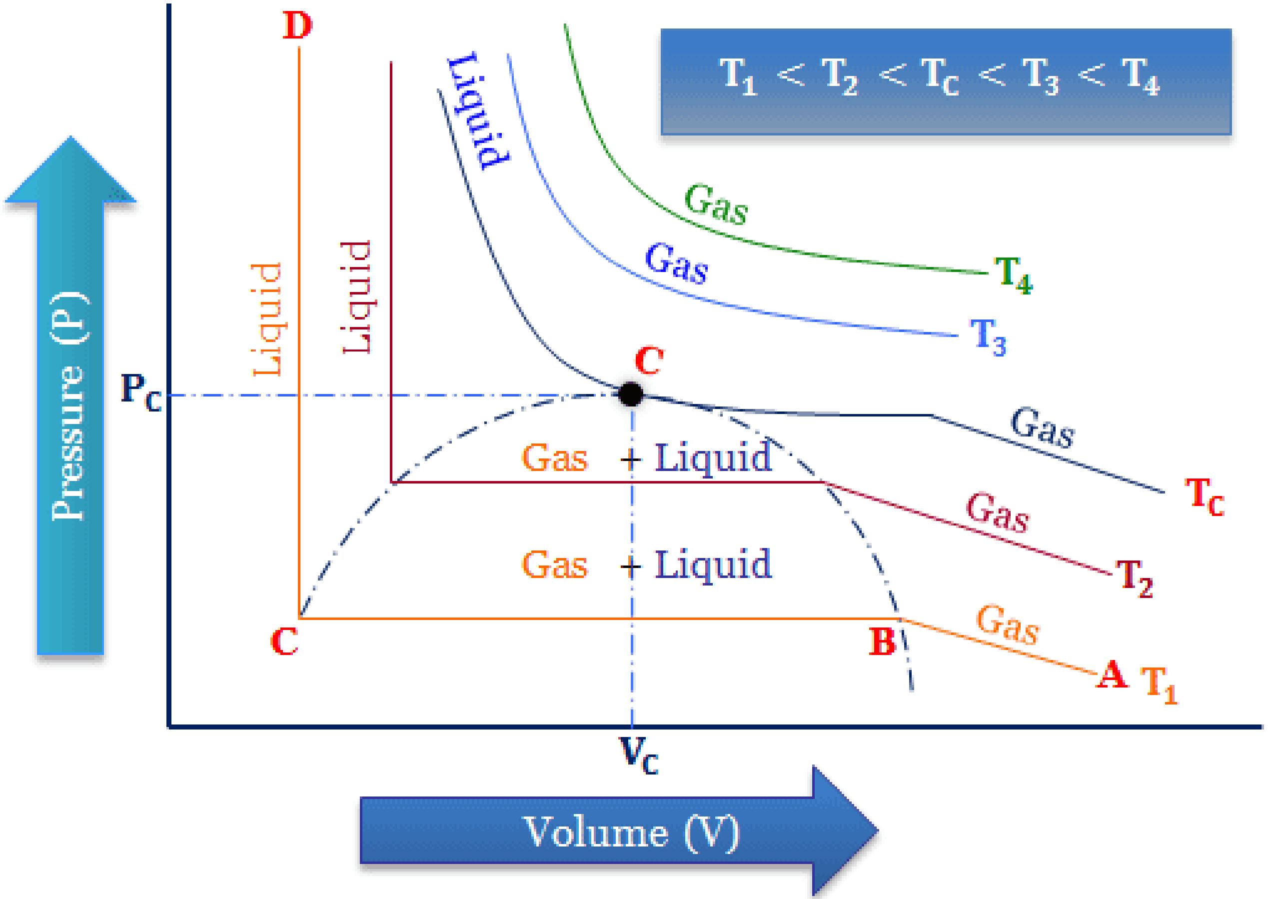
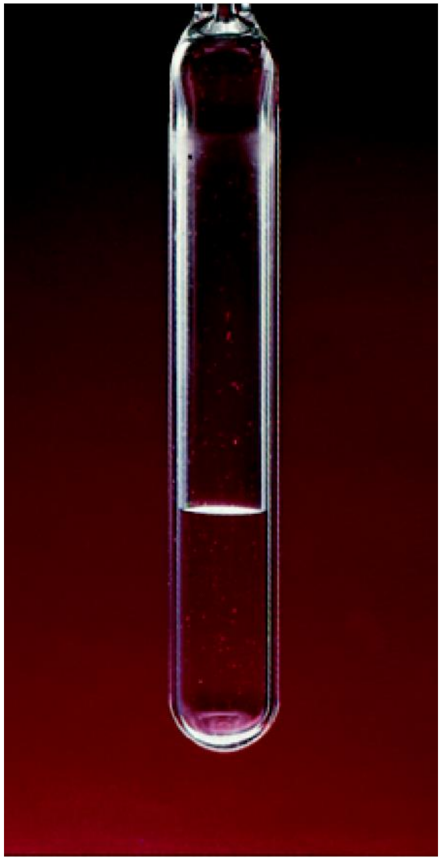


Table 12.6 **Critical Temperatures and Critical Pressures of Selected Substances**

Substance	**T_c(°C)**	**P_c(atm)**
Ammonia (NH_3)	132.4	111.5
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	288.9	47.9
Carbon dioxide (CO_2)	31.0	73.0
Diethyl ether ($C_2H_5OC_2H_5$)	192.6	35.6
Ethanol (C_2H_5OH)	243	63.0
Mercury (Hg)	1462	1036
Methane (CH_4)	−83.0	45.6
Molecular hydrogen (H_2)	−239.9	12.8
Molecular nitrogen (N_2)	−147.1	33.5
Molecular oxygen (O_2)	−118.8	49.7
Sulfur hexafluoride (SF_6)	45.5	37.6
Water (H_2O)	374.4	219.5


$T_1 < T_2 < T_C < T_3 < T_4$
Pressure (P)
Volume (V)
P_C
V_C
D
C
C
B
A
Liquid
Liquid
Liquid
Gas
Gas
Gas
Gas
Gas
Gas + Liquid
Gas + Liquid
T_4
T_3
T_C
T_2
T_1

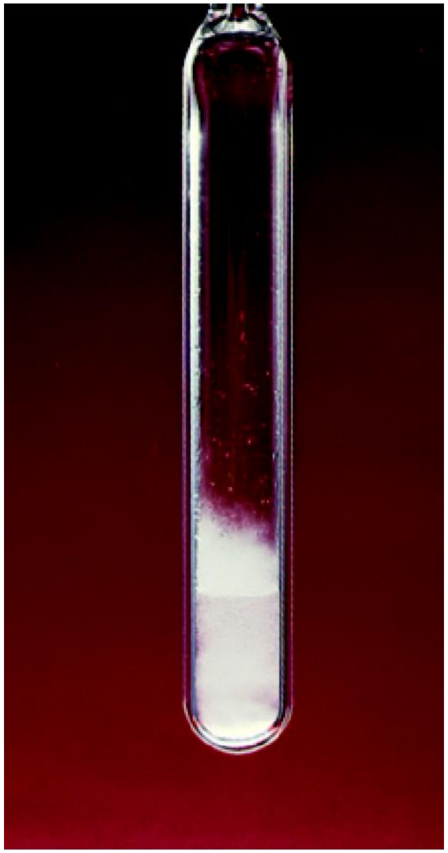
The Critical Phenomenon of SF_6



$T < T_c$

$T > T_c$

$T \sim T_c$



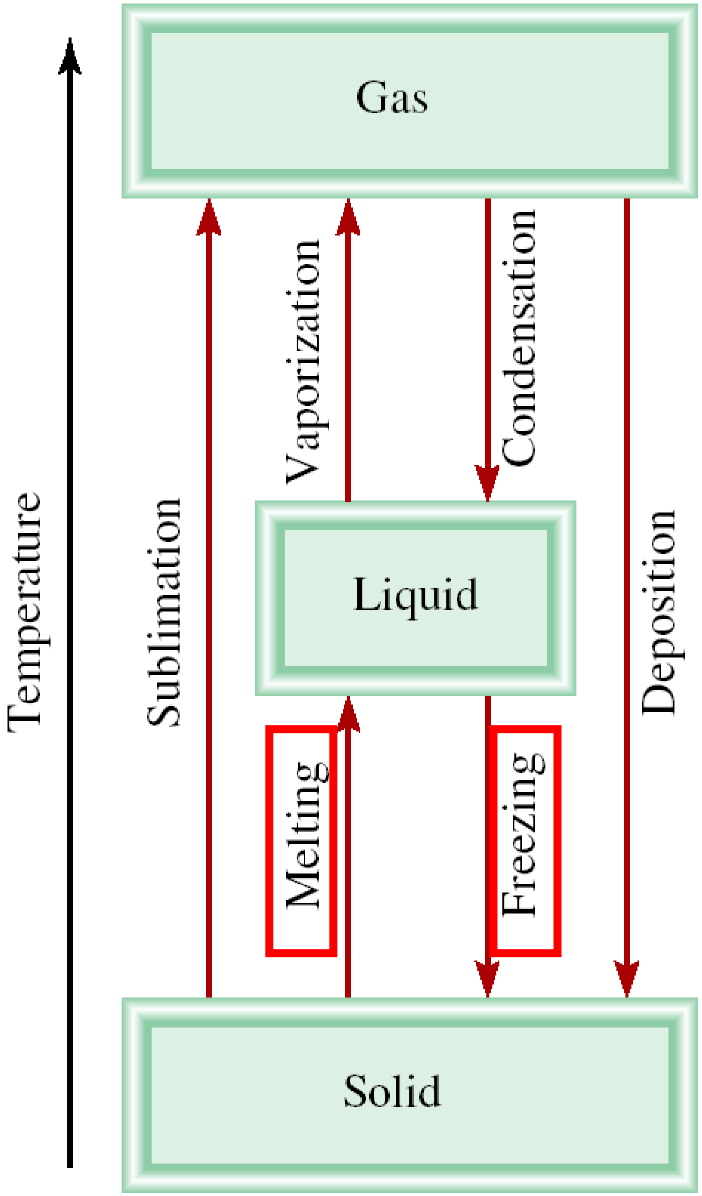
$T < T_c$

Solid-Liquid Equilibrium

$H_2O\ (s) \rightleftharpoons H_2O\ (l)$

The ***melting point*** of a solid or the ***freezing point*** of a liquid is the temperature at which the solid and liquid phases coexist in equilibrium.

Normal freezing point or melting point : the Temp. at which a substance melt or freeze at 1 atm pressure



Molar heat of fusion (ΔH_{fus}) is the energy required to melt 1 mole of a solid substance at its freezing point.

For every substance $\Delta H_{fus} < \Delta H_{vap}$

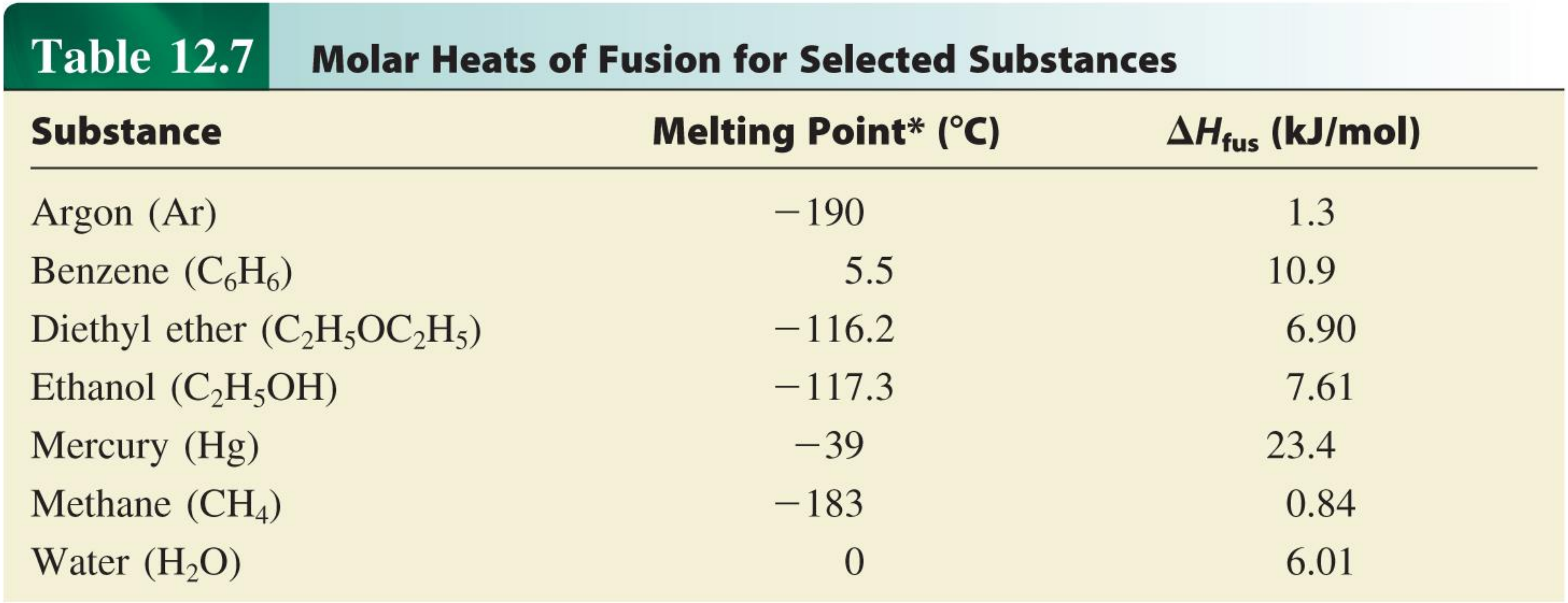
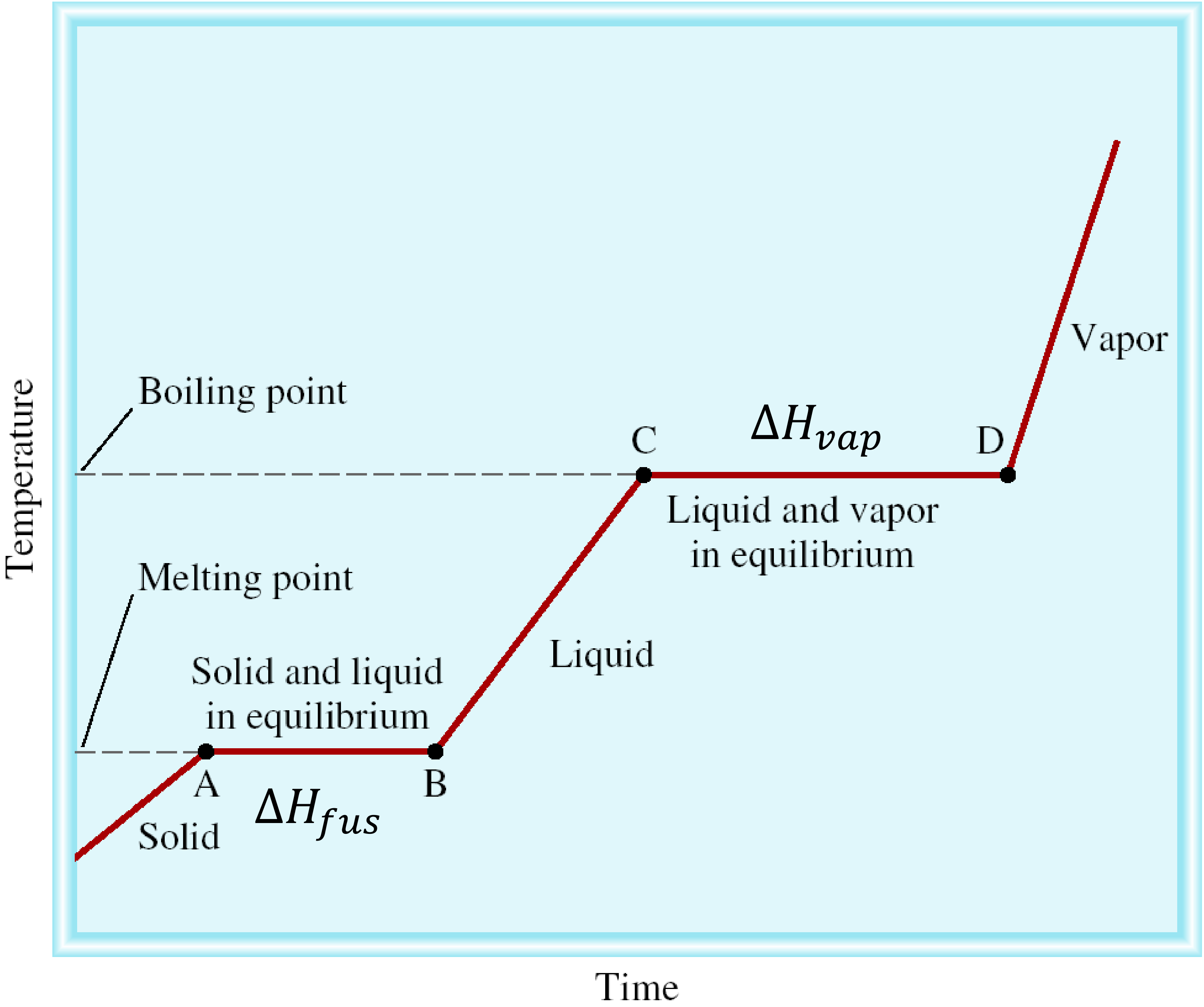


Table 12.7 **Molar Heats of Fusion for Selected Substances**

Substance	Melting Point* (°C)	ΔH_{fus} (kJ/mol)
Argon (Ar)	−190	1.3
Benzene (C_6H_6)	5.5	10.9
Diethyl ether ($C_2H_5OC_2H_5$)	−116.2	6.90
Ethanol (C_2H_5OH)	−117.3	7.61
Mercury (Hg)	−39	23.4
Methane (CH_4)	−183	0.84
Water (H_2O)	0	6.01

Heating Curve



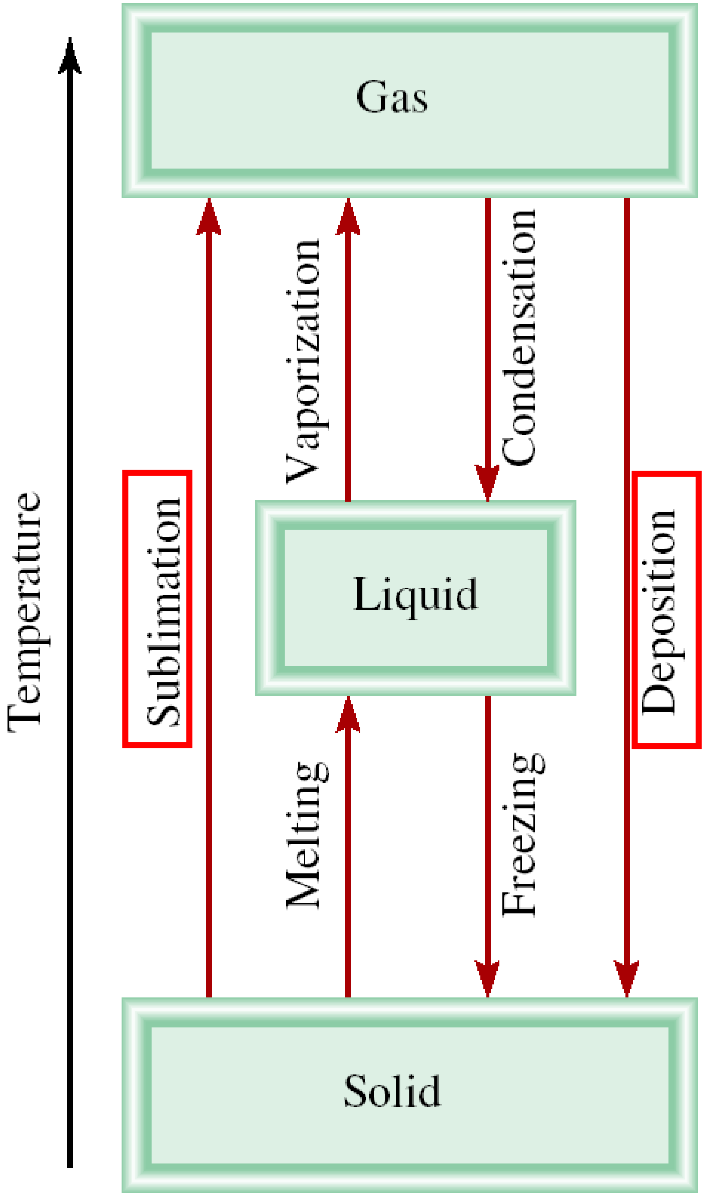
Solid-Gas Equilibrium

$$H_2O\ (s) \rightleftharpoons H_2O\ (g)$$

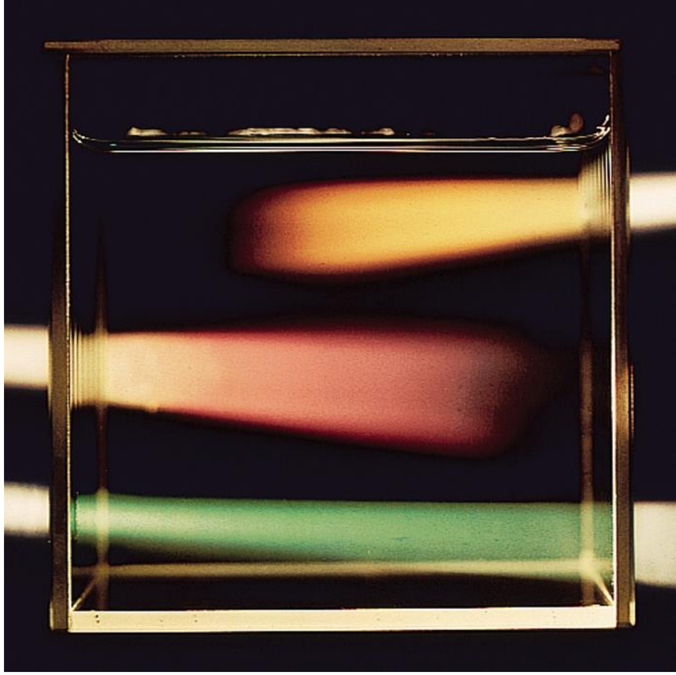
Molar heat of sublimation (ΔH_{sub}) is the energy required to sublime 1 mole of a solid.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

(Hess's Law)



Good Luck



Physical Properties of Solutions

Chapter 12

A ***solution*** is a homogenous mixture of 2 or more substances

The ***solute*** is(are) the substance(s) present in the smaller amount(s)

The ***solvent*** is the substance present in the larger amount

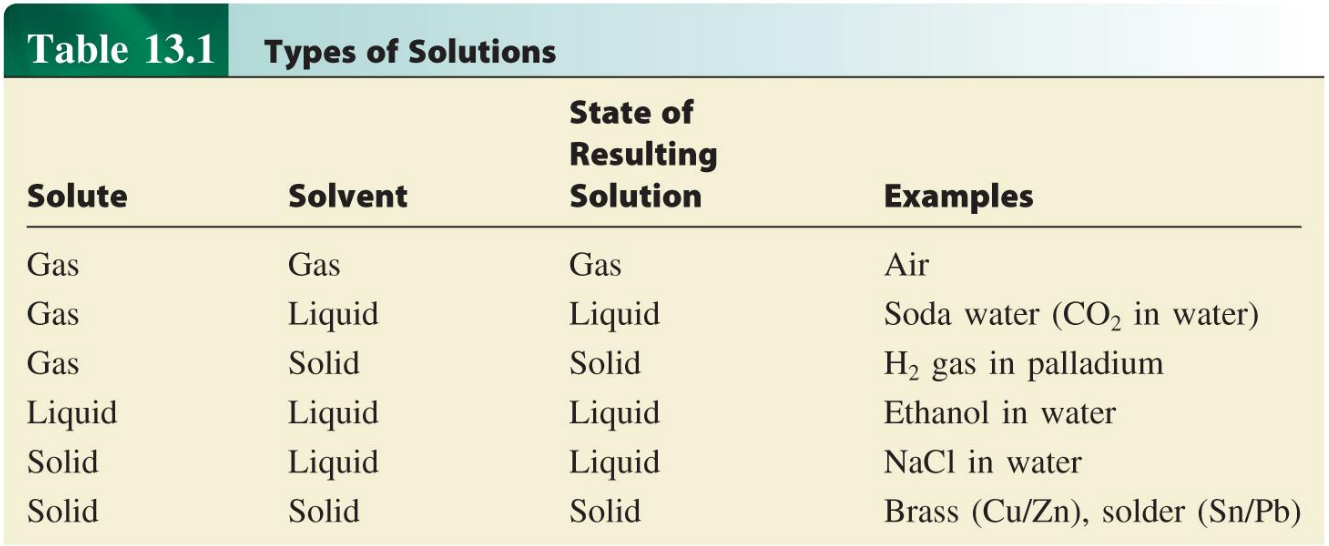


Table 13.1 **Types of Solutions**

Solute	Solvent	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO_2 in water)
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

Solute can be :

- Electrolyte: dissociate into ions when dissolve in solvent and conduct electricity

- Strong electrolyte: dissociate completely

Ex : $NaCl \longrightarrow Na^+ + Cl^-$

- Weak electrolyte: dissociate incompletely

Ex: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

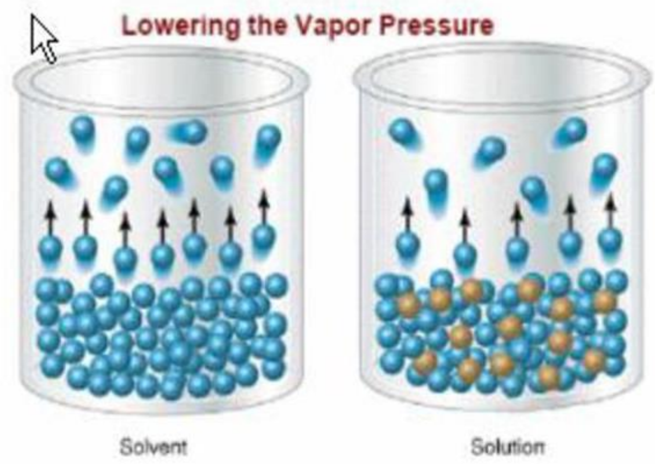
- Non-electrolyte: do not dissociate into ions when dissolve in solvent (Ex: Glucose $C_6H_{12}O_6$)

Colligative Properties of Nonelectrolyte Solutions
(*solvent + nonelectrolyte solute*)

Colligative properties are properties that depend *only on the* ***number*** *of solute particles* in solution and not on the **nature** of the solute particles.

1-Vapor-Pressure Lowering

- Nonvolatile solutes reduce the ability of surface solvent molecules to escape the liquid.
- Therefore, vapor pressure is lowered.
- The amount of vapor pressure lowering depends upon the *number of solute particles* (a colligative property)



Nonvolatile solute: substance which do not vaporize rapidly

1-Vapor-Pressure Lowering

$$\boxed{P_1 = X_1 P_1^0}$$

Raoult's law

$P1$ = vapor pressure of solvent above solution

P_1^0 = vapor pressure of **pure** solvent

X_1 = mole fraction of the solvent

If the solution contains only one solute:

$X_1 = 1 – X_2$

X_2 = mole fraction of the solute

$$P_1^0 - P_1 = \Delta P = X_2 P_1^0$$

$$\boxed{\therefore\ \Delta P = X_2 . P_1^{\circ}}$$

↓

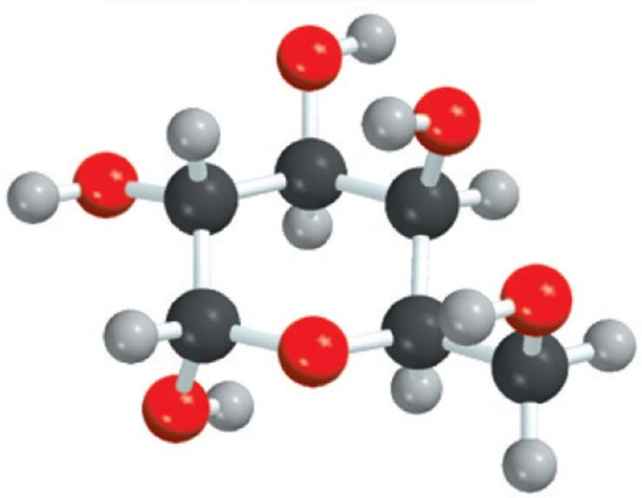
Vapor pressure lowering

Example 13.6

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30°C.

What is the vapor-pressure lowering?

The vapor pressure of pure water at 30°C is given in Table 5.2 (p. 157). Assume the density of the solvent is 1.00 g/mL.



Example 13.6

Strategy We need Raoult's law [Equation (13.6)] to determine the vapor pressure of a solution. Note that glucose is a nonvolatile solute.

Solution The vapor pressure of a solution (P_1) is

$$\underset{\text{want to calculate}}{P_1} = \overset{\text{need to find}}{X_1}\underset{\text{given}}{P_1^\circ}$$

First we calculate the number of moles of glucose and water in the solution:

$$n_1(\text{water}) = 460\ \cancel{\text{mL}} \times \frac{1.00\ \cancel{\text{g}}}{1\ \cancel{\text{mL}}} \times \frac{1\ \text{mol}}{18.02\ \cancel{\text{g}}} = 25.5\ \text{mol}$$

$$n_2(\text{glucose}) = 218\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{180.2\ \cancel{\text{g}}} = 1.21\ \text{mol}$$

Example 13.6

The mole fraction of water, X_1, is given by

$$X_1 = \frac{n_1}{n_1 + n_2} = \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955$$

From Table 5.2, we find the vapor pressure of water at 30°C to be 31.82 mmHg. Therefore, the vapor pressure of the glucose solution is

$$P_1 = 0.955 \times 31.82 \text{ mmHg}$$

$$= 30.4 \text{ mmHg}$$

Finally, the vapor-pressure lowering (ΔP) is (31.82 − 30.4) mmHg, or 1.4 mmHg.

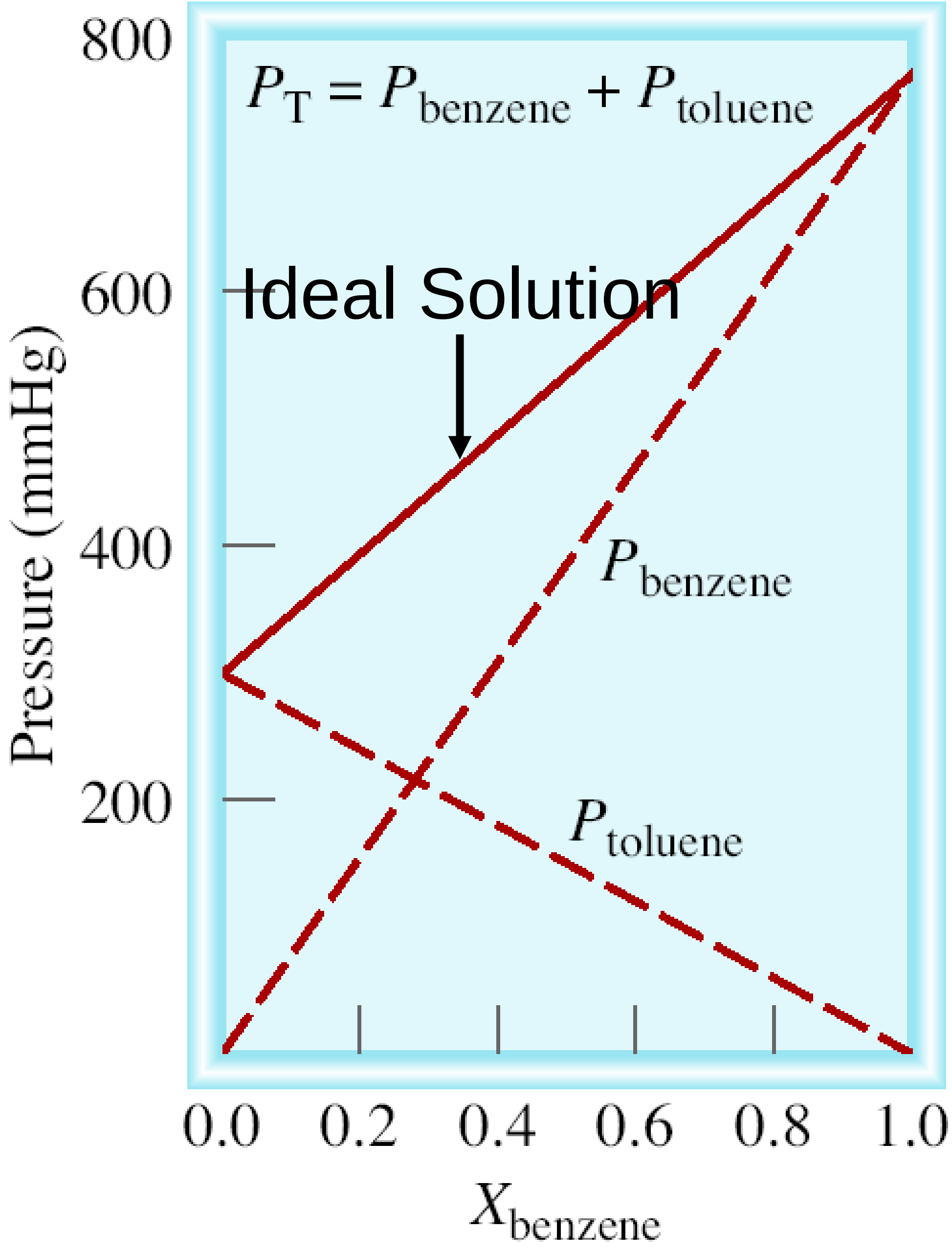
If both components are volatile(volatile solvent + volatile solute)

In this case we have two types of solutions :

1- Ideal solution: any solution obey Raoult's law ($P_i = X_i . P_i^{\circ}$)

In this solution, A-B interactions are same as A-A, and B-B (assume A=solvent, B=solute), then $\Delta H_{solution}$=zero

(ex: Benzene &Toluene solution)



$$P_A = X_A P_A^0$$

$$P_B = X_B P_B^0$$

$$P_T = P_A + P_B$$

$$P_T = X_A P_A^0 + X_B P_B^0$$

2- Real solution : solution that does not obey Raoult's law

In this solution, A-B interactions are different from A-A, and B-B

- positive deviation from Raoult's law:

A-B interactions are weaker than A-A, and B-B.

$\Delta H_{solution} >$ zero(endothermic)

$P_i(real) > P_i(ideal), then\ P_{total}(real) > P_{total}(ideal)$

- Negative deviation from Raoult's law:

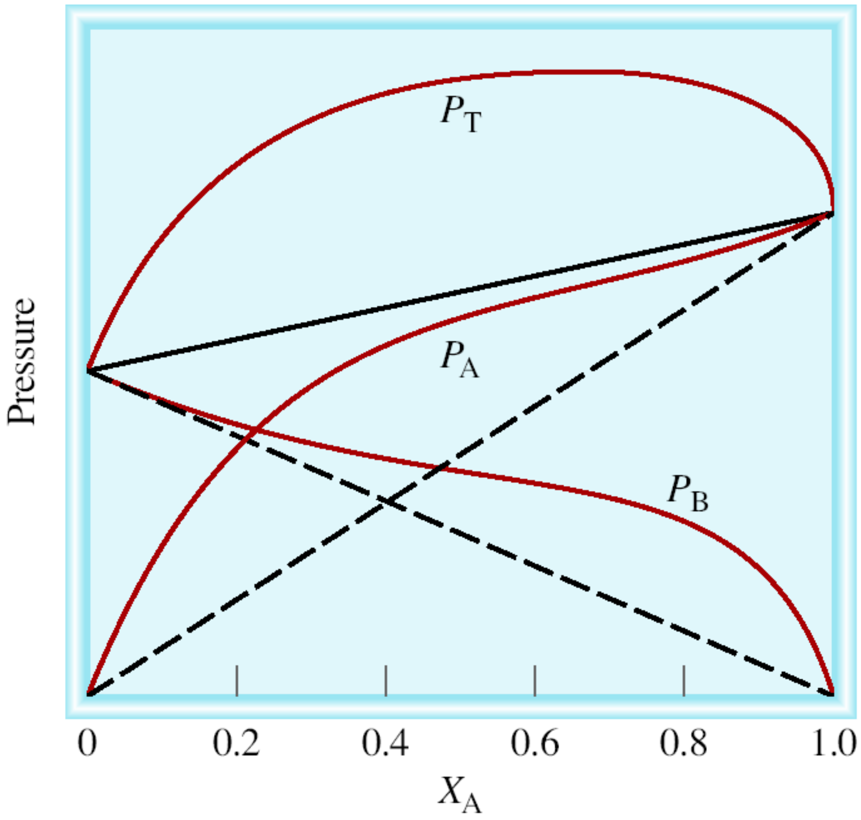
A-B interactions are stronger than A-A, and B-B.

$\Delta H_{solution} <$ zero(exothermic)

$P_i(real) < P_i(ideal), then\ P_{total}(real) < P_{total}(ideal)$

P_T is greater than predicted by Raoult’s law

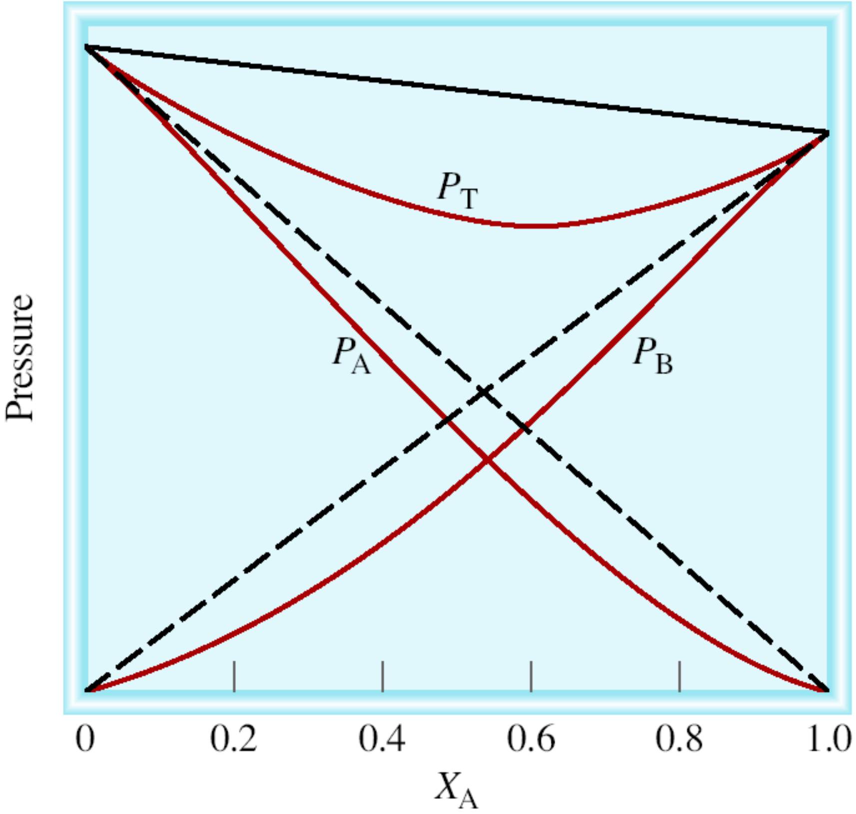
(Positive deviation)



Force A-B < Force A-A & Force B-B

P_T is less than predicted by Raoult’s law

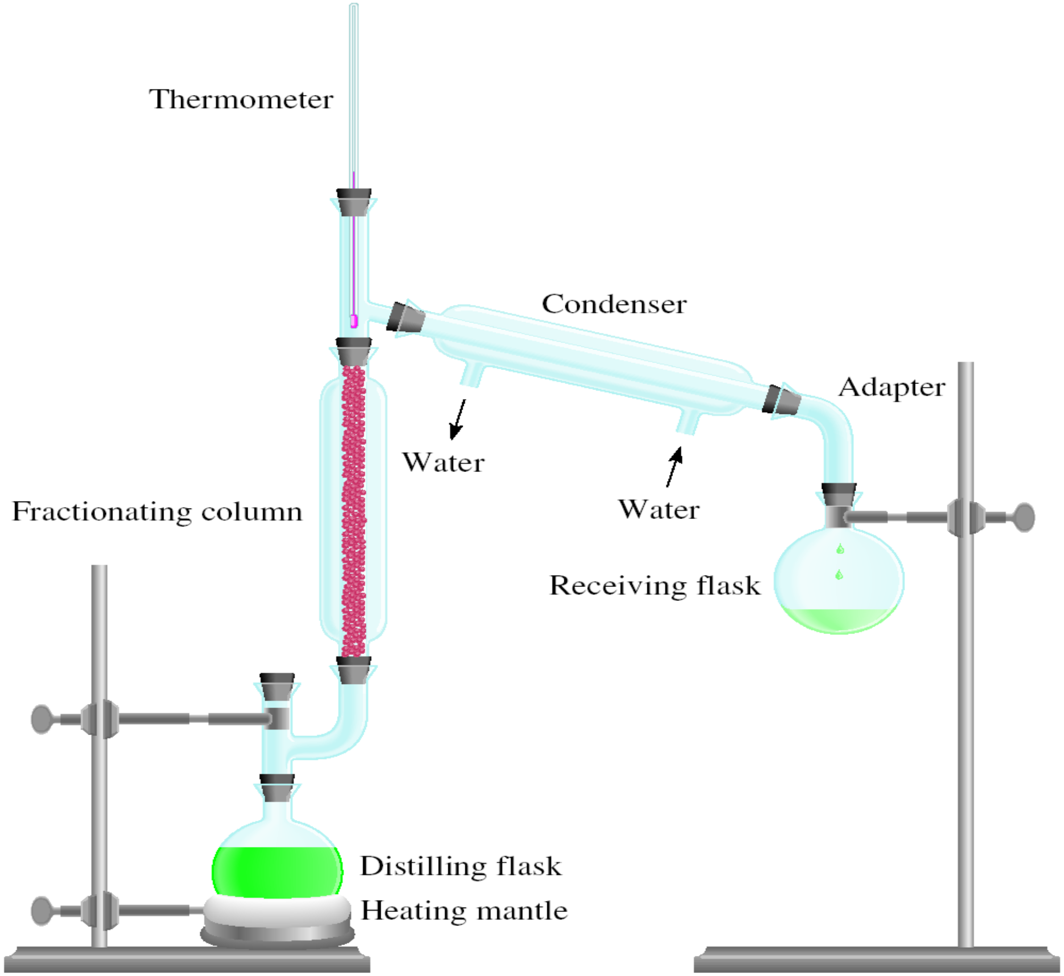
(Negative deviation)



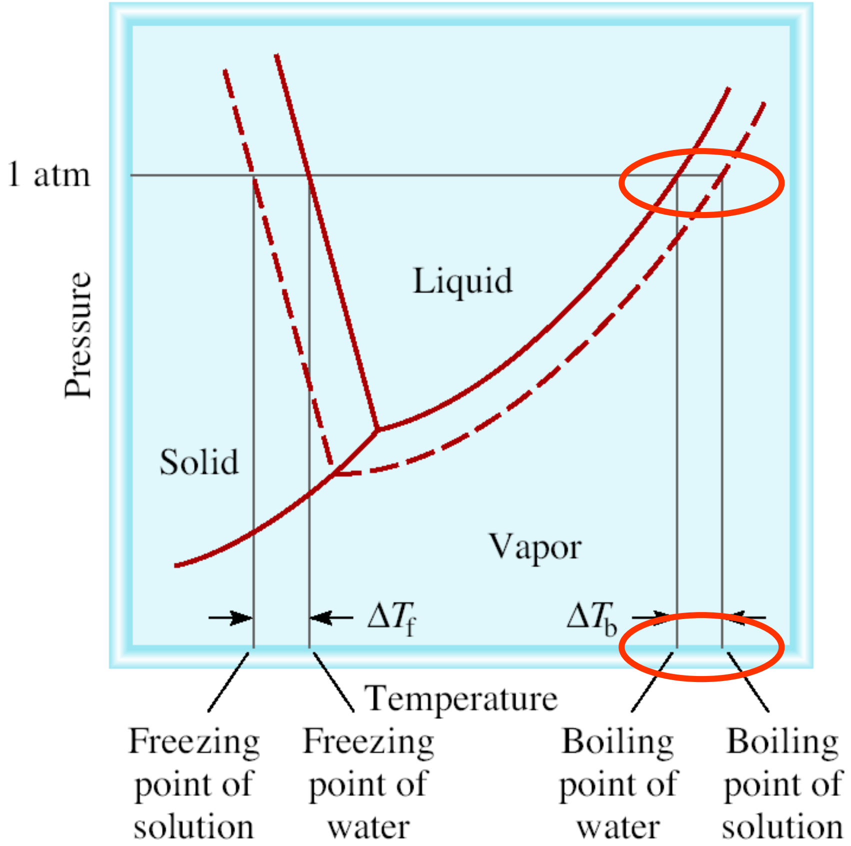
Force A-B > Force A-A & Force B-B

Fractional Distillation Apparatus

Fractional Distillation: process to separate liquids components of solution based On their boiling points



2- Boiling-Point Elevation



$$\Delta T_b = T_b - T_b^0$$

T_b^0 is the boiling point of the pure solvent

T_b is the boiling point of the solution

$T_b > T_b^0$ $\Delta T_b > 0$

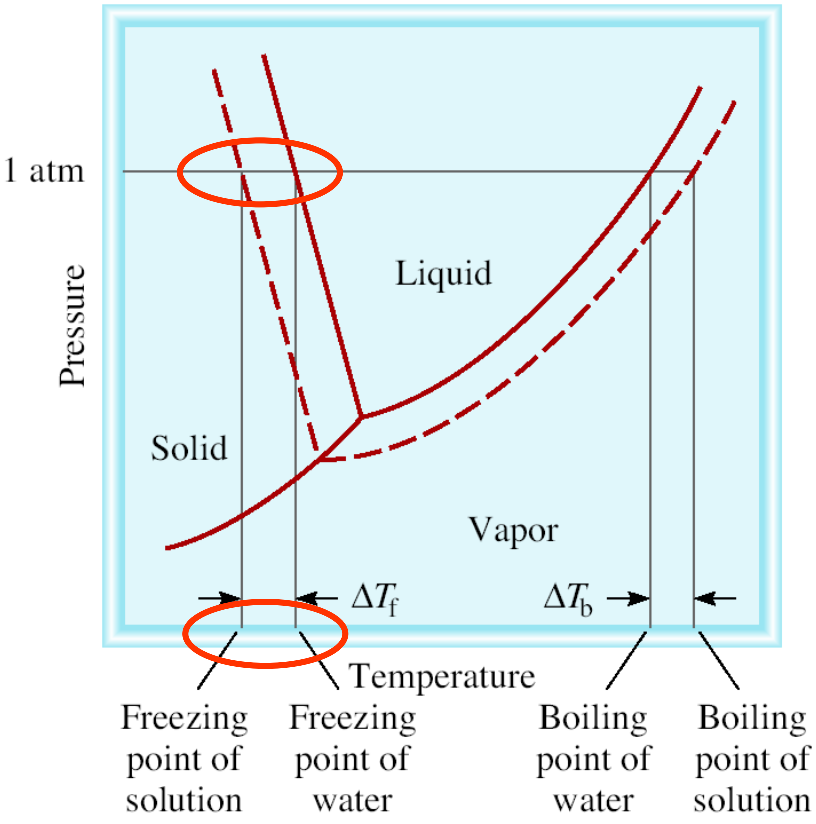
$$\boxed{\Delta T_b = K_b\, m}$$

m is the molality of the solution

$$m = \frac{mole\ of\ solute}{Kg\ solvent}$$

K_b is the molal boiling-point elevation constant (^{0}C/*m*) for a given solvent

3-Freezing-Point Depression



$$\Delta T_f = T_f^0 - T_f$$

T_f^0 is the freezing point of the pure solvent

T_f is the freezing point of the solution

$T_f^0 > T_f \qquad \Delta T_f > 0$

$$\boxed{\Delta T_f = K_f\, m}$$

m is the molality of the solution

K_f is the molal freezing-point depression constant (^{0}C/*m*) for a given solvent

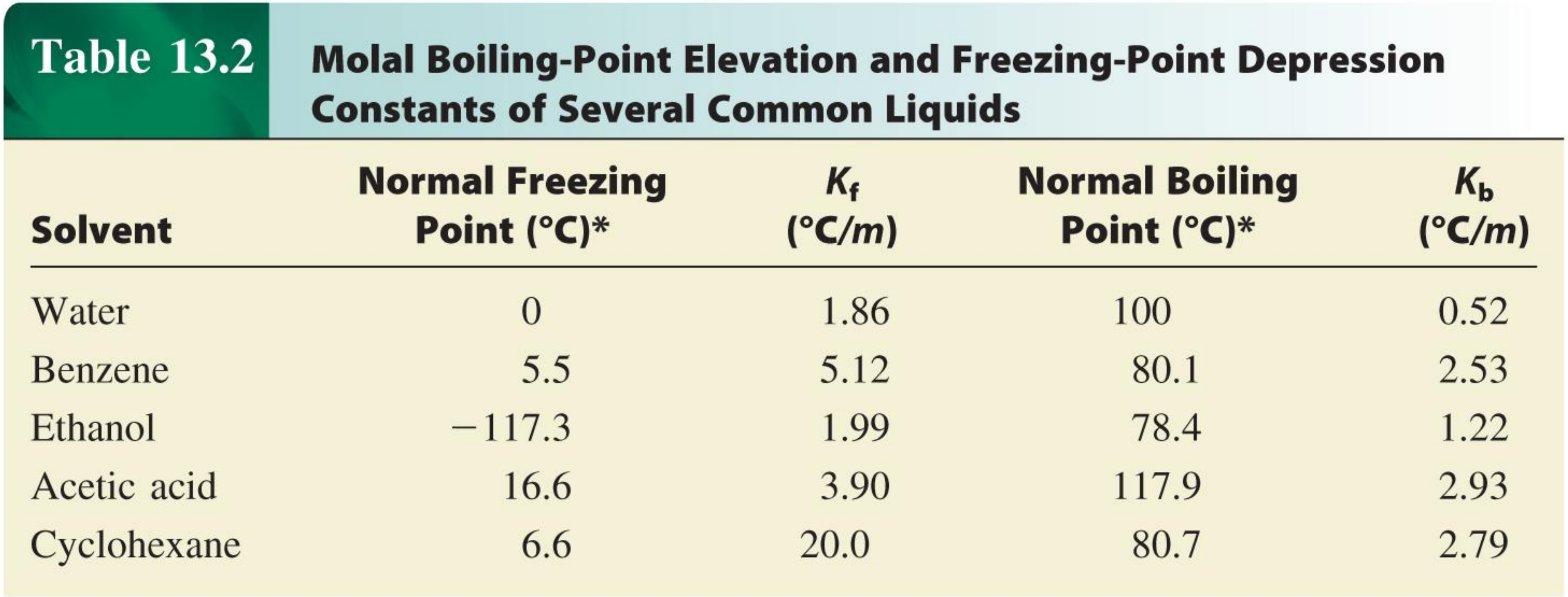


Table 13.2 **Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids**

Solvent	Normal Freezing Point (°C)*	K_f (°C/*m*)	Normal Boiling Point (°C)*	K_b (°C/*m*)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	−117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

Example 13.7

Ethylene glycol (EG), $CH_2(OH)CH_2(OH)$, is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p. 197°C).

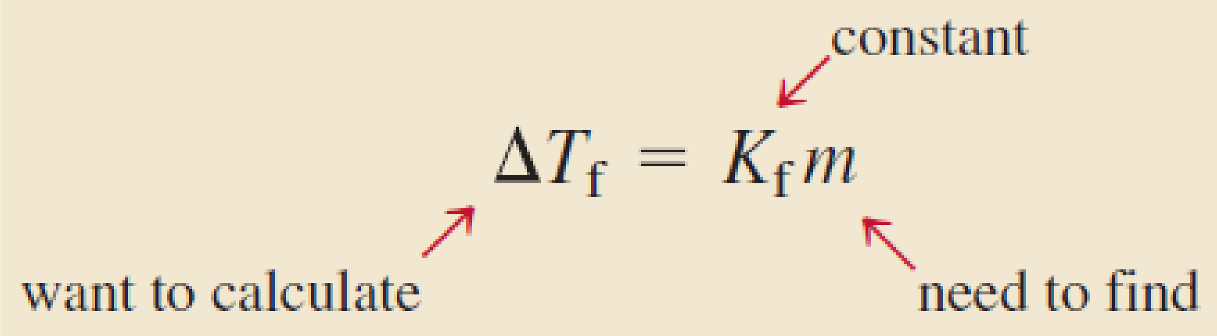
Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water.

Would you keep this substance in your car radiator during the summer?

The molar mass of ethylene glycol is 62.07 g.

Example 13.7

Strategy This question asks for the depression in freezing point of the solution.



$$\underset{\text{want to calculate}}{\Delta T_{\mathrm{f}}} = \overset{\text{constant}}{K_{\mathrm{f}}}\,\underset{\text{need to find}}{m}$$

The information given enables us to calculate the molality of the solution and we refer to Table 13.2 for the K_{f} of water.

Solution To solve for the molality of the solution, we need to know the number of moles of EG and the mass of the solvent in kilograms.

Example 13.7

We find the molar mass of EG, and convert the mass of the solvent to 2.505 kg, and calculate the molality as follows:

$$651\ \cancel{\text{g EG}} \times \frac{1\ \text{mol EG}}{62.07\ \cancel{\text{g EG}}} = 10.5\ \text{mol EG}$$

$$\begin{aligned} m &= \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \\ &= \frac{10.5\ \text{mol EG}}{2.505\ \text{kg H}_2\text{O}} = 4.19\ \text{mol EG/kg H}_2\text{O} \\ &= 4.19\ m \end{aligned}$$

From Equation (13.9) and Table 13.2 we write

$$\begin{aligned} \Delta T_f &= K_f m \\ &= (1.86^\circ\text{C}/m)(4.19\ m) \end{aligned}$$

= 7.79°C

Example 13.7

Because pure water freezes at 0°C, the solution will freeze at -7.79 °C (7.79= 0 − T)

We can calculate boiling-point elevation in the same way as follows:

$$\begin{aligned}\Delta T_b &= K_b m \\ &= (0.52°\text{C}/m)(4.19\ m)\end{aligned}$$

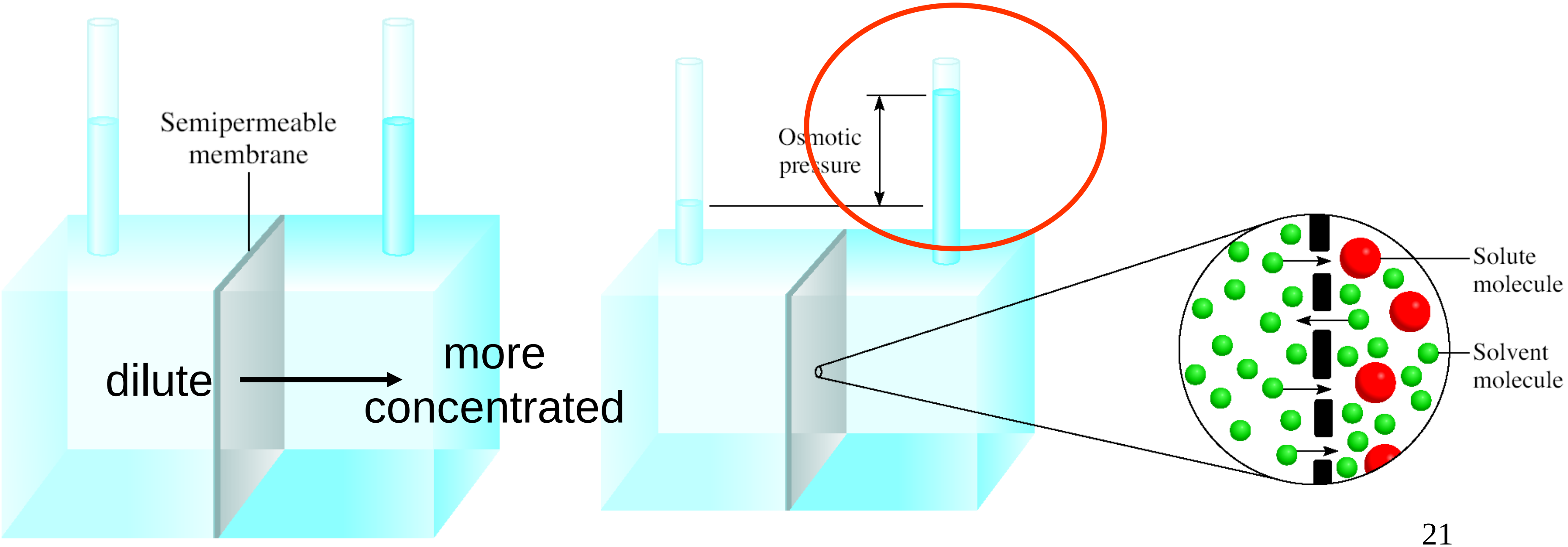
Because the solution will boil at (100 + 2.2)°C, or 102.2°C, it would be preferable to leave the antifreeze in your car radiator in summer to prevent the solution from boiling.

4- Osmotic Pressure (π)

Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

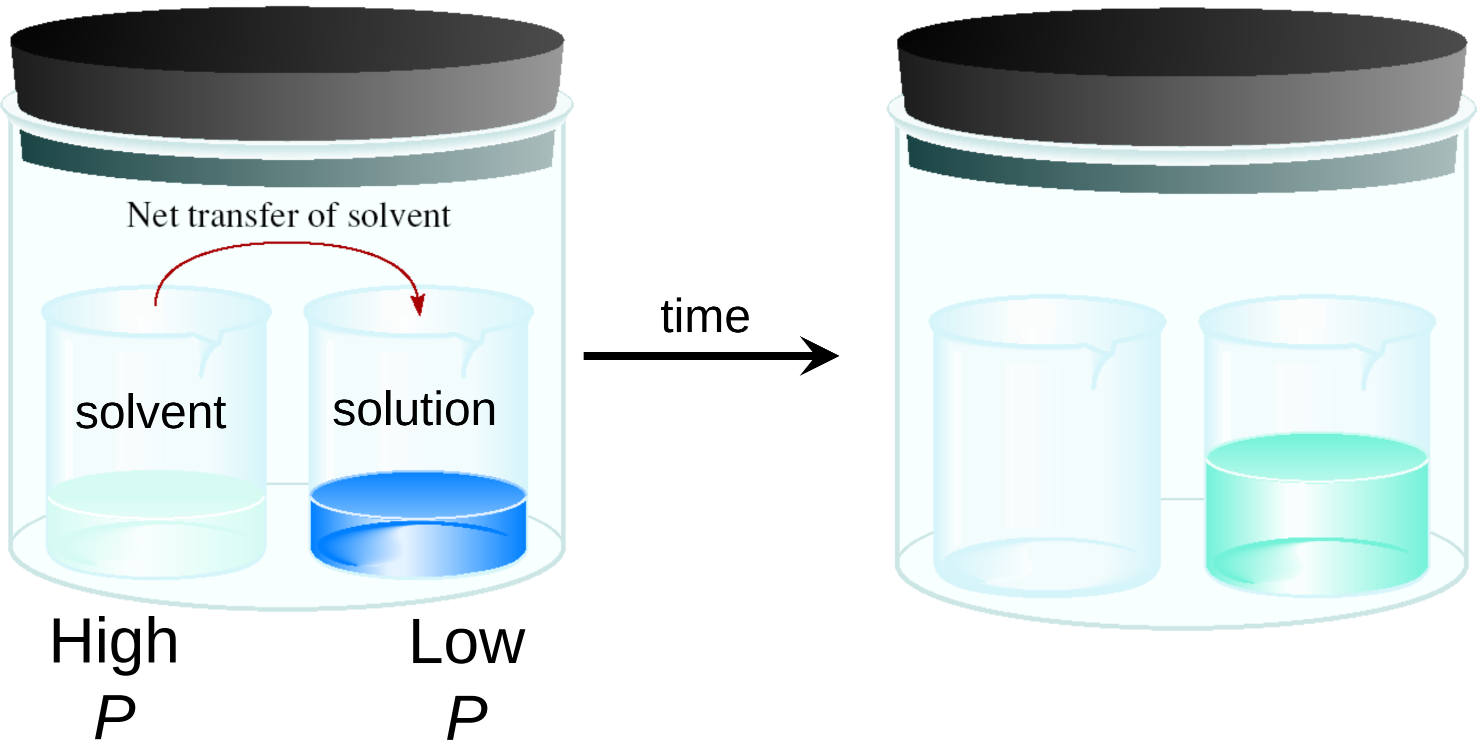
A ***semipermeable membrane*** allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (π) is the pressure required to stop osmosis.



dilute → more concentrated

Osmotic Pressure (π)



$$\boxed{\pi = MRT}$$

M is the molarity of the solution

R is the gas constant

T is the temperature (in K)

- If we have two solutions with same concentrations, so they have same osmotic pressures(Isotonic)
- If we have two solutions with different concentrations, so the More concentrated one called (Hypertonic)

  & The less concentrated one called (Hypotonic)

(osmosis : solvent molecules move from Hypotonic to Hypertonic)

Colligative Properties of Nonelectrolyte Solutions

Vapor-Pressure Lowering $P_1 = X_1 P_1^{\circ}$

Boiling-Point Elevation $\Delta T_b = K_b m$

Freezing-Point Depression $\Delta T_f = K_f m$

Osmotic Pressure (π) $\pi = MRT$

Example 13.8

A 7.85-g sample of a compound with the empirical formula C_5H_4 is dissolved in 301 g of benzene.

The freezing point of the solution is 1.05°C below that of pure benzene.

What are the molar mass and molecular formula of this compound?

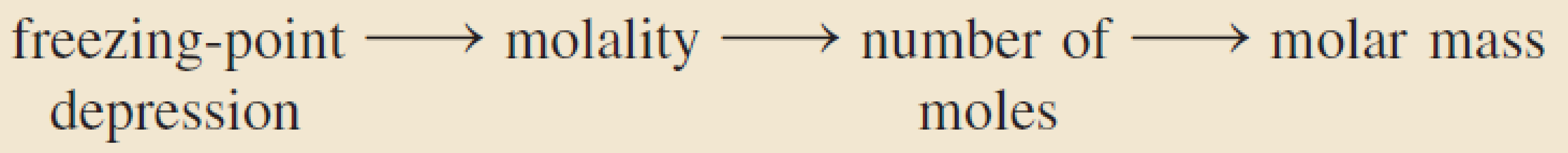
Example 13.8

Strategy Solving this problem requires three steps. First, we calculate the molality of the solution from the depression in freezing point.

Next, from the molality we determine the number of moles in 7.85 g of the compound and hence its molar mass.

Finally, comparing the experimental molar mass with the empirical molar mass enables us to write the molecular formula.

Solution The sequence of conversions for calculating the molar mass of the compound is



$$\begin{array}{c}\text{freezing-point}\\ \text{depression}\end{array} \longrightarrow \text{molality} \longrightarrow \begin{array}{c}\text{number of}\\ \text{moles}\end{array} \longrightarrow \text{molar mass}$$

Example 13.8

Our first step is to calculate the molality of the solution. From Equation (13.9) and Table 13.2 we write

$$\text{molality} = \frac{\Delta T_f}{K_f} = \frac{1.05°\text{C}}{5.12°\text{C}/m} = 0.205\ m$$

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

$$0.301\ \text{kg} \times \frac{0.205\ \text{mol}}{1\ \text{kg}} = 0.0617\ \text{mol}$$

Example 13.8

Thus, the molar mass of the solute is

$$\begin{aligned}\text{molar mass} &= \frac{\text{grams of compound}}{\text{moles of compound}}\\ &= \frac{7.85\ \text{g}}{0.0617\ \text{mol}} = 127\ \text{g/mol}\end{aligned}$$

Now we can determine the ratio

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{127\ \text{g/mol}}{64\ \text{g/mol}} \approx 2$$

Therefore, the molecular formula is $(C_5H_4)_2$ or $C_{10}H_8$ (naphthalene).

Example 13.9

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume.

If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, calculate the molar mass of hemoglobin.

Example 13.9

Strategy We are asked to calculate the molar mass of Hb. The steps are similar to those outlined in Example 13.8.

From the osmotic pressure of the solution, we calculate the molarity of the solution.

Then, from the molarity, we determine the number of moles in 35.0 g of Hb and hence its molar mass. What units should we use for π and temperature?

Solution The sequence of conversions is as follows:

$$\text{osmotic pressure} \longrightarrow \text{molarity} \longrightarrow \text{number of moles} \longrightarrow \text{molar mass}$$

Example 13.9

First we calculate the molarity using Equation (13.10)

$$\begin{aligned}
\pi &= MRT \\
M &= \frac{\pi}{RT} \\
&= \frac{10.0\ \text{mmHg} \times \dfrac{1\ \text{atm}}{760\ \text{mmHg}}}{(0.0821\ \text{L} \cdot \text{atm/K} \cdot \text{mol})(298\ \text{K})} \\
&= 5.38 \times 10^{-4}\, M
\end{aligned}$$

The volume of the solution is 1 L, so it must contain 5.38×10^{-4} mol of Hb.

Example 13.9

We use this quantity to calculate the molar mass:

$$\text{moles of Hb} = \frac{\text{mass of Hb}}{\text{molar mass of Hb}}$$

$$\begin{aligned}\text{molar mass of Hb} &= \frac{\text{mass of Hb}}{\text{moles of Hb}} \\ &= \frac{35.0\ \text{g}}{5.38 \times 10^{-4}\ \text{mol}} \\ &= 6.51 \times 10^{4}\ \text{g/mol}\end{aligned}$$

Colligative Properties of Electrolyte Solutions

0.1 m NaCl solution → 0.1 m Na^+ ions & 0.1 m Cl^- ions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

0.1 m NaCl solution → 0.2 m ions in solution

$$\textbf{\textit{van't Hoff factor (i)}} = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$$

	i should be
nonelectrolytes	1
NaCl	2
$CaCl_2$	3

Colligative Properties of Electrolyte Solutions

Boiling-Point Elevation $\Delta T_b = i\,K_b\,m$

Freezing-Point Depression $\Delta T_f = i\,K_f\,m$

Osmotic Pressure (π) $\pi = iMRT$

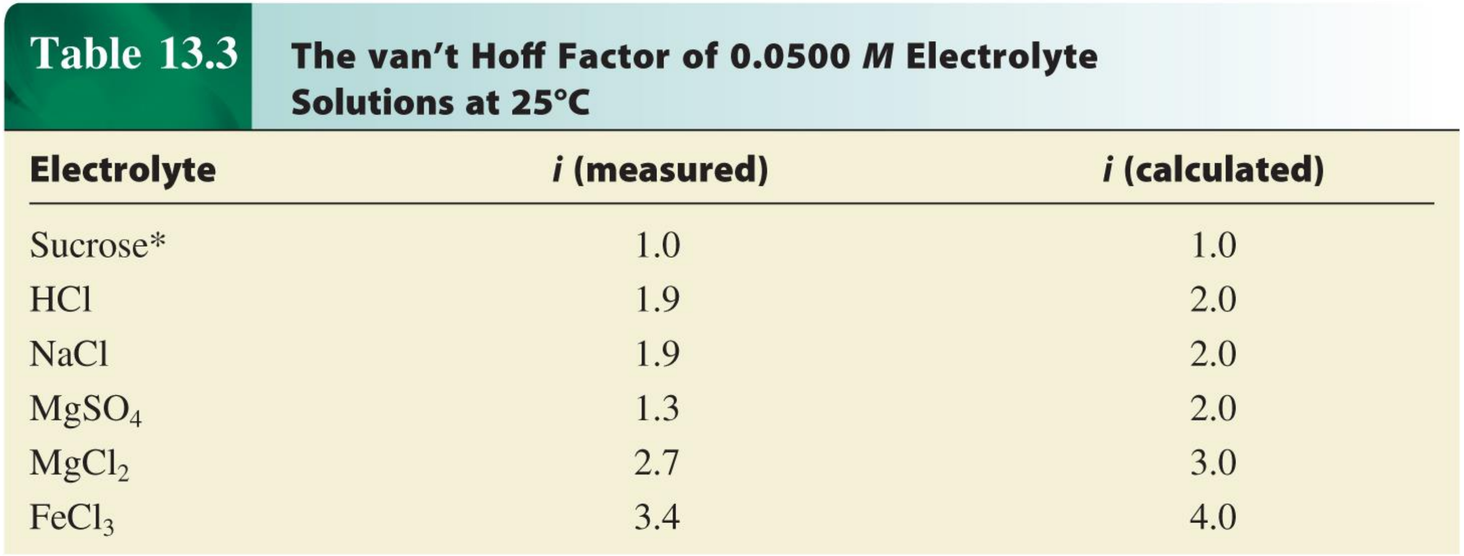


Table 13.3 The van't Hoff Factor of 0.0500 *M* Electrolyte Solutions at 25°C

Electrolyte	*i* (measured)	*i* (calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
$MgSO_4$	1.3	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0

Example 13.10

The osmotic pressure of a 0.010 *M* potassium iodide (KI) solution at 25°C is 0.465 atm.

Calculate the van’t Hoff factor for KI at this concentration.

Example 13.10

Strategy Note that KI is a strong electrolyte, so we expect it to dissociate completely in solution. If so, its osmotic pressure would be

$$2(0.010\,M)(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(298\ \text{K}) = 0.489\ \text{atm}$$

However, the measured osmotic pressure is only 0.465 atm. The smaller than predicted osmotic pressure means that there is ion-pair formation, which reduces the number of solute particles (K^+ and I^- ions) in solution.

Example 13.10

Solution From Equation (13.13) we have

$$\begin{aligned} i &= \frac{\pi}{MRT} \\ &= \frac{0.465\ \text{atm}}{(0.010\ M)(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(298\ \text{K})} \\ &= \boxed{1.90} \end{aligned}$$

Chemical Equilibrium

Chapter 14

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

Chemical equilibrium is achieved when:

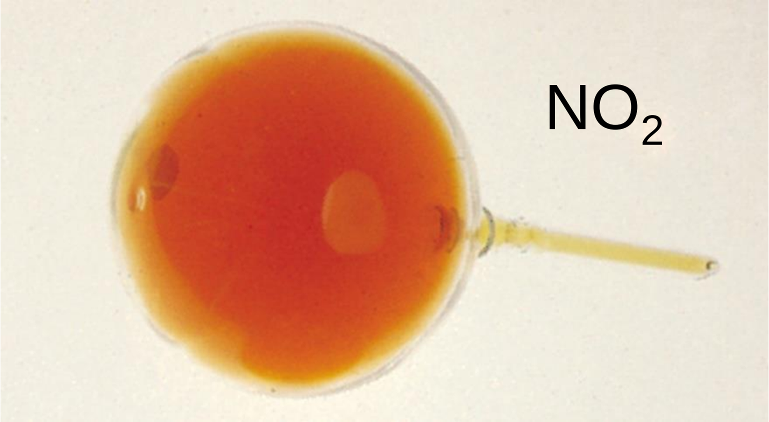
- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant

Physical equilibrium

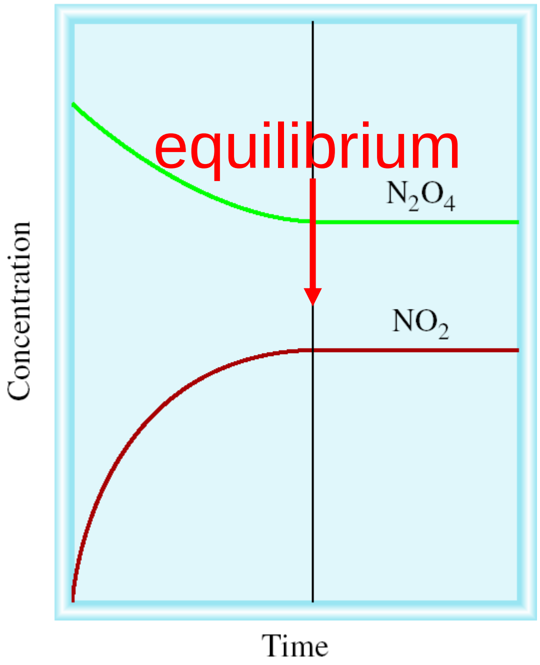
$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

Chemical equilibrium

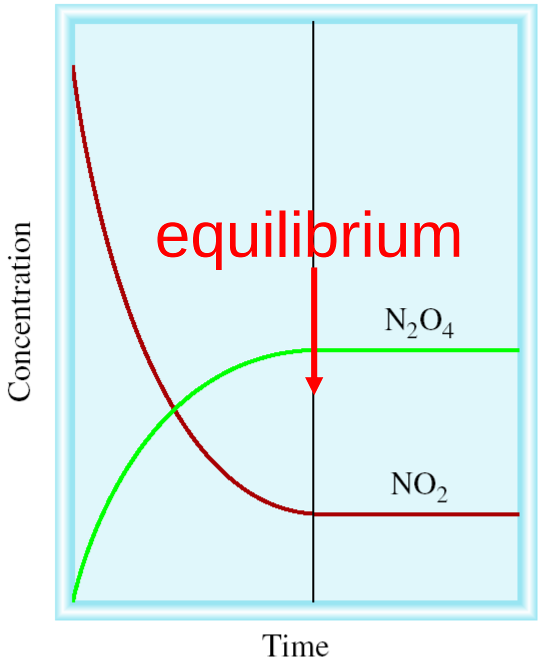
$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$



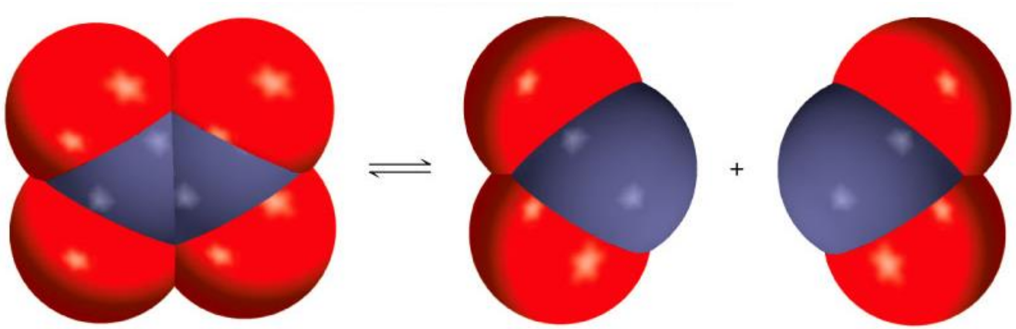
$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$



Start with N_2O_4



Start with NO_2



Equilibrium constant

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

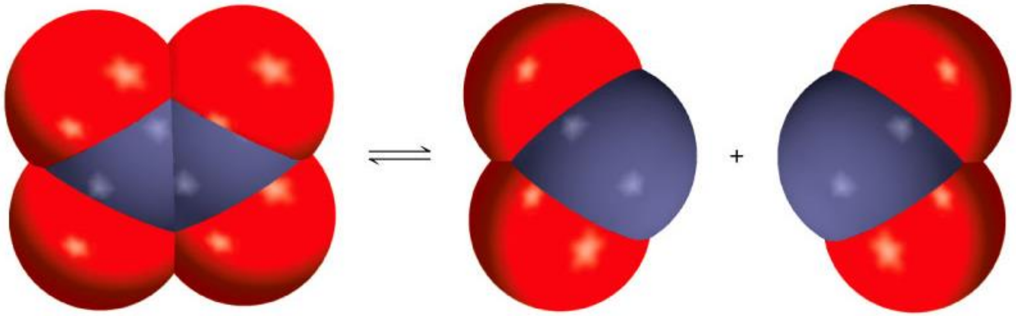
$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{[C]_{eq}^{\,c}\ [D]_{eq}^{\,d}}{[A]_{eq}^{\,a}\ [B]_{eq}^{\,b}}$$

Law of Mass Action

Equilibrium constant



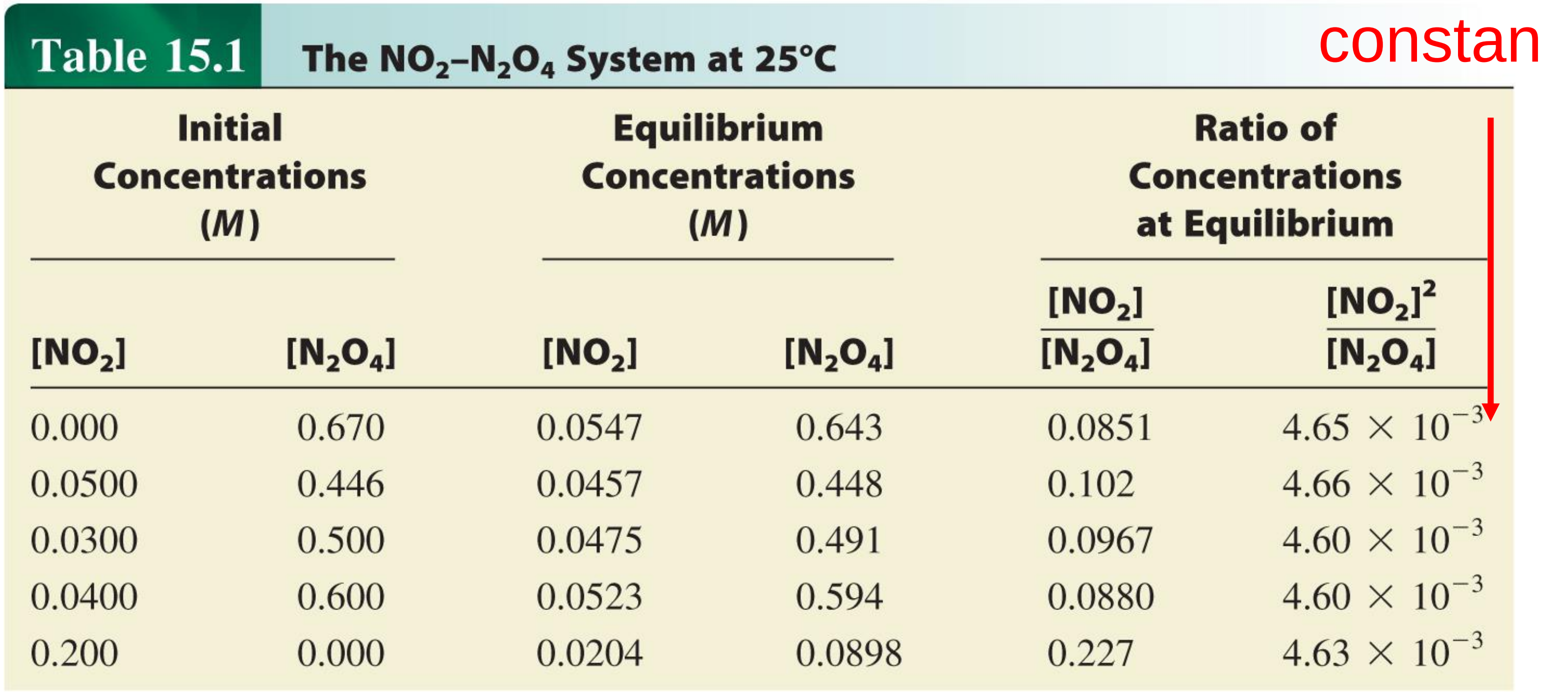


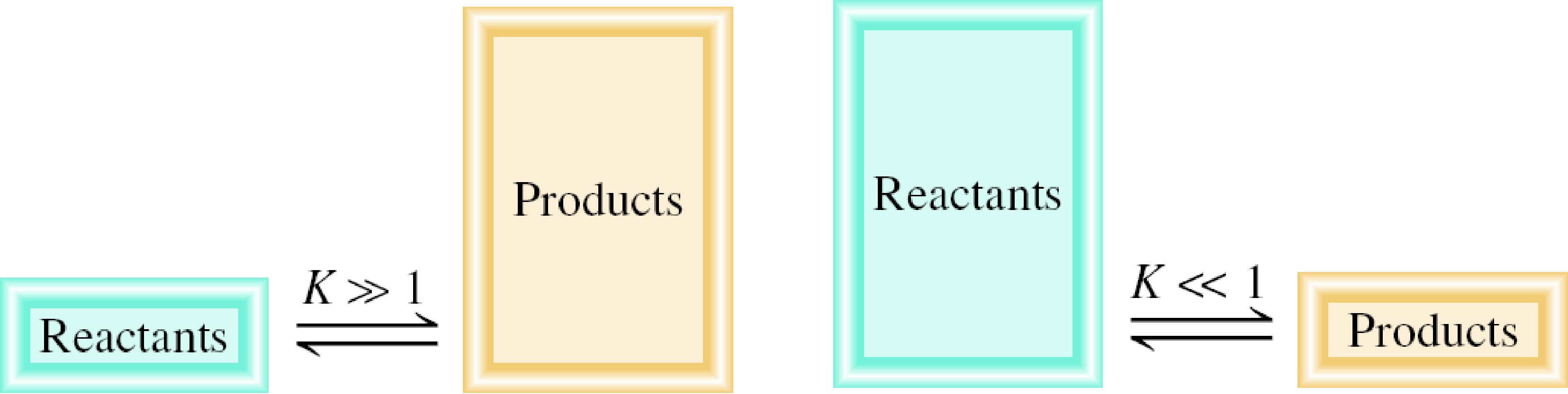
Table 15.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

constant

$$K = \frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{A}]^{a}[\mathrm{B}]^{b}} \qquad a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

	Equilibrium Will	
$K >> 1$	Lie to the right	Favor products
$K << 1$	Lie to the left	Favor reactants



Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase.**

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P_{NO_2}^{\ 2}}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$aA\ (g) + bB\ (g) \rightleftharpoons cC\ (g) + dD\ (g)$$

$$K_p = K_c(RT)^{\Delta n}$$

Δn = moles of gaseous products – moles of gaseous reactants

$= (c + d) – (a + b)$

Homogeneous Equilibrium

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

$$K_c' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

$$[H_2O] = \text{constant}$$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = K_c'\,[H_2O]$$

General practice **not** to include units for the equilibrium constant.

Example 15.1

Write expressions for K_c, and K_P if applicable, for the following reversible reactions at equilibrium:

(a) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

(b) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

(c) $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$

Example 15.1

Strategy

Keep in mind the following facts: (1) the K_P expression applies only to gaseous reactions and (2) the concentration of solvent (usually water) does not appear in the equilibrium constant expression.

Example 15.1

Solution

(a) Because there are no gases present, K_P does not apply and we have only K_c.

$$K'_c = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$$

HF is a weak acid, so that the amount of water consumed in acid ionizations is negligible compared with the total amount of water present as solvent. Thus, we can rewrite the equilibrium constant as

$$\boldsymbol{K_c = \frac{[H_3O^+][F^-]}{[HF]}}$$

Example 15.1

(b)

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_p = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}}$$

(c) The equilibrium constant $K_c^{'}$ is given by

$$K_c^{'} = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Because the water produced in the reaction is negligible compared with the water solvent, the concentration of water does not change. Thus, we can write the new equilibrium constant as

$$K_c = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

Example 15.2

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

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

is found to be 1.05 at 250°C. If the equilibrium partial pressures of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?

Example 15.2

Strategy

The concentrations of the reacting gases are given in atm, so we can express the equilibrium constant in K_P. From the known K_P value and the equilibrium pressures of PCl_3 and PCl_5, we can solve for P_{Cl_2}.

Example 15.2

Solution

First, we write K_P in terms of the partial pressures of the reacting species

$$K_p = \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}}$$

Knowing the partial pressures, we write

$$1.05 = \frac{(0.463)(P_{Cl_2})}{(0.875)}$$

or

$$P_{Cl_2} = \frac{(1.05)(0.875)}{(0.463)} = \mathbf{1.98\ atm}$$

Example 15.2

Check

Note that we have added atm as the unit for P_{Cl_2}.

Example 15.3

Methanol (CH_3OH) is manufactured industrially by the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

The equilibrium constant (K_c) for the reaction is 10.5 at 220°C. What is the value of K_P at this temperature?

Example 15.3

Strategy

The relationship between K_c and K_P is given by Equation (15.5). What is the change in the number of moles of gases from reactants to product? Recall that

Δn = moles of gaseous products - moles of gaseous reactants

What unit of temperature should we use?

Example 15.3

Solution

The relationship between K_c and K_P is

$$K_P = K_c(0.0821T)^{\Delta n}$$

Because $T = 273 + 220 = 493$ K and $\Delta n = 1 - 3 = -2$, we have

$$K_P = (10.5)(0.0821 \times 493)^{-2}$$
$$= \mathbf{6.41 \times 10^{-3}}$$

Example 15.3

Check

Note that K_P, like K_c, is a dimensionless quantity. This example shows that we can get a quite different value for the equilibrium constant for the same reaction, depending on whether we express the concentrations in moles per liter or in atmospheres.

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases.**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_c' = \frac{[CaO][CO_2]}{[CaCO_3]}$$

$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = [CO_2] = K_c' \times \frac{[CaCO_3]}{[CaO]}$$

$$K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

Example 15.4

Consider the following heterogeneous equilibrium:

$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$

At 800°C, the pressure of CO_2 is 0.236 atm. Calculate (a) K_P and (b) K_c for the reaction at this temperature.

Example 15.4

Strategy

Remember that pure solids do not appear in the equilibrium constant expression. The relationship between K_P and K_c is given by Equation (15.5).

Solution

(a) Using Equation (15.8) we write

$$K_P = P_{CO_2}$$
$$= \mathbf{0.236}$$

Example 15.4

(b) From Equation (15.5), we know

$$K_P = K_c(0.0821T)^{\Delta n}$$

In this case, $T = 800 + 273 = 1073$ K and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$0.236 = K_c(0.0821 \times 1073)$$
$$K_c = \mathbf{2.68 \times 10^{-3}}$$

Multiple equilibrium

$$A + B \rightleftharpoons \cancel{C} + \cancel{D} \qquad K_c'$$

$$\cancel{C} + \cancel{D} \rightleftharpoons E + F \qquad K_c''$$

$$A + B \rightleftharpoons E + F \qquad K_c$$

$$K_c' = \frac{[C][D]}{[A][B]} \qquad K_c'' = \frac{[E][F]}{[C][D]}$$

$$K_c = \frac{[E][F]}{[A][B]}$$

$$K_c = K_c' \times K_c''$$

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ $2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3} \qquad K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

- When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

  - The value of K depend also on how the chemical equation is balanced

Ex $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

$$Kc = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$\frac{1}{2}\,N_2O_4\,(g) \rightleftharpoons NO_2\,(g)$

$$K`c = \frac{[NO_2]}{[N_2O_4]^{1/2}}$$

$$K`c = \sqrt{K_c} = \sqrt{(4.63\times10^{-3})} = 0.068$$

Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in *M*. In the gaseous phase, the concentrations can be expressed in *M* or in atm.
2. The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
3. The equilibrium constant is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
5. If a reaction can be expressed as a sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

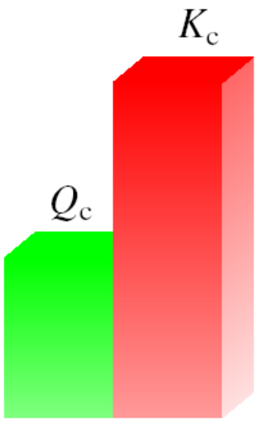
The ***reaction quotient (Q_c)*** is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant (K_c) expression.

- To determine the direction in which the net reaction will proceed to achieve equilibrium we compare the values of Qc & Kc

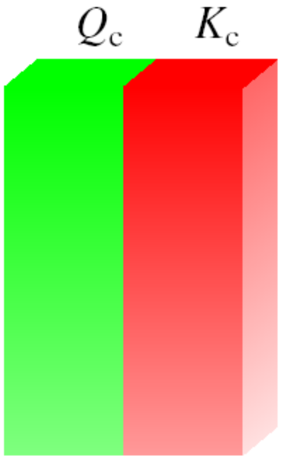
$$Q_c = \frac{[C]_i^c [D]_i^d}{[A]_i^a [B]_i^b} \text{ (before equilibrium)}$$

IF

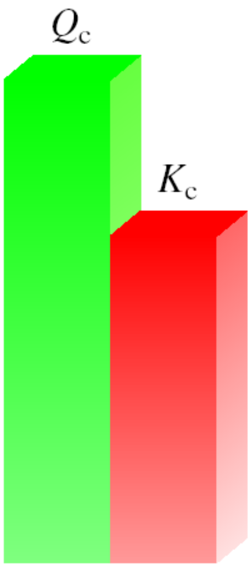
- $Q_c < K_c$ system proceeds from left to right to reach equilibrium
- $Q_c = K_c$ the system is at equilibrium
- $Q_c > K_c$ system proceeds from right to left to reach equilibrium



Reactants → Products



Equilibrium : no net change



Reactants ← Products

Example 15.5

At the start of a reaction, there are 0.249 mol N_2, 3.21×10^{-2} mol H_2, and 6.42×10^{-4} mol NH_3 in a 3.50-L reaction vessel at 375°C. If the equilibrium constant (K_c) for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

Example 15.5

Strategy

We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations and hence the reaction quotient (Q_c). How does a comparison of Q_c with K_c enable us to determine if the system is at equilibrium or, if not, in which direction will the net reaction proceed to reach equilibrium?

Example 15.5

Solution

The initial concentrations of the reacting species are

$$[N_2]_o = \frac{0.249\text{ mol}}{3.50\text{ L}} = 0.0711\ M$$

$$[H_2]_o = \frac{3.21 \times 10^{-2}\text{ mol}}{3.50\text{ L}} = 9.17 \times 10^{-3}\ M$$

$$[NH_3]_o = \frac{6.42 \times 10^{-4}\text{ mol}}{3.50\text{ L}} = 1.83 \times 10^{-4}\ M$$

Example 15.5

Next we write

$$Q_{\mathbf{c}} = \frac{[\mathrm{NH_3}]_{\mathbf{o}}^2}{[\mathrm{N_2}]_{\mathbf{o}}[\mathrm{H_2}]_{\mathbf{o}}^3} = \frac{(1.83 \times 10^{-4})^2}{(0.0711)(9.17 \times 10^{-3})^3} = 0.611$$

Because Q_c is smaller than K_c (1.2), the system is not at equilibrium. The net result will be an increase in the concentration of NH_3 and a decrease in the concentrations of N_2 and H_2. That is, the net reaction will proceed from left to right until equilibrium is reached.

Calculating Equilibrium Concentrations

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown x, which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x.
3. Having solved for x, calculate the equilibrium concentrations of all species.

Example 15.6

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.3 at this temperature. Calculate the concentrations of H_2, I_2, and HI at equilibrium.

Example 15.6

Strategy

We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations. Because initially no HI was present, the system could not be at equilibrium. Therefore, some H_2 would react with the same amount of I_2 (why?) to form HI until equilibrium was established.

Example 15.6

Solution We follow the preceding procedure to calculate the equilibrium concentrations.

Step 1: The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let *x* be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be 2*x*. We summarize the changes in concentrations as follows:

	H_2 +	I_2	$\rightleftharpoons$	2HI
Initial (*M*):	0.500	0.500		0.000
Change (*M*):	$-x$	$-x$		$+2x$
Equilibrium (*M*):	$(0.500 - x)$	$(0.500 - x)$		$2x$

Example 15.6

Step 2: The equilibrium constant is given by

$$K_{\mathbf{c}} = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}$$

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$

$$x = 0.393\ M$$

Example 15.6

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.500 - 0.393)\ M = \mathbf{0.107}\ \boldsymbol{M}$$

$$[I_2] = (0.500 - 0.393)\ M = \mathbf{0.107}\ \boldsymbol{M}$$

$$[HI] = 2 \times 0.393\ M = \mathbf{0.786}\ \boldsymbol{M}$$

Check You can check your answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.

Example 15.7

For the same reaction and temperature as in Example 15.6, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 *M*, 0.00414 *M*, and 0.0224 *M*, respectively. Calculate the concentrations of these species at equilibrium.

Example 15.7

Strategy

From the initial concentrations we can calculate the reaction quotient (Q_c) to see if the system is at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium. A comparison of Q_c with K_c also enables us to determine if there will be a depletion in H_2 and I_2 or HI as equilibrium is established.

Example 15.7

Solution

First we calculate Q_c as follows:

$$Q_c = \frac{[\mathrm{HI}]_0^2}{[\mathrm{H_2}]_0[\mathrm{I_2}]_0} = \frac{(0.0224)^2}{(0.00623)(0.00414)} = 19.5$$

Because Q_c (19.5) is smaller than K_c (54.3), we conclude that the net reaction will proceed from left to right until equilibrium is reached (see Figure 15.4); that is, there will be a depletion of H_2 and I_2 and a gain in HI.

Example 15.7

Step 1: Let *x* be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be 2*x*. Next we write

	H_2 +	I_2	$\rightleftharpoons$	2HI
Initial (*M*):	0.00623	0.00414		0.0224
Change (*M*):	$-x$	$-x$		$+2x$
Equilibrium (*M*):	$(0.00623 - x)$	$(0.00414 - x)$		$(0.0224 + 2x)$

Example 15.7

Step 2: The equilibrium constant is

$$K_\mathbf{c} = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]}$$

Substituting, we get

$$54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

It is not possible to solve this equation by the square root shortcut, as the starting concentrations $[H_2]$ and $[I_2]$ are unequal. Instead, we must first carry out the multiplications

$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$

Example 15.7

Collecting terms, we get

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation (see Appendix 4) is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here we have $a = 50.3$, $b = -0.654$, and $c = 8.98 \times 10^{-4}$, so that

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$$x = 0.0114\ M \qquad \text{or} \qquad x = 0.00156\ M$$

Example 15.7

The first solution is physically impossible because the amounts of H_2 and I_2 reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for x is easy.

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.00623 - 0.00156)\ M = \mathbf{0.00467}\ \boldsymbol{M}$$

$$[I_2] = (0.00414 - 0.00156)\ M - \mathbf{0.00258}\ \boldsymbol{M}$$

$$[HI] = (0.0224 + 2 \times 0.00156)\ M = \mathbf{0.0255}\ \boldsymbol{M}$$

Example 15.7

Check

You can check the answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.

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Acids and Bases

Chapter 15

Acids

Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.

React with certain metals to produce hydrogen gas.

React with carbonates and bicarbonates to produce carbon dioxide gas.

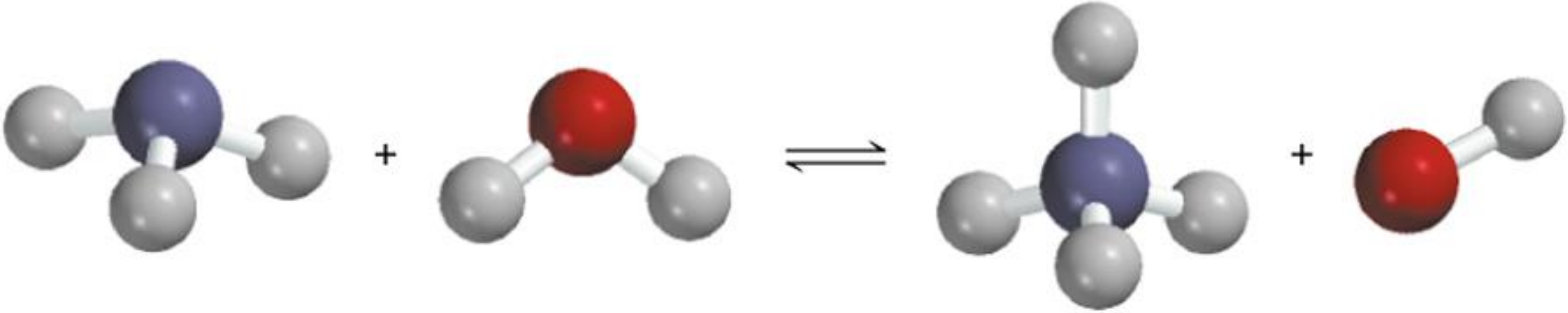
Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.

A Brønsted acid is a proton donor

A Brønsted base is a proton acceptor



$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

base	acid	$\rightleftharpoons$	acid	base
base	acid		conjugate acid	conjugate base

Example 16.1

Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in aqueous solution

$$NH_3(aq) + HF(aq) \rightleftharpoons NH_4^+(aq) + F^-(aq)$$

Example 16.1

Strategy

Remember that a conjugate base always has one fewer H atom and one more negative charge (or one fewer positive charge) than the formula of the corresponding acid.

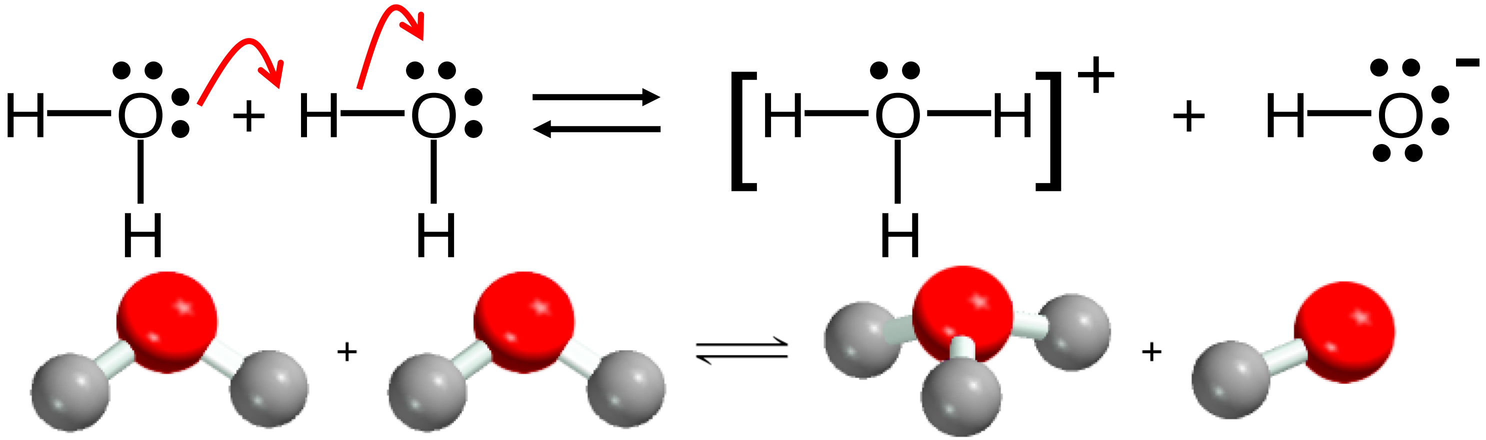
Solution

NH_3 has one fewer H atom and one fewer positive charge than NH_4^+. F^- has one fewer H atom and one more negative charge than HF. Therefore, the conjugate acid-base pairs are (1) NH_4^+ and NH_3 and (2) HF and F^-.

Acid-Base Properties of Water

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

autoionization of water



base

conjugate acid

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

acid

conjugate base

The Ion Product of Water

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq) \qquad K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad [H_2O] = \text{constant}$$

$$K_c[H_2O] = K_w = [H^+][OH^-]$$

The ***ion-product constant*** (***K_w***) is the product of the molar concentrations of H^+ and OH^- ions **at a particular temperature.**

$$\boxed{\begin{array}{c}\text{At } 25^0\text{C} \\ K_w = [H^+][OH^-] = 1.0 \times 10^{-14}\end{array}}$$

	Solution Is
$[H^+] = [OH^-]$	neutral
$[H^+] > [OH^-]$	acidic
$[H^+] < [OH^-]$	basic

Example 16.2

The concentration of OH^- ions in a certain household ammonia cleaning solution is 0.0025 *M*. Calculate the concentration of H^+ ions.

Example 16.2

Strategy

We are given the concentration of the OH^- ions and asked to calculate $[H^+]$. The relationship between $[H^+]$ and $[OH^-]$ in water or an aqueous solution is given by the ion-product of water, K_w [Equation (16.4)].

Example 16.2

Solution

Rearranging Equation (16.4), we write

$$[\mathrm{H}^{+}] = \frac{K_{\mathrm{w}}}{[\mathrm{OH}^{-}]} = \frac{1.0 \times 10^{-14}}{0.0025} = \mathbf{4.0 \times 10^{-12}}\ \boldsymbol{M}$$

Check

Because $[\mathrm{H}^{+}] < [\mathrm{OH}^{-}]$, the solution is basic, as we would expect from the earlier discussion of the reaction of ammonia with water.

pH – A Measure of Acidity

$$\boxed{\text{pH} = -\log [\text{H}^+]}$$

Solution Is		**At 25^0C**	
neutral	$[\text{H}^+] = [\text{OH}^-]$	$[\text{H}^+] = 1.0 \times 10^{-7}$	$\text{pH} = 7$
acidic	$[\text{H}^+] > [\text{OH}^-]$	$[\text{H}^+] > 1.0 \times 10^{-7}$	$\text{pH} < 7$
basic	$[\text{H}^+] < [\text{OH}^-]$	$[\text{H}^+] < 1.0 \times 10^{-7}$	$\text{pH} > 7$

$$\text{pH} \uparrow \qquad [\text{H}^+] \downarrow$$

Other important relationships

$$pOH = -\log [OH^-]$$

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

$$-\log [H^+] - \log [OH^-] = 14.00$$

$$pH + pOH = 14.00$$

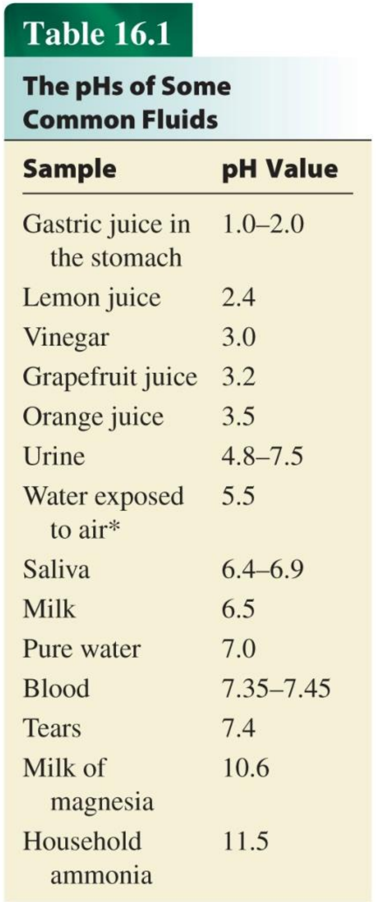


Table 16.1

The pHs of Some Common Fluids

Sample	pH Value
Gastric juice in the stomach	1.0–2.0
Lemon juice	2.4
Vinegar	3.0
Grapefruit juice	3.2
Orange juice	3.5
Urine	4.8–7.5
Water exposed to air*	5.5
Saliva	6.4–6.9
Milk	6.5
Pure water	7.0
Blood	7.35–7.45
Tears	7.4
Milk of magnesia	10.6
Household ammonia	11.5

pH Meter

Example 16.3

The concentration of H^+ ions in a bottle of table wine was 3.2×10^{-4} *M* right after the cork was removed. Only half of the wine was consumed. The other half, after it had been standing open to the air for a month, was found to have a hydrogen ion concentration equal to 1.0×10^{-3} *M.* Calculate the pH of the wine on these two occasions.

Example 16.3

Strategy

We are given the H^+ ion concentration and asked to calculate the pH of the solution. What is the definition of pH?

Example 16.3

Solution

According to Equation (16.5), pH = -log [H^+]. When the bottle was first opened, [H^+] = 3.2 x 10^{-4} *M*, which we substitute in Equation (16.5)

$$\text{pH} = -\log\,[\text{H}^+]$$

$$= -\log\,(3.2 \times 10^{-4}) = \mathbf{3.49}$$

On the second occasion, [H^+] = 1.0 x 10^{-3} *M*, so that

$$\text{pH} = -\log\,(1.0 \times 10^{-3}) = \mathbf{3.00}$$

Example 16.3

Comment

The increase in hydrogen ion concentration (or decrease in pH) is largely the result of the conversion of some of the alcohol (ethanol) to acetic acid, a reaction that takes place in the presence of molecular oxygen.

Example 16.4

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. Calculate the H^+ ion concentration of the rainwater.

Example 16.4

Strategy

Here we are given the pH of a solution and asked to calculate $[H^+]$. Because pH is defined as pH = −log $[H^+]$, we can solve for $[H^+]$ by taking the antilog of the pH; that is, $[H^+] = 10^{-pH}$, as shown in Equation (16.6).

Example 16.4

Solution

From Equation (16.5)

$$pH = -\log [H^+] = 4.82$$

Therefore,

$$\log [H^+] = -4.82$$

To calculate $[H^+]$, we need to take the antilog of −4.82

$$[H^+] = 10^{-4.82} = \mathbf{1.5 \times 10^{-5}}\ \boldsymbol{M}$$

Example 16.4

Check

Because the pH is between 4 and 5, we can expect $[H^+]$ to be between 1 x 10^{-4} *M* and 1 x 10^{-5} *M*. Therefore, the answer is reasonable.

Example 16.5

In a NaOH solution $[OH^-]$ is 2.9×10^{-4} *M*. Calculate the pH of the solution.

Example 16.5

Strategy

Solving this problem takes two steps. First, we need to calculate pOH using Equation (16.8). Next, we use Equation (16.10) to calculate the pH of the solution.

Solution

We use Equation (16.8):

$$\begin{aligned} \text{pOH} &= -\log\,[\text{OH}^-] \\ &= -\log\,(2.9 \times 10^{-4}) \\ &= 3.54 \end{aligned}$$

Example 16.5

Now we use Equation (16.10):

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pH} = 14.00 - \text{pOH}$$

$$= 14.00 - 3.54 = \mathbf{10.46}$$

Alternatively, we can use the ion-product constant of water, $K_w = [H^+][OH^-]$ to calculate $[H^+]$, and then we can calculate the pH from the $[H^+]$. Try it.

Check The answer shows that the solution is basic (pH > 7), which is consistent with a NaOH solution.

Strong Electrolyte – 100% dissociation

$$\text{NaCl}\ (s) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+\ (aq) + \text{Cl}^-\ (aq)$$

Weak Electrolyte – not completely dissociated

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^-\ (aq) + \text{H}^+\ (aq)$$

Strong Acids are strong electrolytes

$$\text{HCl}\ (aq) + \text{H}_2\text{O}\ (l) \boxed{\longrightarrow} \text{H}_3\text{O}^+\ (aq) + \text{Cl}^-\ (aq)$$

$$\text{HNO}_3\ (aq) + \text{H}_2\text{O}\ (l) \longrightarrow \text{H}_3\text{O}^+\ (aq) + \text{NO}_3^-\ (aq)$$

$$\text{HClO}_4\ (aq) + \text{H}_2\text{O}\ (l) \longrightarrow \text{H}_3\text{O}^+\ (aq) + \text{ClO}_4^-\ (aq)$$

$$\text{H}_2\text{SO}_4\ (aq) + \text{H}_2\text{O}\ (l) \longrightarrow \text{H}_3\text{O}^+\ (aq) + \text{HSO}_4^-\ (aq)$$

Weak Acids are weak electrolytes

$$\mathrm{HF}\ (aq) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}\ (aq) + \mathrm{F^-}\ (aq)$$

$$\mathrm{HNO_2}\ (aq) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}\ (aq) + \mathrm{NO_2^-}\ (aq)$$

$$\mathrm{HSO_4^-}\ (aq) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}\ (aq) + \mathrm{SO_4^{2-}}\ (aq)$$

$$\mathrm{H_2O}\ (l) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}\ (aq) + \mathrm{OH^-}\ (aq)$$

Strong Bases are strong electrolytes

$$\mathrm{NaOH}\ (s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}\ (aq) + \mathrm{OH^-}\ (aq)$$

$$\mathrm{KOH}\ (s) \xrightarrow{\mathrm{H_2O}} \mathrm{K^+}\ (aq) + \mathrm{OH^-}\ (aq)$$

$$\mathrm{Ba(OH)_2}\ (s) \xrightarrow{\mathrm{H_2O}} \mathrm{Ba^{2+}}\ (aq) + 2\mathrm{OH^-}\ (aq)$$

Weak Bases are weak electrolytes

$F^- (aq) + H_2O (l) \rightleftharpoons OH^- (aq) + HF (aq)$

$NO_2^- (aq) + H_2O (l) \rightleftharpoons OH^- (aq) + HNO_2 (aq)$

Conjugate acid-base pairs:

- The conjugate base of a strong acid has no measurable strength.
- H_3O^+ is the strongest acid that can exist in aqueous solution.
- The OH^- ion is the strongest base that can exist in aqueous solution.

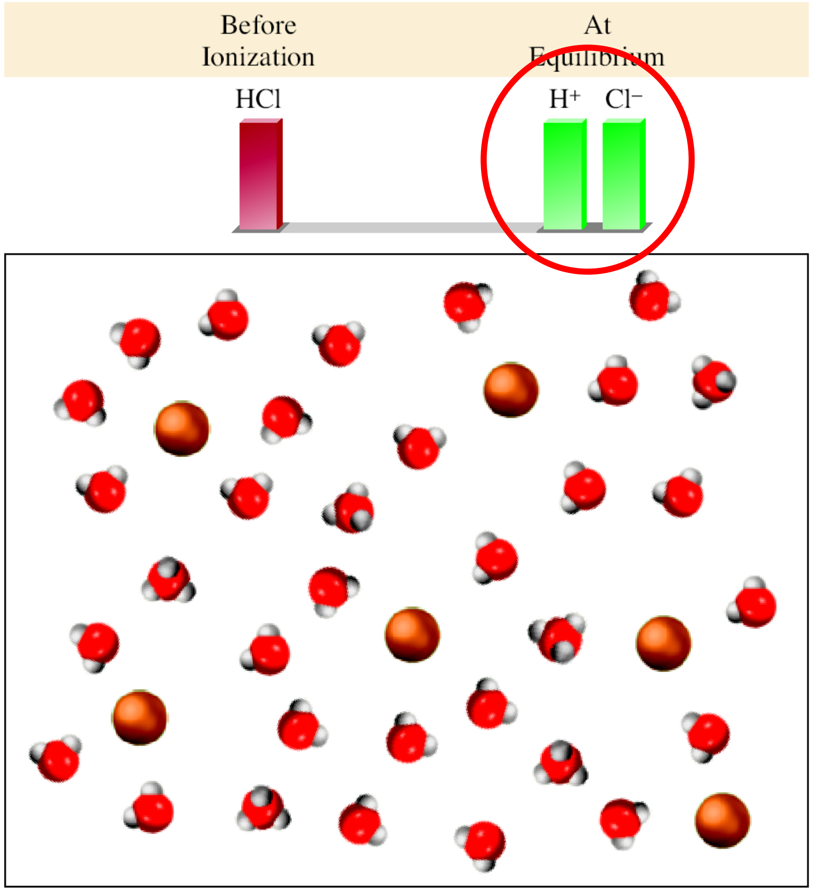
Table 16.2 Relative Strengths of Conjugate Acid-Base Pairs

Acid strength increases

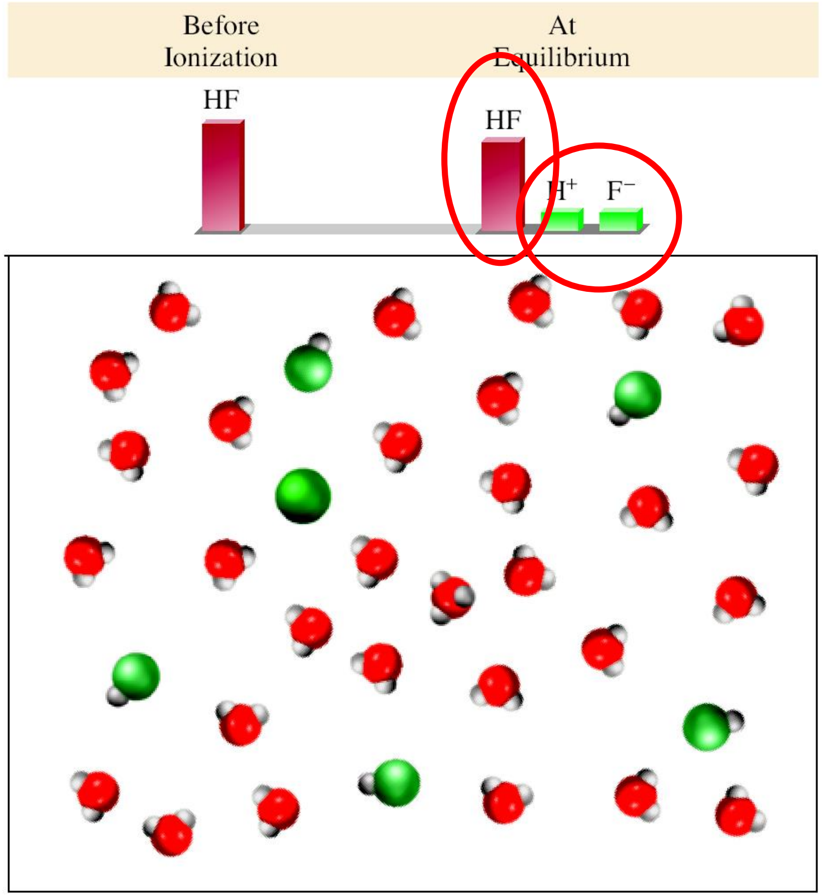
	Acid	Conjugate Base
Strong acids	$HClO_4$ (perchloric acid)	ClO_4^- (perchlorate ion)
	HI (hydroiodic acid)	I^- (iodide ion)
	HBr (hydrobromic acid)	Br^- (bromide ion)
	HCl (hydrochloric acid)	Cl^- (chloride ion)
	H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)
	HNO_3 (nitric acid)	NO_3^- (nitrate ion)
	H_3O^+ (hydronium ion)	H_2O (water)
Weak acids	HSO_4^- (hydrogen sulfate ion)	SO_4^{2-} (sulfate ion)
	HF (hydrofluoric acid)	F^- (fluoride ion)
	HNO_2 (nitrous acid)	NO_2^- (nitrite ion)
	HCOOH (formic acid)	$HCOO^-$ (formate ion)
	CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)
	NH_4^+ (ammonium ion)	NH_3 (ammonia)
	HCN (hydrocyanic acid)	CN^- (cyanide ion)
	H_2O (water)	OH^- (hydroxide ion)
	NH_3 (ammonia)	NH_2^- (amide ion)

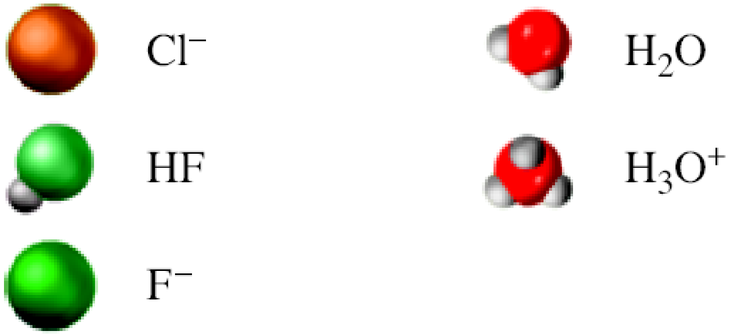
Base strength increases

Strong Acid (HCl)



Weak Acid (HF)





Example 16.6

Calculate the pH of a

(a) 1.0×10^{-3} *M* HCl solution

(b) 0.020 *M* $Ba(OH)_2$ solution

Example 16.6

Strategy

Keep in mind that HCl is a strong acid and $Ba(OH)_2$ is a strong base. Thus, these species are completely ionized and no HCl or $Ba(OH)_2$ will be left in solution.

Solution

(a) The ionization of HCl is

$$HCl(\mathit{aq}) \longrightarrow H^+(\mathit{aq}) + Cl^-(\mathit{aq})$$

Example 16.6

The concentrations of all the species (HCl, H^+, and Cl^-) before and after ionization can be represented as follows:

	$HCl(aq)$	→	$H^+(aq)$	+	$Cl^-(aq)$
Initial (*M*):	1.0×10^{-3}		0.0		0.0
Change (*M*):	-1.0×10^{-3}		$+1.0 \times 10^{-3}$		$+1.0 \times 10^{-3}$
Final (*M*):	0.0		1.0×10^{-3}		1.0×10^{-3}

A positive (+) change represents an increase and a negative (-) change indicates a decrease in concentration. Thus,

$$[H^+] = 1.0 \times 10^{-3}\ M$$

$$pH = -\log (1.0 \times 10^{-3})$$

$$= \mathbf{3.00}$$

Example 16.6

(b) $Ba(OH)_2$ is a strong base; each $Ba(OH)_2$ unit produces two OH^- ions:

$$Ba(OH)_2(aq) \longrightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

The changes in the concentrations of all the species can be represented as follows:

	$Ba(OH)_2(aq)$	$\rightarrow$	$Ba^{2+}(aq)$	+	$2OH^-(aq)$
Initial (*M*):	0.020		0.00		0.00
Change (*M*):	- 0.020		+ 0.020		+2(0.020)
Final (*M*):	0.00		0.020		0.040

Example 16.6

Thus,

$$[OH^-] = 0.040\ M$$
$$pOH = -\log 0.040 = 1.40$$

Therefore, from Equation (16.10),

$$pH = 14.00 - pOH$$
$$= 14.00 - 1.40$$
$$= \mathbf{12.60}$$

Check Note that in both (a) and (b) we have neglected the contribution of the autoionization of water to $[H^+]$ and $[OH^-]$ because $1.0 \times 10^{-7}\ M$ is so small compared with $1.0 \times 10^{-3}\ M$ and $0.040\ M$.

Example 16.7

Predict the direction of the following reaction in aqueous solution:

$$HNO_2(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NO_2^-(aq)$$

Example 16.7

Strategy

The problem is to determine whether, at equilibrium, the reaction will be shifted to the right, favoring HCN and NO_2^-, or to the left, favoring HNO_2 and CN^-. Which of the two is a stronger acid and hence a stronger proton donor: HNO_2 or HCN? Which of the two is a stronger base and hence a stronger proton acceptor: CN^- or NO_2^-? Remember that the stronger the acid, the weaker its conjugate base.

Example 16.7

Solution

In Table 16.2 we see that HNO_2 is a stronger acid than HCN. Thus, CN^- is a stronger base than NO_2^-. The net reaction will proceed from left to right as written because HNO_2 is a better proton donor than HCN (and CN^- is a better proton acceptor than NO_2^-).

Weak Acids (HA) and Acid Ionization Constants

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

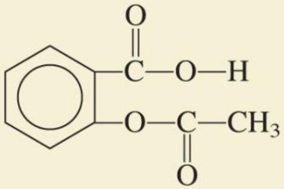
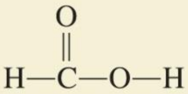
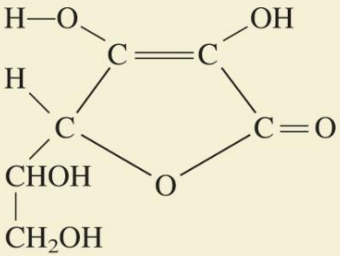
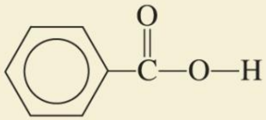
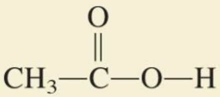
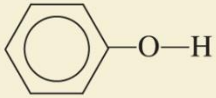
$$HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-\,(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a is the ***acid ionization constant***

K_a ↑ weak acid strength ↑

Table 16.3 Ionization Constants of Some Weak Acids and Their Conjugate Bases at 25°C

Name of Acid	**Formula**	**Structure**	K_a	**Conjugate Base**	K_b
Hydrofluoric acid	HF	$H-F$	7.1×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	$O=N-O-H$	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
Acetylsalicylic acid (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	$C_9H_7O_4^-$	3.3×10^{-11}
Formic acid	$HCOOH$	 $H-\overset{\overset{O}{\Vert}}{C}-O-H$	1.7×10^{-4}	$HCOO^-$	5.9×10^{-11}
Ascorbic acid*	$C_6H_8O_6$		8.0×10^{-5}	$C_6H_7O_6^-$	1.3×10^{-10}
Benzoic acid	C_6H_5COOH		6.5×10^{-5}	$C_6H_5COO^-$	1.5×10^{-10}
Acetic acid	CH_3COOH	 $CH_3-\overset{\overset{O}{\Vert}}{C}-O-H$	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
Hydrocyanic acid	HCN	$H-C\equiv N$	4.9×10^{-10}	CN^-	2.0×10^{-5}
Phenol	C_6H_5OH		1.3×10^{-10}	$C_6H_5O^-$	7.7×10^{-5}

Solving **weak acid** ionization problems:

1. Identify the major species that can affect the pH.
    - In most cases, you can ignore the autoionization of water.
    - Ignore [OH^-] because it is determined by [H^+].
2. Use ICE to express the equilibrium concentrations in terms of single unknown x.
3. Write K_a in terms of equilibrium concentrations. Solve for x by the approximation method. If approximation is not valid, solve for x exactly.
4. Calculate concentrations of all species and/or pH of the solution.

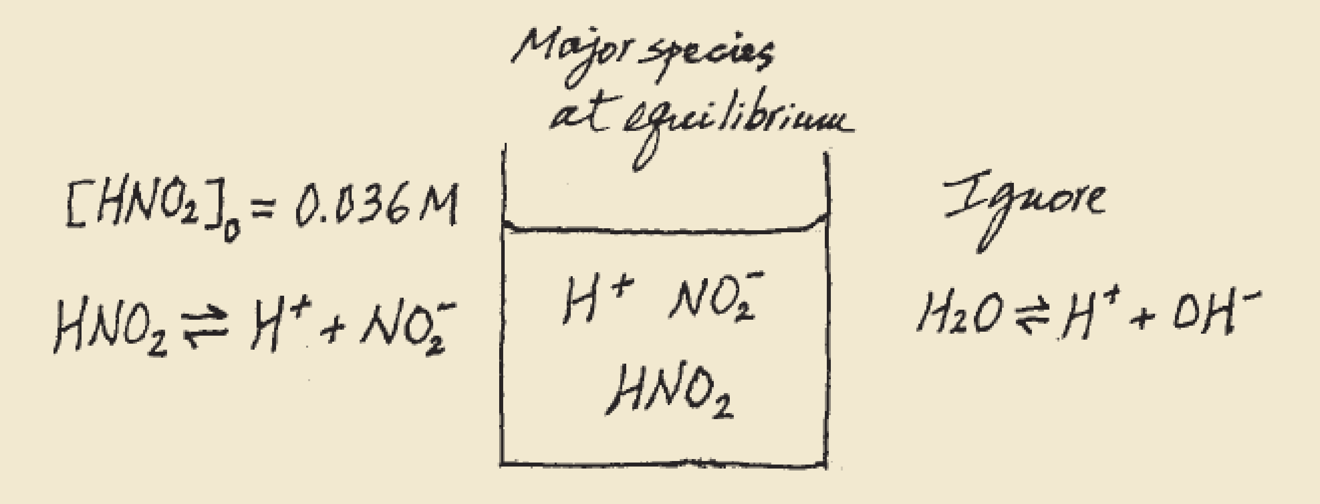
Example 16.8

Calculate the pH of a 0.036 *M* nitrous acid (HNO_2) solution:

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$$

Example 16.8

Strategy Recall that a weak acid only partially ionizes in water. We are given the initial concentration of a weak acid and asked to calculate the pH of the solution at equilibrium. It is helpful to make a sketch to keep track of the pertinent species.



As in Example 16.6, we ignore the ionization of H_2O so the major source of H^+ ions is the acid. The concentration of OH^- ions is very small as we would expect from an acidic solution so it is present as a minor species.

Example 16.8

Solution We follow the procedure already outlined.

Step 1: The species that can affect the pH of the solution are HNO_2, H^+, and the conjugate base NO_2^-. We ignore water's contribution to $[H^+]$.

Step 2: Letting x be the equilibrium concentration of H^+ and NO_2^- ions in mol/L, we summarize:

	$HNO_2(aq)$	$\rightleftharpoons$	$H^+(aq)$ +	$NO_2^-(aq)$
Initial (*M*):	0.036		0.00	0.00
Change (*M*):	$-x$		$+x$	$+x$
Equilibrium (*M*):	$0.036 - x$		x	x

Example 16.8

Step 3: From Table 16.3 we write

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

$$4.5 \times 10^{-4} = \frac{x^2}{0.036-x}$$

Applying the approximation 0.036 - *x* ≈ 0.036, we obtain

$$4.5 \times 10^{-4} = \frac{x^2}{0.036-x} \approx \frac{x^2}{0.036}$$

$$x^2 = 1.62 \times 10^{-5}$$

$$x = 4.0 \times 10^{-3}\ M$$

Example 16.8

To test the approximation,

$$\frac{4.0 \times 10^{-3}\ M}{0.036\ M} \times 100\% = 11\%$$

Because this is greater than 5%, our approximation is not valid and we must solve the quadratic equation, as follows:

$$x^2 + 4.5 \times 10^{-4}x - 1.62 \times 10^{-5} = 0$$

$$x = \frac{-4.5 \times 10^{-4} \pm \sqrt{\left(4.5 \times 10^{-4}\right)^2 - 4(1)(-1.62 \times 10^{-5})}}{2(1)}$$

$$= 3.8 \times 10^{-3}\ M \text{ or } -4.3 \times 10^{-3}\ M$$

Example 16.8

The second solution is physically impossible, because the concentration of ions produced as a result of ionization cannot be negative. Therefore, the solution is given by the positive root, $x = 3.8 \times 10^{-3}\ M$.

Step 4: At equilibrium

$$[\mathrm{H}^+] = 3.8 \times 10^{-3}\ M$$

$$\mathrm{pH} = -\log\,(3.8 \times 10^{-3})$$

$$= \mathbf{2.42}$$

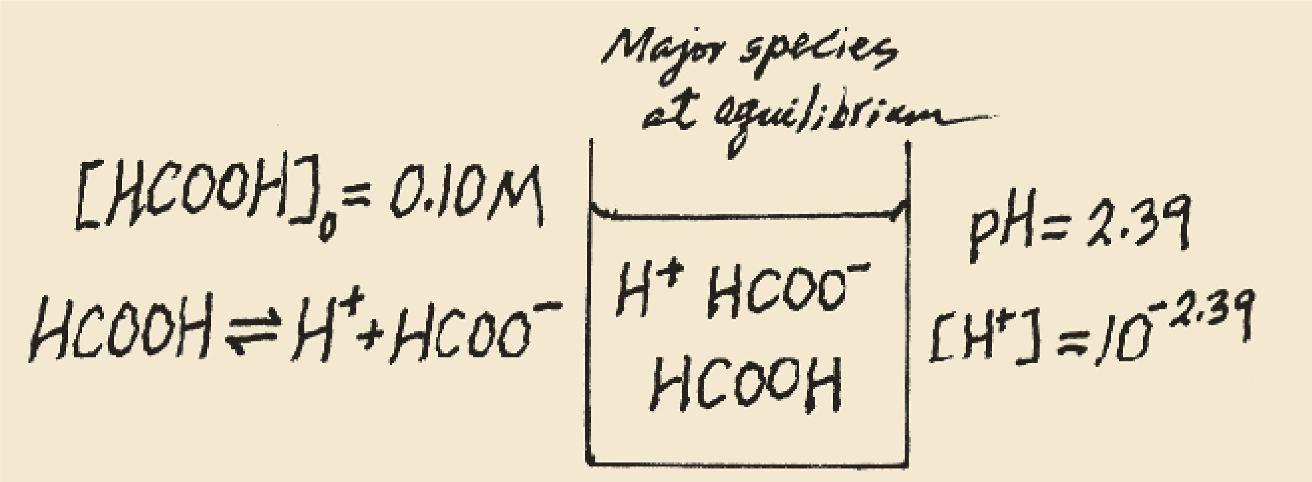
Check Note that the calculated pH indicates that the solution is acidic, which is what we would expect for a weak acid solution. Compare the calculated pH with that of a 0.036 *M* strong acid solution such as HCl to convince yourself of the difference between a strong acid and a weak acid.

Example 16.9

The pH of a 0.10 *M* solution of formic acid (HCOOH) is 2.39. What is the K_a of the acid?

Example 16.9

Strategy Formic acid is a weak acid. It only partially ionizes in water. Note that the concentration of formic acid refers to the initial concentration, before ionization has started. The pH of the solution, on the other hand, refers to the equilibrium state. To calculate K_a, then, we need to know the concentrations of all three species: $[H^+]$, $[HCOO^-]$, and $[HCOOH]$ at equilibrium. As usual, we ignore the ionization of water. The following sketch summarizes the situation.



Example 16.9

Solution We proceed as follows.

Step 1: The major species in solution are HCOOH, H^+, and the conjugate base $HCOO^-$.

Step 2: First we need to calculate the hydrogen ion concentration from the pH value

$$\mathrm{pH} = -\log [H^+]$$

$$2.39 = -\log [H^+]$$

Taking the antilog of both sides, we get

$$[H^+] = 10^{-2.39} = 4.1 \times 10^{-3}\ M$$

Example 16.9

Next we summarize the changes:

	$HCOOH(aq) \rightleftharpoons$	$H^+(aq)$ +	$HCOO^-(aq)$
Initial (*M*):	0.10	0.00	0.00
Change (*M*):	-4.1×10^{-3}	$+4.1 \times 10^{-3}$	$+4.1 \times 10^{-3}$
Equilibrium (*M*):	$(0.10 - 4.1 \times 10^{-3})$	4.1×10^{-3}	4.1×10^{-3}

Note that because the pH and hence the H^+ ion concentration is known, it follows that we also know the concentrations of HCOOH and $HCOO^-$ at equilibrium.

Example 16.9

Step 3: The ionization constant of formic acid is given by

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$= \frac{(4.1 \times 10^{-3})(4.1 \times 10^{-3})}{(0.10 - 4.1 \times 10^{-3})}$$

$$= \mathbf{1.8 \times 10^{-4}}$$

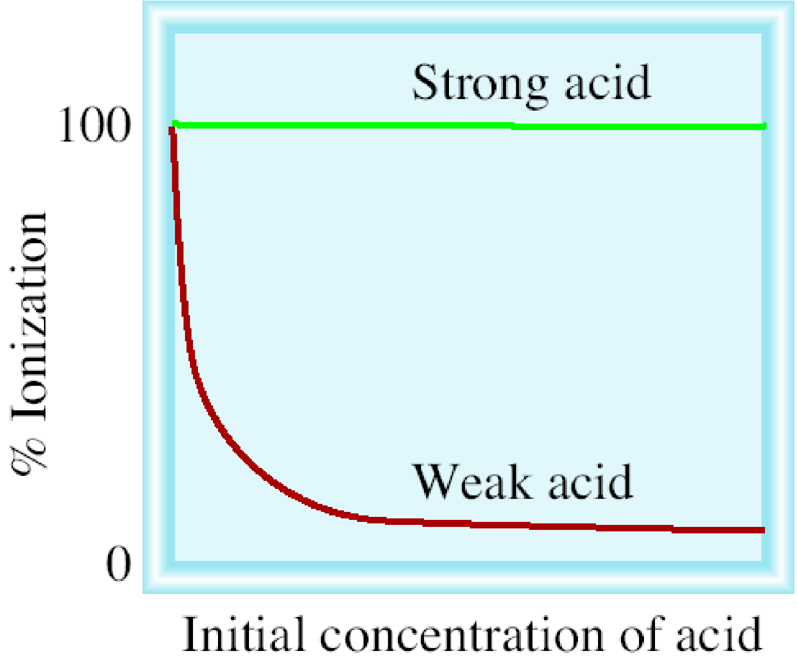
Check

The K_a value differs slightly from the one listed in Table 16.3 because of the rounding-off procedure we used in the calculation.

$$\textbf{\textit{percent ionization}} = \frac{\text{Ionized acid concentration at equilibrium}}{\text{Initial concentration of acid}} \times 100\%$$

For a monoprotic acid HA,

$$\text{Percent ionization} = \frac{[\mathrm{H^+}]}{[\mathrm{HA}]_0} \times 100\% \qquad [\mathrm{HA}]_0 = \text{initial concentration}$$



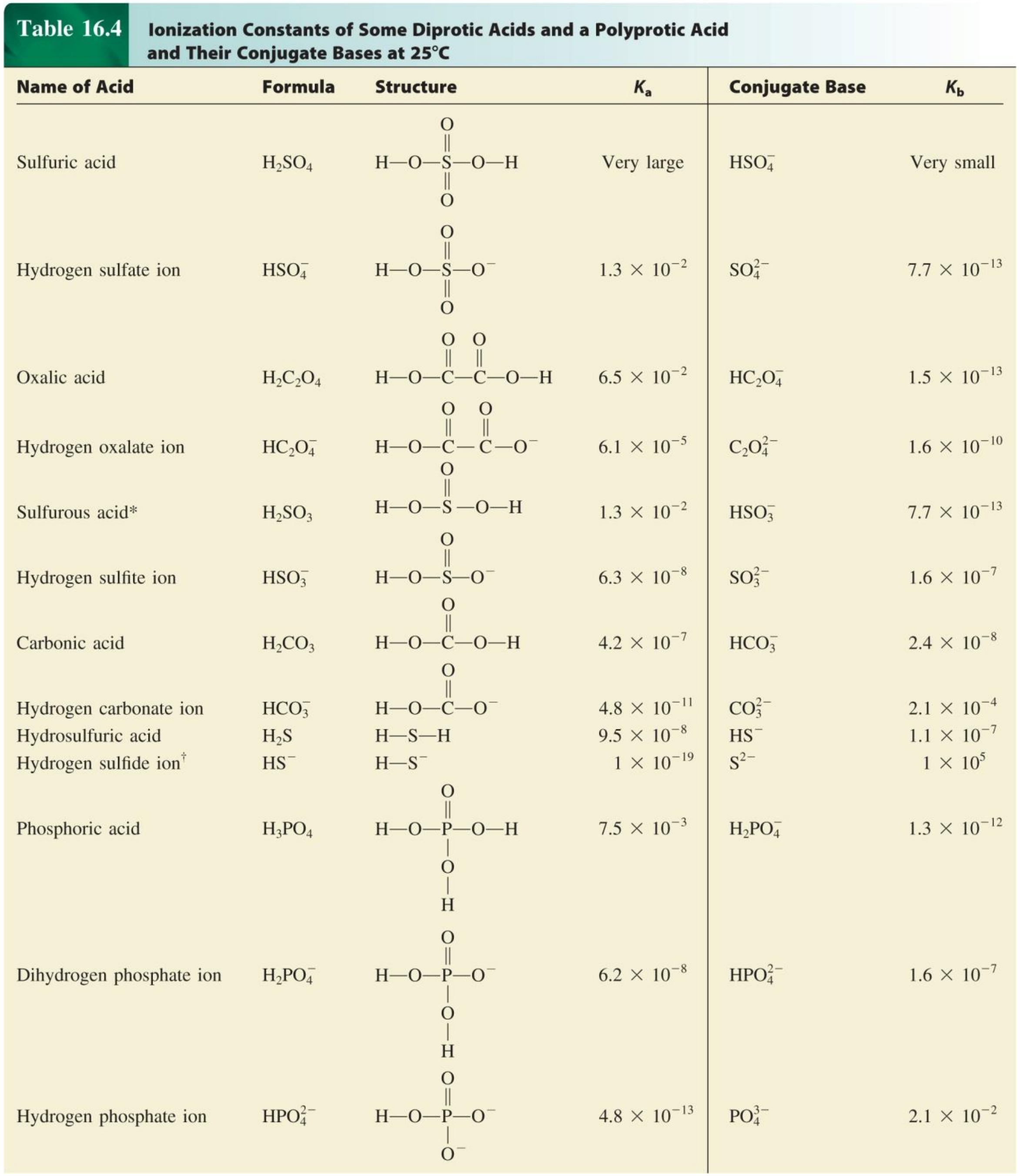


Table 16.4 Ionization Constants of Some Diprotic Acids and a Polyprotic Acid and Their Conjugate Bases at 25°C

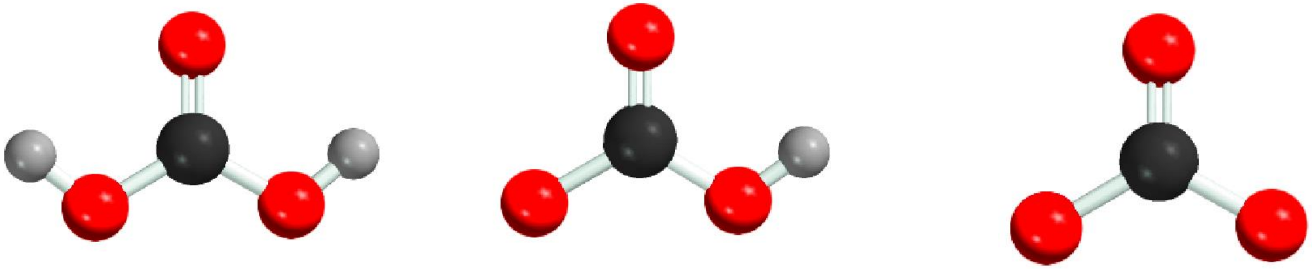
Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b
Sulfuric acid	H_2SO_4	$H-O-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-O-H$	Very large	HSO_4^-	Very small
Hydrogen sulfate ion	HSO_4^-	$H-O-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-O^-$	1.3×10^{-2}	SO_4^{2-}	7.7×10^{-13}
Oxalic acid	$H_2C_2O_4$	$H-O-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-O-H$	6.5×10^{-2}	$HC_2O_4^-$	1.5×10^{-13}
Hydrogen oxalate ion	$HC_2O_4^-$	$H-O-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-O^-$	6.1×10^{-5}	$C_2O_4^{2-}$	1.6×10^{-10}
Sulfurous acid*	H_2SO_3	$H-O-\overset{\overset{O}{\parallel}}{S}-O-H$	1.3×10^{-2}	HSO_3^-	7.7×10^{-13}
Hydrogen sulfite ion	HSO_3^-	$H-O-\overset{\overset{O}{\parallel}}{S}-O^-$	6.3×10^{-8}	SO_3^{2-}	1.6×10^{-7}
Carbonic acid	H_2CO_3	$H-O-\overset{\overset{O}{\parallel}}{C}-O-H$	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}
Hydrogen carbonate ion	HCO_3^-	$H-O-\overset{\overset{O}{\parallel}}{C}-O^-$	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrosulfuric acid	H_2S	$H-S-H$	9.5×10^{-8}	HS^-	1.1×10^{-7}
Hydrogen sulfide ion[†]	HS^-	$H-S^-$	1×10^{-19}	S^{2-}	1×10^{5}
Phosphoric acid	H_3PO_4	$H-O-\overset{\overset{O}{\parallel}}{\underset{\underset{\underset{\underset{H}{\vert}}{O}}{\vert}}{P}}-O-H$	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}
Dihydrogen phosphate ion	$H_2PO_4^-$	$H-O-\overset{\overset{O}{\parallel}}{\underset{\underset{\underset{\underset{H}{\vert}}{O}}{\vert}}{P}}-O^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
Hydrogen phosphate ion	HPO_4^{2-}	$H-O-\overset{\overset{O}{\parallel}}{\underset{\underset{O^-}{\vert}}{P}}-O^-$	4.8×10^{-13}	PO_4^{3-}	2.1×10^{-2}

Diprotic and Triprotic Acids

- May yield more than one hydrogen ion per molecule.
- Ionize in a stepwise manner; that is, they lose one proton at a time.
- An ionization constant expression can be written for each ionization stage.
- Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$



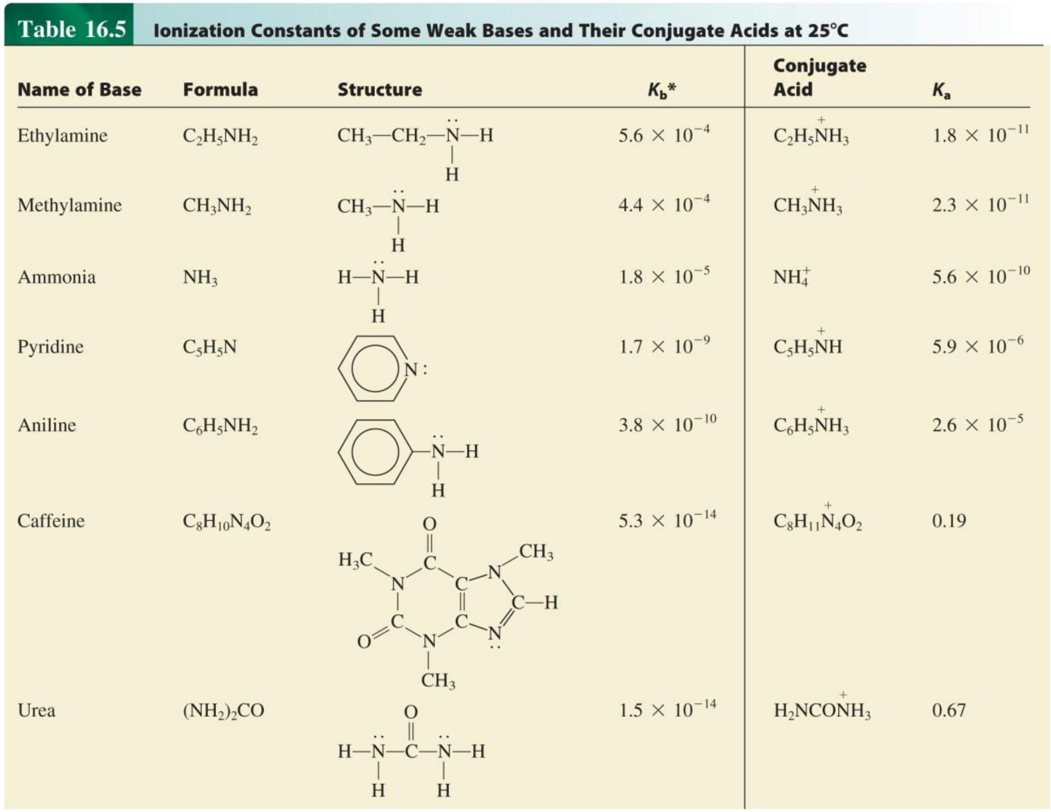


Table 16.5 Ionization Constants of Some Weak Bases and Their Conjugate Acids at 25°C

Name of Base	Formula	Structure	K_b*	Conjugate Acid	K_a
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\ddot{N}-H$ (with H below N)	5.6×10^{-4}	$C_2H_5\overset{+}{N}H_3$	1.8×10^{-11}
Methylamine	CH_3NH_2	$CH_3-\ddot{N}-H$ (with H below N)	4.4×10^{-4}	$CH_3\overset{+}{N}H_3$	2.3×10^{-11}
Ammonia	NH_3	$H-\ddot{N}-H$ (with H below N)	1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Pyridine	C_5H_5N		1.7×10^{-9}	$C_5H_5\overset{+}{N}H$	5.9×10^{-6}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}	$C_6H_5\overset{+}{N}H_3$	2.6×10^{-5}
Caffeine	$C_8H_{10}N_4O_2$		5.3×10^{-14}	$C_8H_{11}\overset{+}{N}_4O_2$	0.19
Urea	$(NH_2)_2CO$	$H-\ddot{N}(H)-C(=O)-\ddot{N}(H)-H$	1.5×10^{-14}	$H_2NCO\overset{+}{N}H_3$	0.67

Example 16.10

Oxalic acid ($H_2C_2O_4$) is a poisonous substance used chiefly as a bleaching and cleansing agent (for example, to remove bathtub rings). Calculate the concentrations of all the species present at equilibrium in a 0.10 *M* solution.

Example 16.10

Strategy

Determining the equilibrium concentrations of the species of a diprotic acid in aqueous solution is more involved than for a monoprotic acid. We follow the same procedure as that used for a monoprotic acid for each stage, as in Example 16.8. Note that the conjugate base from the first stage of ionization becomes the acid for the second stage ionization.

Example 16.10

Solution We proceed according to the following steps.

Step 1: The major species in solution at this stage are the nonionized acid, H^+ ions, and the conjugate base, $HC_2O_4^-$.

Step 2: Letting *x* be the equilibrium concentration of H^+ and $HC_2O_4^-$ ions in mol/L, we summarize:

	$H_2C_2O_4(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HC_2O_4^-(aq)$
Initial (*M*):	0.10		0.00		0.00
Change (*M*):	$-x$		$+x$		$+x$
Equilibrium (*M*):	$0.10 - x$		x		x

Example 16.10

Step 3: Table 16.4 gives us

$$K_a = \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]}$$

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x}$$

Applying the approximation 0.10 - $x \approx$ 0.10, we obtain

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x^2 = 6.5 \times 10^{-3}$$

$$x = 8.1 \times 10^{-2}\ M$$

Example 16.10

To test the approximation,

$$\frac{8.1 \times 10^{-2}\ M}{0.10\ M} \times 100\% = 81\%$$

Clearly the approximation is not valid. Therefore, we must solve the quadratic equation

$$x^2 + 6.5 \text{ x } 10^{-2}x - 6.5 \text{ x } 10^{-3} = 0$$

The result is $x = 0.054\ M$.

Example 16.10

Step 4: When the equilibrium for the first stage of ionization is reached, the concentrations are

$$[H^+] = 0.054\ M$$

$$[HC_2O_4^-] = 0.054\ M$$

$$[H_2C_2O_4] = (0.10 - 0.054)\ M = 0.046\ M$$

Next we consider the second stage of ionization.

Step 1: At this stage, the major species are $HC_2O_4^-$, which acts as the acid in the second stage of ionization, H^+, and the conjugate base $C_2O_4^{2-}$.

Example 16.10

Step 2: Letting *y* be the equilibrium concentration of H^+ and $C_2O_4^{2-}$ ions in mol/L, we summarize:

	$HC_2O_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2O_4^{2-}(aq)$
Initial (*M*):	0.054		0.054		0.00
Change (*M*):	$-y$		$+y$		$+y$
Equilibrium (*M*):	$0.054 - y$		$0.054 + y$		y

Step 3: Table 16.4 gives us

$$K_a = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

$$6.1 \times 10^{-5} = \frac{(0.054 + y)(y)}{(0.054 - y)}$$

Example 16.10

Applying the approximation 0.054 + $y \approx$ 0.054 and 0.054 - $y \approx$ 0.054, we obtain

$$\frac{(0.054)(y)}{(0.054)} = y = 6.1 \times 10^{-5}\ M$$

and we test the approximation,

$$\frac{6.1 \times 10^{-5}\ M}{0.054\ M} \times 100\% = 0.11\%$$

The approximation is valid.

Example 16.10

Step 4: At equilibrium,

$$[H_2C_2O_4] = \mathbf{0.046}\ \boldsymbol{M}$$

$$[HC_2O_4^-] = (0.054 - 6.1 \times 10^{-5})\ M = \mathbf{0.054}\ \boldsymbol{M}$$

$$[H^+] = (0.054 + 6.1 \times 10^{-5})\ M = \mathbf{0.054}\ \boldsymbol{M}$$

$$[C_2O_4^{2-}] = \mathbf{6.1 \times 10^{-5}}\ \boldsymbol{M}$$

$$[OH^-] = 1.0 \times 10^{-14}/0.054 = \mathbf{1.9 \times 10^{-13}}\ \boldsymbol{M}$$

Weak Bases and Base Ionization Constants

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

K_b is the ***base ionization constant***

K_b ↑ weak base strength ↑

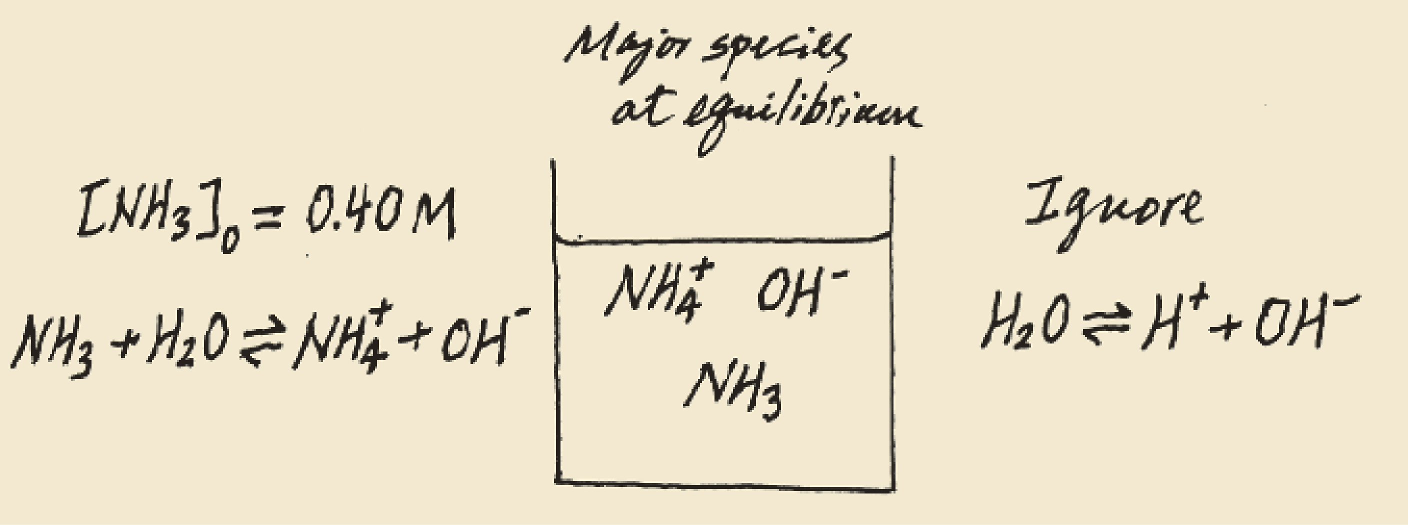
Solve weak base problems like weak acids ***except*** solve for [OH-] instead of [H^+].

Example 16.11

What is the pH of a 0.40 *M* ammonia solution?

Example 16.11

Strategy The procedure here is similar to the one used for a weak acid (see Example 16.8). From the ionization of ammonia, we see that the major species in solution at equilibrium are NH_3, NH_4^+ ,and OH^-. The hydrogen ion concentration is very small as we would expect from a basic solution, so it is present as a minor species. As before, we ignore the ionization of water. We make a sketch to keep track of the pertinent species as follows:



Example 16.11

Solution We proceed according to the following steps.

Step 1: The major species in an ammonia solution are NH_3, NH_4^+, and OH^-. We ignore the very small contribution to OH^- concentration by water.

Step 2: Letting *x* be the equilibrium concentration of NH_4^+ and OH^- ions in mol/L, we summarize:

	$NH_3(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	$+$	$OH^-(aq)$
Initial (*M*):	0.40				0.00		0.00
Change (*M*):	$-x$				$+x$		$+x$
Equilibrium (*M*):	$0.40 - x$				x		x

Example 16.11

Step 3: Table 16.5 gives us K_b:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x}$$

Applying the approximation $0.40 - x \approx 0.40$, we obtain

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40}$$

$$x^2 = 7.2 \times 10^{-6}$$

$$x = 2.7 \times 10^{-3}\ M$$

Example 16.11

To test the approximation, we write

$$\frac{2.7 \times 10^{-3}\ M}{0.40\ M} \times 100\% = 0.68\%$$

Therefore, the approximation is valid.

Step 4: At equilibrium, $[OH^-] = 2.7 \times 10^{-3}$ *M*. Thus,

$$\begin{aligned} pOH &= -\log(2.7 \times 10^{-3}) \\ &= 2.57 \\ pH &= 14.00 - 2.57 \\ &= \mathbf{11.43} \end{aligned}$$

Example 16.11

Check

Note that the pH calculated is basic, which is what we would expect from a weak base solution. Compare the calculated pH with that of a 0.40 *M* strong base solution, such as KOH, to convince yourself of the difference between a strong base and a weak base.

Ionization Constants of Conjugate Acid-Base Pairs

$$\cancel{\mathrm{HA}}\ (aq) \rightleftharpoons \mathrm{H^+}\ (aq) + \cancel{\mathrm{A^-}}\ (aq) \qquad K_a$$

$$\underline{\cancel{\mathrm{A^-}}\ (aq) + \mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{OH^-}\ (aq) + \cancel{\mathrm{HA}}\ (aq)} \qquad K_b$$

$$\mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H^+}\ (aq) + \mathrm{OH^-}\ (aq) \qquad K_w$$

$$\boxed{K_aK_b = K_w}$$

Weak Acid and Its Conjugate Base

$$K_a = \frac{K_w}{K_b} \qquad\qquad K_b = \frac{K_w}{K_a}$$

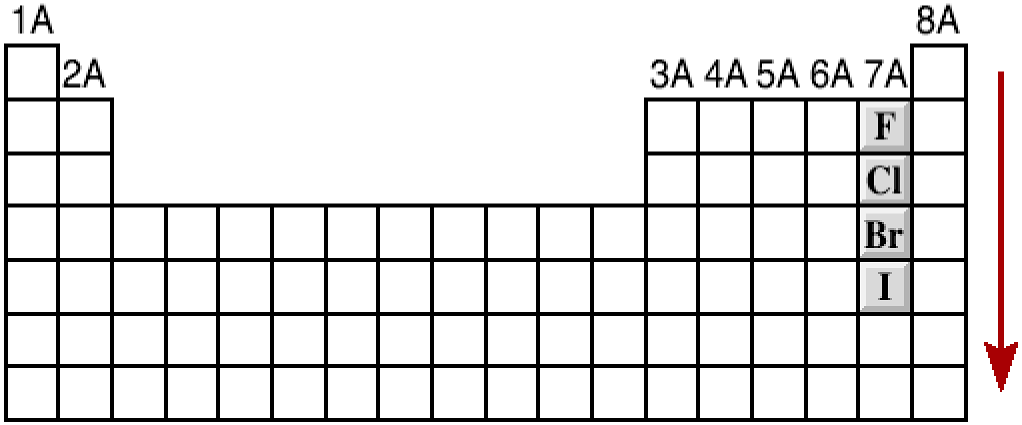
Molecular Structure and Acid Strength

$$H{-}X \longrightarrow H^{+} + X^{-}$$

The stronger the bond

The weaker the acid

$HF \ll HCl < HBr < HI$



acidity increases

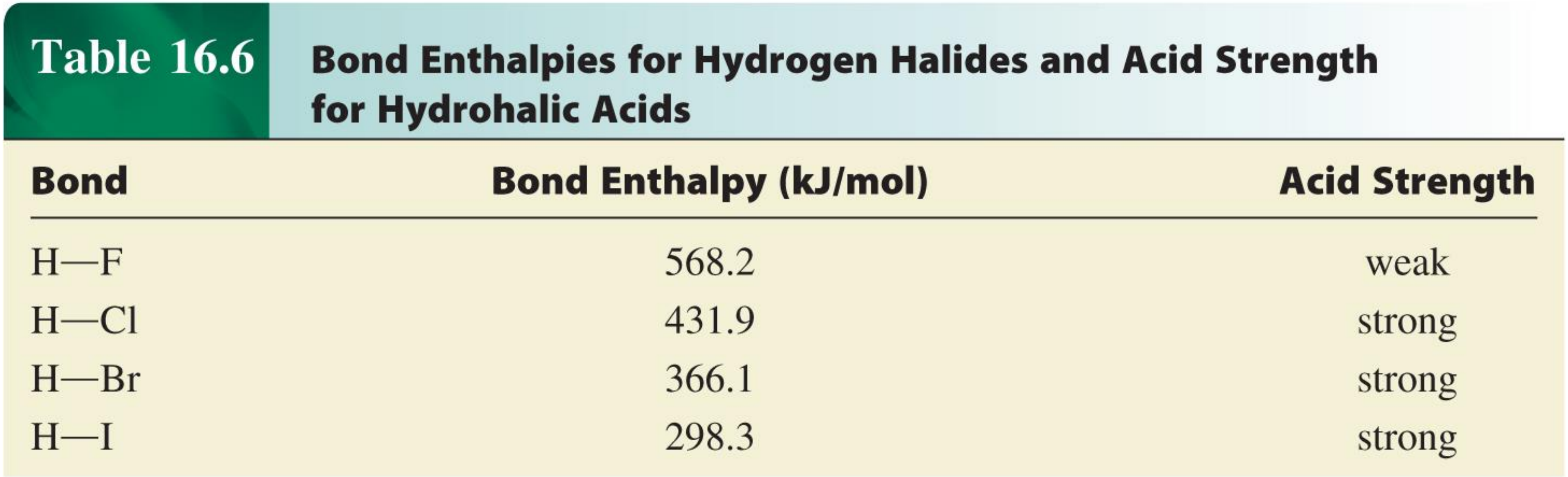


Table 16.6 **Bond Enthalpies for Hydrogen Halides and Acid Strength for Hydrohalic Acids**

Bond	Bond Enthalpy (kJ/mol)	Acid Strength
H—F	568.2	weak
H—Cl	431.9	strong
H—Br	366.1	strong
H—I	298.3	strong

Acid-Base Properties of Salts

Neutral Solutions:

Salts containing an alkali metal or alkaline earth metal ion (except Be^{2+}) **and** the conjugate base of a **strong** acid (*e.g.* Cl^-, Br^-, and NO_3^-).

$$NaCl\ (s) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$

Basic Solutions:

Salts derived from a strong base **and** a **weak** acid.

$$CH_3COONa\ (s) \xrightarrow{H_2O} Na^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (aq) + \enclose{circle}{OH^-}\ (aq)$$

Example 16.13

Calculate the pH of a 0.25 *M* solution of potassium fluoride (KF). What is the percent hydrolysis?

Example 16.13

Strategy

What is a salt? In solution, KF dissociates completely into K^+ and F^- ions. The K^+ ion does not react with water and has no effect on the pH of the solution because potassium is an alkali metal. The F^- ion is the conjugate base of the weak acid HF (Table 16.3). Therefore, we expect that it will react to a certain extent with water to produce HF and OH^-, and the solution will be basic.

Example 16.13

Solution

Step 1: Because we started with a 0.25 *M* potassium fluoride solution, the concentrations of the ions are also equal to 0.25 *M* after dissociation*:*

	$\mathrm{KF}(aq)$	→	$\mathrm{K}^+(aq)$ +	$\mathrm{F}^-(aq)$
Initial (*M*):	0.25		0	0
Change (*M*):	−0.25		+0.25	+0.25
Final (*M*):	0		0.25	0.25

Of these ions, only the fluoride ion will react with water

$$\mathrm{F}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HF}(aq) + \mathrm{OH}^-(aq)$$

Example 16.13

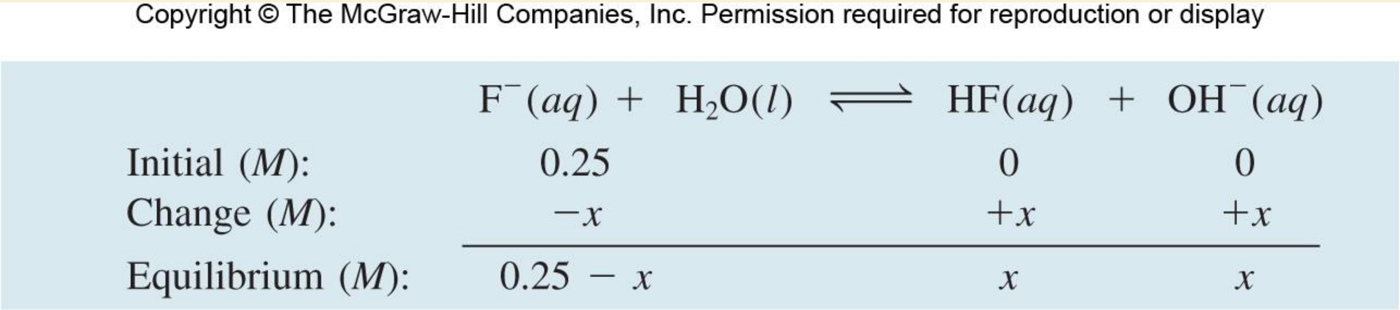
At equilibrium, the major species in solution are HF, F^-, and OH^-. The concentration of the H^+ ion is very small as we would expect for a basic solution, so it is treated as a minor species. We ignore the ionization of water.

Step 2: Let *x* be the equilibrium concentration of HF and OH^- ions in mol/L, we summarize:

	$F^-(aq)$	+	$H_2O\ (l)$	$\rightleftharpoons$	$HF(aq)$	+	$OH^-(aq)$
Initial (*M*):	0.25				0.00		0.00
Change (*M*):	$-x$				$+x$		$+x$
Equilibrium (*M*):	$0.25 - x$				x		x

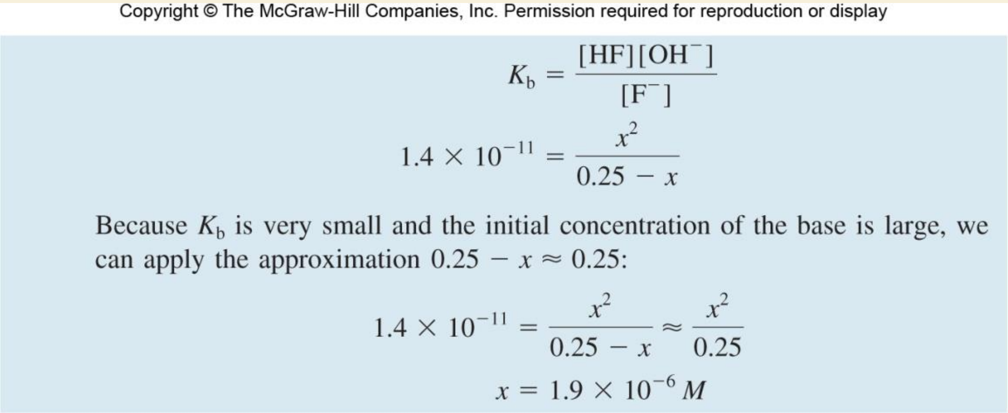
Example 16.13

Step 3: From the preceding discussion and Table 16.3 we write the equilibrium constant of hydrolysis, or the base ionization constant, as



	$F^-(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$HF(aq)$	$+$	$OH^-(aq)$
Initial (M):	0.25				0		0
Change (M):	$-x$				$+x$		$+x$
Equilibrium (M):	$0.25 - x$				x		x

Because K_b is very small and the initial concentration of the base is large, we can apply the approximation $0.25 - x \approx 0.25$:



$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

$$1.4 \times 10^{-11} = \frac{x^2}{0.25 - x}$$

Because K_b is very small and the initial concentration of the base is large, we can apply the approximation $0.25 - x \approx 0.25$:

$$1.4 \times 10^{-11} = \frac{x^2}{0.25 - x} \approx \frac{x^2}{0.25}$$

$$x = 1.9 \times 10^{-6}\ M$$

Example 16.13

Step 4: At equilibrium:

$$[OH^-] = 1.9 \text{ x } 10^{-6}\ M$$

$$pOH = -\log (1.9 \text{ x } 10^{-6})$$

$$= 5.72$$

$$pH = 14.00 - 5.72$$

$$= 8.28$$

Thus the solution is basic, as we would expect. The percent hydrolysis is given by

$$\% \text{ hydrolysis} = \frac{[F^-]_{\text{hydrolyzed}}}{[F^-]_{\text{initial}}}$$

$$= \frac{1.9 \times 10^{-6}}{0.25} \times 100\%$$

$$= 0.00076\%$$

Example 16.13

Check

The result shows that only a very small amount of the anion undergoes hydrolysis. Note that the calculation of percent hydrolysis takes the same form as the test for the approximation, which is valid in this case.

Acid-Base Properties of Salts

Acid Solutions:

Salts derived from a strong acid and a weak base.

$$NH_4Cl\ (s) \xrightarrow{H_2O} NH_4^+\ (aq) + Cl^-\ (aq)$$

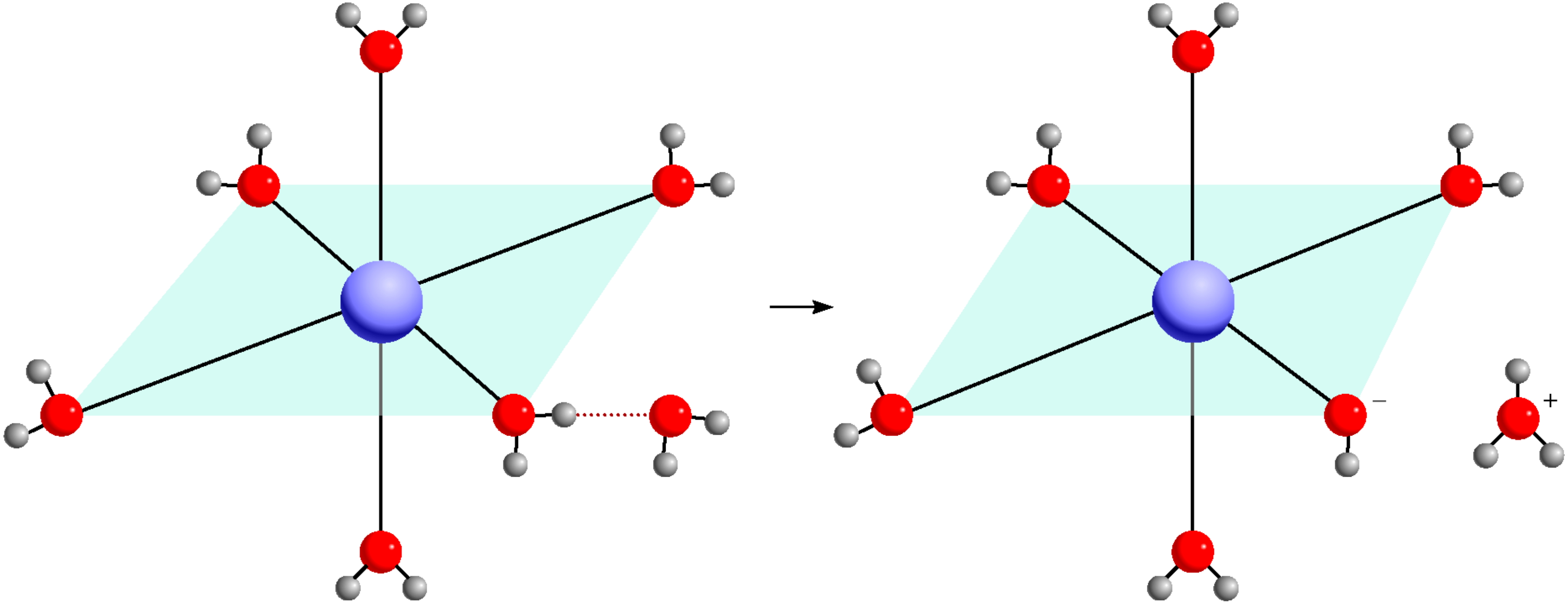
$$NH_4^+\ (aq) \rightleftharpoons NH_3\ (aq) + \boxed{H^+}\ (aq)$$

Salts with small, highly charged metal cations (*e.g.* Al^{3+}, Cr^{3+}, and Be^{2+}) and the conjugate base of a strong acid.

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+\ (aq)$$

Acid Hydrolysis of Al^{3+}

$$\mathrm{Al(H_2O)_6^{3+}} + \mathrm{H_2O} \longrightarrow \mathrm{Al(OH)(H_2O)_5^{2+}} + \mathrm{H_3O^+}$$



Acid-Base Properties of Salts

Solutions in which both the cation and the anion hydrolyze:

- K_b for the anion > K_a for the cation, solution will be basic
- K_b for the anion < K_a for the cation, solution will be acidic
- K_b for the anion $\approx$ K_a for the cation, solution will be neutral

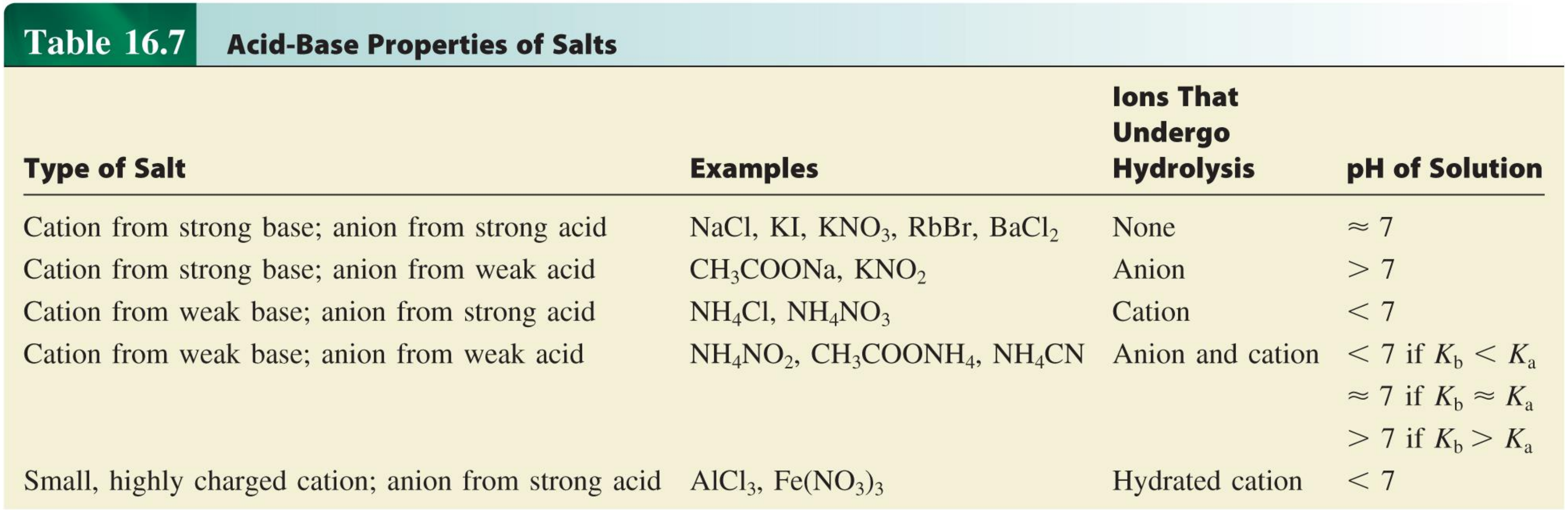


Table 16.7 **Acid-Base Properties of Salts**

Type of Salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KI, KNO_3, RbBr, $BaCl_2$	None	≈ 7
Cation from strong base; anion from weak acid	CH_3COONa, KNO_2	Anion	> 7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3	Cation	< 7
Cation from weak base; anion from weak acid	NH_4NO_2, CH_3COONH_4, NH_4CN	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small, highly charged cation; anion from strong acid	$AlCl_3$, $Fe(NO_3)_3$	Hydrated cation	< 7

Example 16.14

Predict whether the following solutions will be acidic, basic, or nearly neutral:

(a)NH_4I

(b) $NaNO_2$

(c) $FeCl_3$

(d) NH_4F

Example 16.14

Strategy

In deciding whether a salt will undergo hydrolysis, ask yourself the following questions: Is the cation a highly charged metal ion or an ammonium ion? Is the anion the conjugate base of a weak acid? If yes to either question, then hydrolysis will occur. In cases where both the cation and the anion react with water, the pH of the solution will depend on the relative magnitudes of K_a for the cation and K_b for the anion (see Table 16.7).

Example 16.14

Solution

We first break up the salt into its cation and anion components and then examine the possible reaction of each ion with water.

(a)The cation is NH_4^+, which will hydrolyze to produce NH_3 and H^+. The I^- anion is the conjugate base of the strong acid HI. Therefore, I^- will not hydrolyze and the solution is acidic.

(b) The Na^+ cation does not hydrolyze. The NO_2^- is the conjugate base of the weak acid HNO_2 and will hydrolyze to give HNO_2 and OH^-. The solution will be basic.

Example 16.14

(c) Fe^{3+} is a small metal ion with a high charge and hydrolyzes to produce H^+ ions. The Cl^- does not hydrolyze. Consequently, the solution will be acidic.

(d) Both the NH_4^+ and F^- ions will hydrolyze. From Tables 16.5 and 16.3 we see that the K_a of NH_4^+ (5.6×10^{-10}) is greater than the K_b for F^- (1.4×10^{-11}). Therefore, the solution will be acidic.

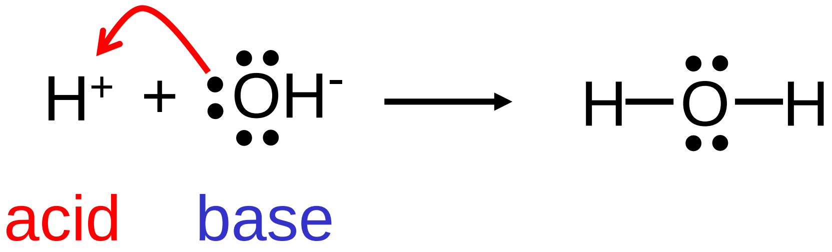
Definition of An Acid

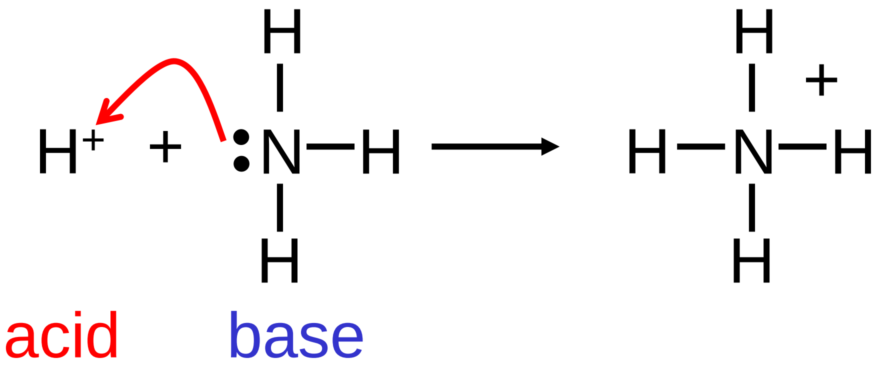
Arrhenius acid is a substance that produces H^+ (H_3O^+) in water

A ***Brønsted acid*** is a proton donor

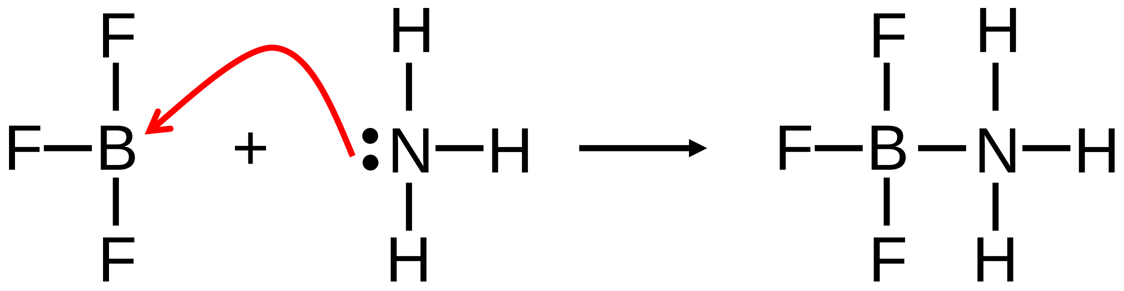
A ***Lewis acid*** is a substance that can accept a pair of electrons

A ***Lewis base*** is a substance that can donate a pair of electrons





Lewis Acids and Bases



acid

base

No protons donated or accepted!

Example 16.15

Identify the Lewis acid and Lewis base in each of the following reactions:

(a) $C_2H_5OC_2H_5 + AlCl_3 \rightleftharpoons (C_2H_5)_2OAlCl_3$

(b) $Hg^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Hg(CN)_4^{2-}(aq)$

Example 16.15

Strategy

In Lewis acid-base reactions, the acid is usually a cation or an electron-deficient molecule, whereas the base is an anion or a molecule containing an atom with lone pairs.

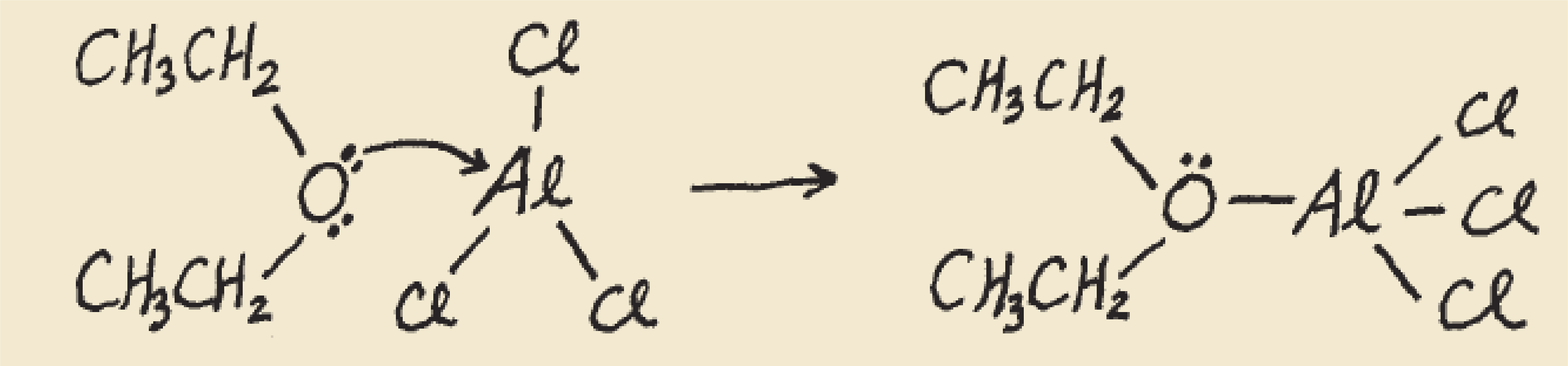
(a) Draw the molecular structure for $C_2H_5OC_2H_5$. What is the hybridization state of Al in $AlCl_3$?

(b) Which ion is likely to be an electron acceptor? An electron donor?

Example 16.15

Solution

(a) The Al is *sp*^{2}-hybridized in $AlCl_3$ with an empty 2p_z orbital. It is electron deficient, sharing only six electrons. Therefore, the Al atom has a tendency to gain two electrons to complete its octet. This property makes $AlCl_3$ a Lewis acid. On the other hand, the lone pairs on the oxygen atom in $C_2H_5OC_2H_5$ make the compound a Lewis base:



Example 16.15

(b) Here the Hg^{2+} ion accepts four pairs of electrons from the CN^- ions. Therefore, Hg^{2+} is the Lewis acid and CN^- is the Lewis base.

Thermochemistry

Chapter 6

Energy is the capacity to do work.

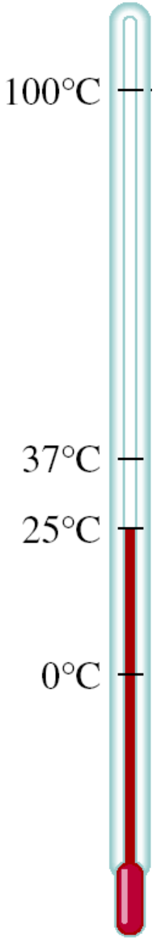
- ***Radiant energy*** comes from the sun and is earth’s primary energy source
- ***Thermal energy*** is the energy associated with the random motion of atoms and molecules
- ***Chemical energy*** is the energy stored within the bonds of chemical substances
- ***Nuclear energy*** is the energy stored within the collection of neutrons and protons in the atom
- ***Potential energy*** is the energy available by virtue of an object’s position

Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.

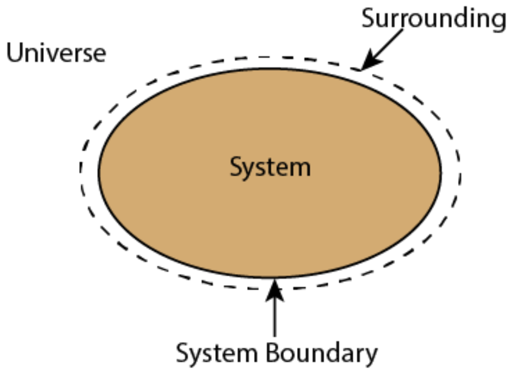
Temperature is a measure of the **thermal energy**.

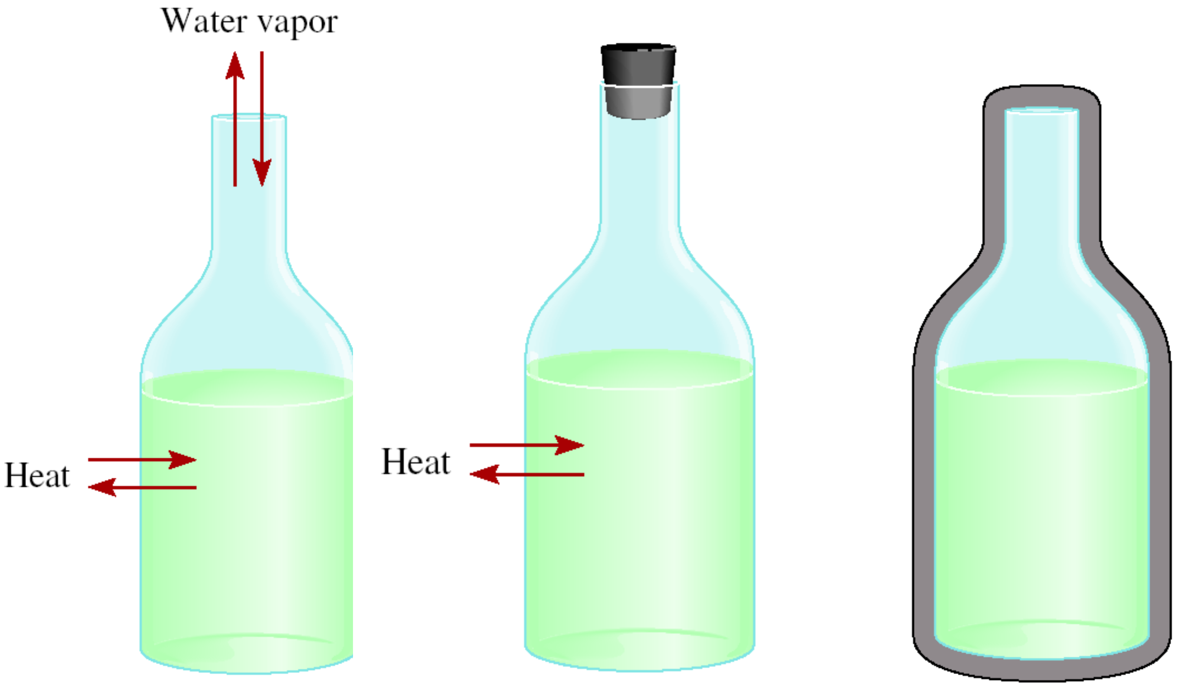
Temperature ≠ Thermal Energy



Thermochemistry is the study of heat change in chemical reactions.

The ***system*** is the specific part of the universe that is of interest in the study.





	open	closed	isolated
Exchange:	mass & energy	energy	nothing

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l) + \text{energy}$$

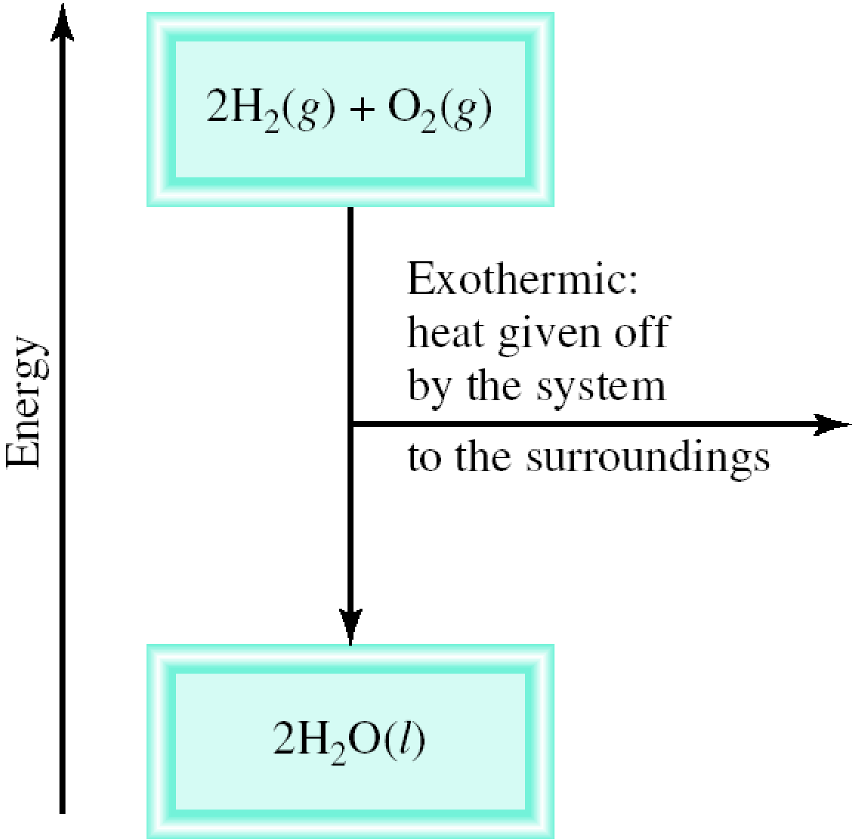
$$H_2O\ (g) \longrightarrow H_2O\ (l) + \text{energy}$$

Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

$$\text{energy} + 2HgO\ (s) \longrightarrow 2Hg\ (l) + O_2\ (g)$$

$$\text{energy} + H_2O\ (s) \longrightarrow H_2O\ (l)$$

Schematic of Exothermic and Endothermic Processes

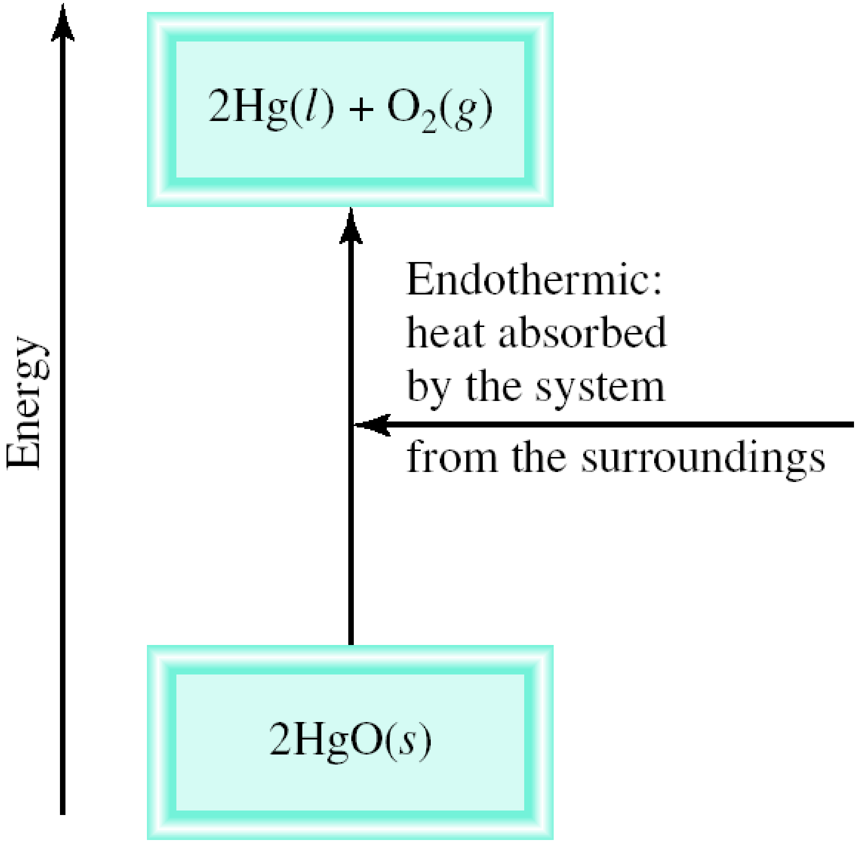


Energy

$2H_2(g) + O_2(g)$

Exothermic:
heat given off
by the system
to the surroundings

$2H_2O(l)$



Energy

$2Hg(l) + O_2(g)$

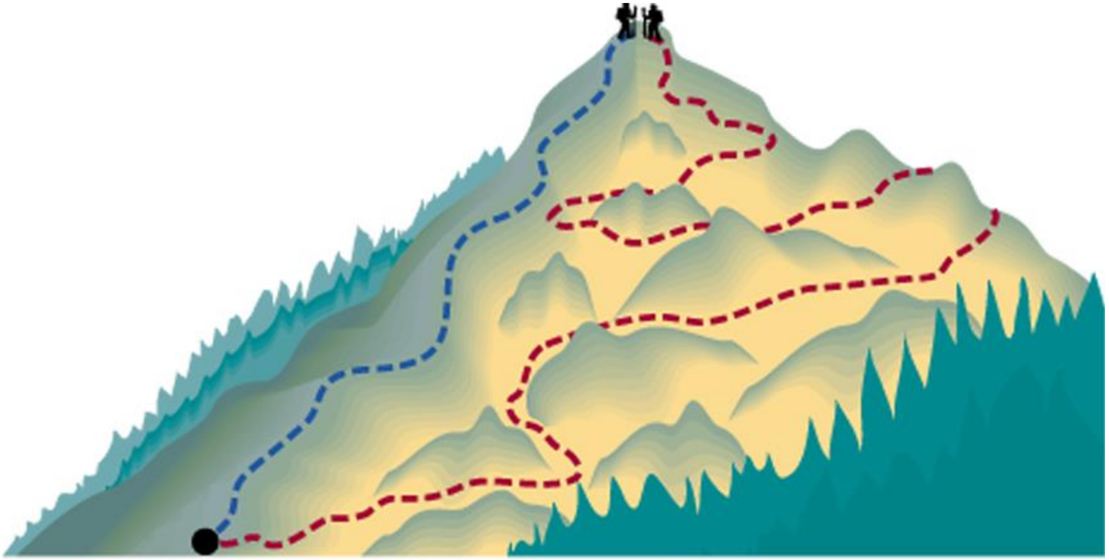
Endothermic:
heat absorbed
by the system
from the surroundings

$2HgO(s)$

Thermodynamics is the scientific study of the interconversion of heat and other kinds of energy.

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature



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

$$\Delta P = P_{final} - P_{initial}$$

$$\Delta V = V_{final} - V_{initial}$$

$$\Delta T = T_{final} - T_{initial}$$

Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

First law of thermodynamics – energy can be converted from one form to another, but cannot be created or destroyed.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

Exothermic chemical reaction!

Chemical energy **lost** by combustion = Energy **gained** by the surroundings

$$\Delta E_{system} + \Delta E_{surroundings} = 0$$

or

$$\Delta E_{system} = -\Delta E_{surroundings}$$

Another form of the ***first law*** for ΔE_{system}

$\Delta E = q + w$

ΔE is the change in internal energy of a system

q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

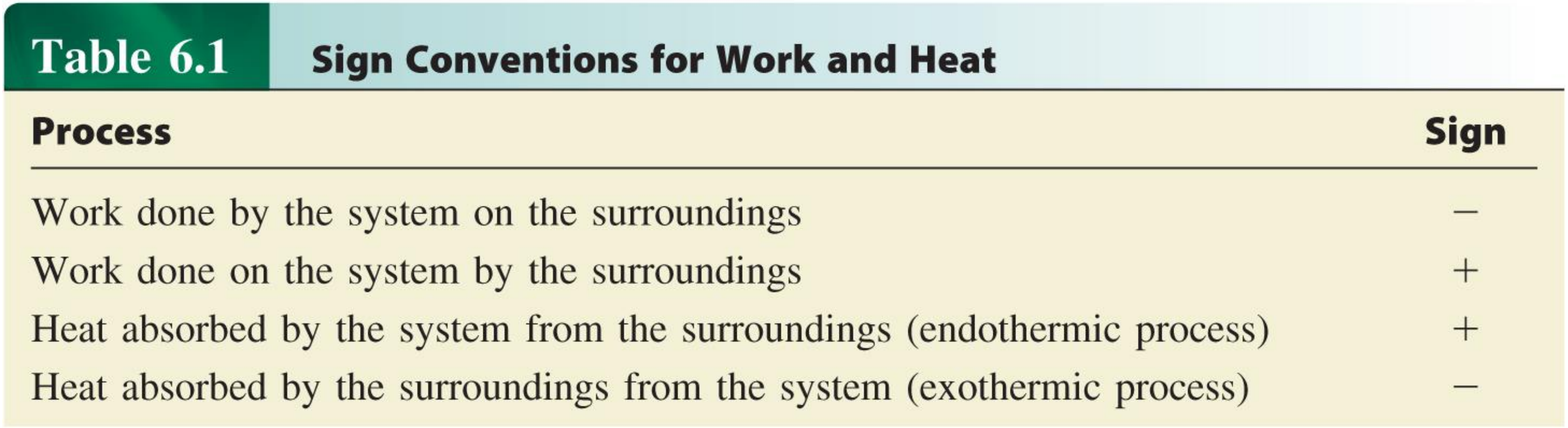


Table 6.1 Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	−
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	−

Work Done By the System On the Surroundings

when a gas expands against a constant external pressure

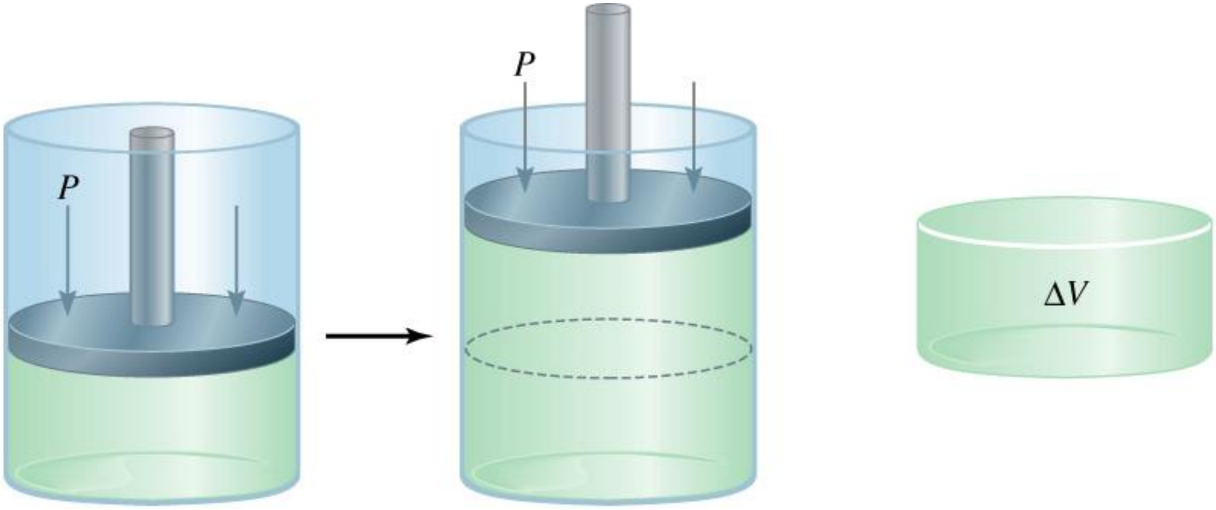
$w = F \times d$

$w = -P \Delta V$

$\Delta V > 0$

$-P\Delta V < 0$

$w < 0$



initial

final

Work is not a state function.

$\Delta w \cancel{=} w_{final} - w_{initial}$

Example 6.1

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature.

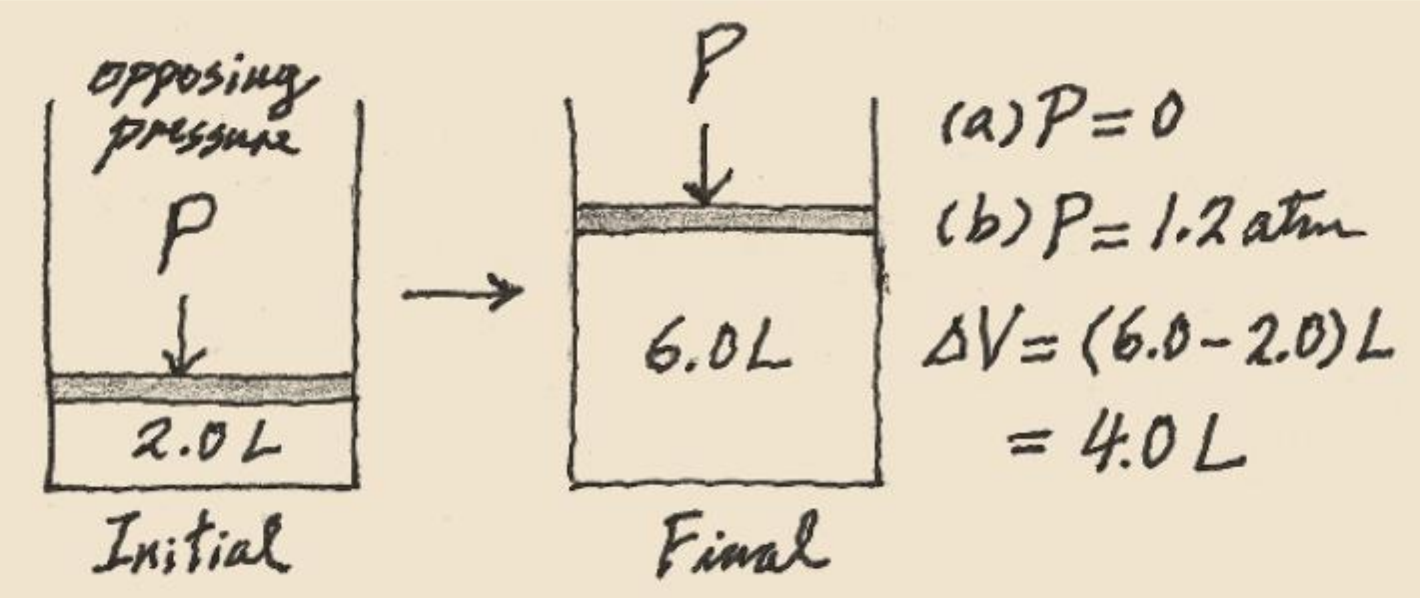
Calculate the work done by the gas if it expands

(a) against a vacuum

(b) against a constant pressure of 1.2 atm

Example 6.1

Strategy A simple sketch of the situation is helpful here:



The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

What is the conversion factor between L · atm and J?

Example 6.1

Solution

(a) Because the external pressure is zero, no work is done in the expansion.

$$\begin{aligned} w &= -P\Delta V \\ &= -(0)(6.0 - 2.0)\ \text{L} \\ &= 0 \end{aligned}$$

(b) The external, opposing pressure is 1.2 atm, so

$$\begin{aligned} w &= -P\Delta V \\ &= -(1.2\ \text{atm})\ (6.0 - 2.0)\ \text{L} \\ &= -4.8\ \text{L} \cdot \text{atm} \end{aligned}$$

Example 6.1

To convert the answer to joules, we write

$$w = -4.8\ \text{L} \cdot \text{atm} \times \frac{101.3\ \text{J}}{1\ \text{L} \cdot \text{atm}}$$

$$= -4.9 \times 10^2\ \text{J}$$

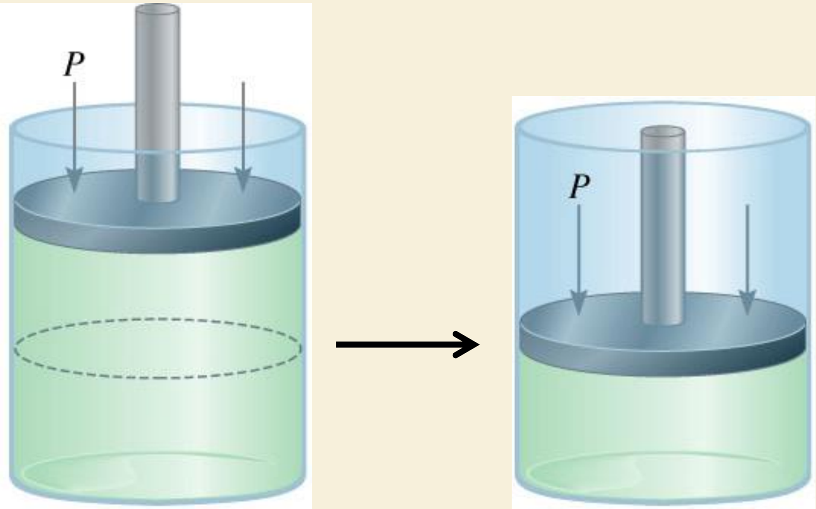
Check Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

Example 6.2

The work done when a gas is compressed in a cylinder like that shown in the figure below is 462 J.

During this process, there is a heat transfer of 128 J from the gas to the surroundings.

Calculate the energy change for this process.



Example 6.2

Strategy

Compression is work done on the gas, so what is the sign for w?

Heat is released by the gas to the surroundings.

Is this an endothermic or exothermic process?

What is the sign for q?

Example 6.2

Solution To calculate the energy change of the gas, we need Equation (6.1). Work of compression is positive and because heat is released by the gas, *q* is negative. Therefore, we have

$$\begin{aligned}\Delta E &= q + w \\ &= -128\ \text{J} + 462\ \text{J} \\ &= 334\ \text{J}\end{aligned}$$

As a result, the energy of the gas increases by 334 J.

Enthalpy and the First Law of Thermodynamics

As most chemical reactions are constant pressure processes

Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

At constant pressure: $\Delta E = q_p + w$

$q_p = \Delta H$ and $w = -P\Delta V$

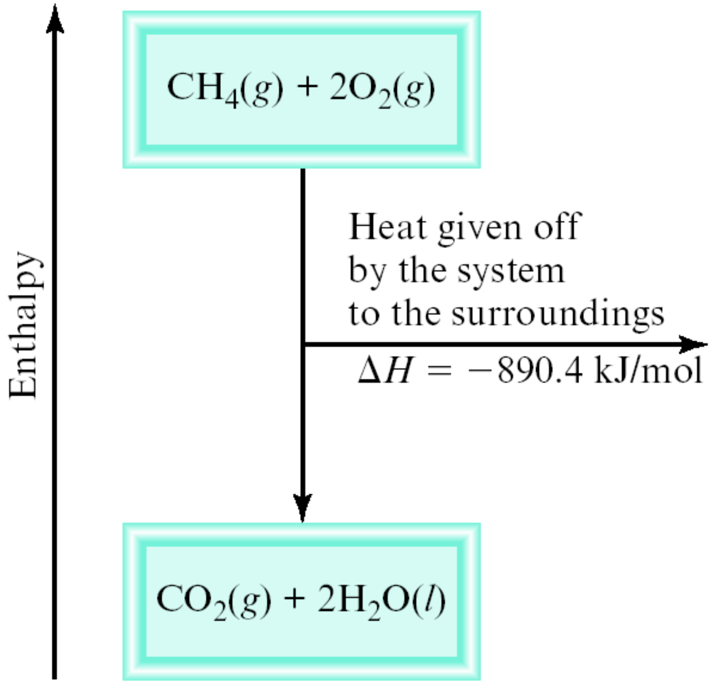
$$\Delta E = \Delta H - P\Delta V$$

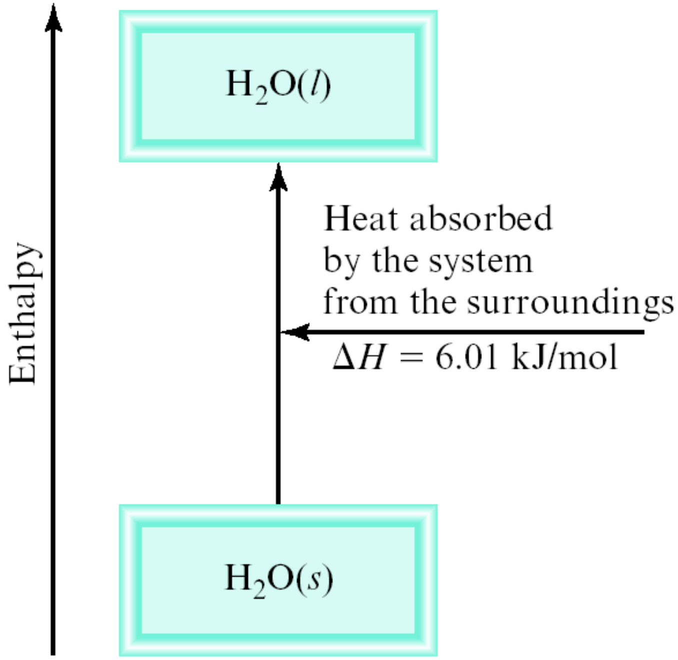
$$\Delta H = \Delta E + P\Delta V$$

$\Delta H = \Delta E + RT\Delta n$ *for ideal gas*

$$\Delta H = H \text{ (products)} - H \text{ (reactants)}$$

ΔH = heat given off or absorbed during a reaction **at constant pressure**





$H_{\text{products}} < H_{\text{reactants}}$

$\Delta H < 0$ exothermic

$H_{\text{products}} > H_{\text{reactants}}$

$\Delta H > 0$ endothermic

A Comparison of ΔH and ΔE

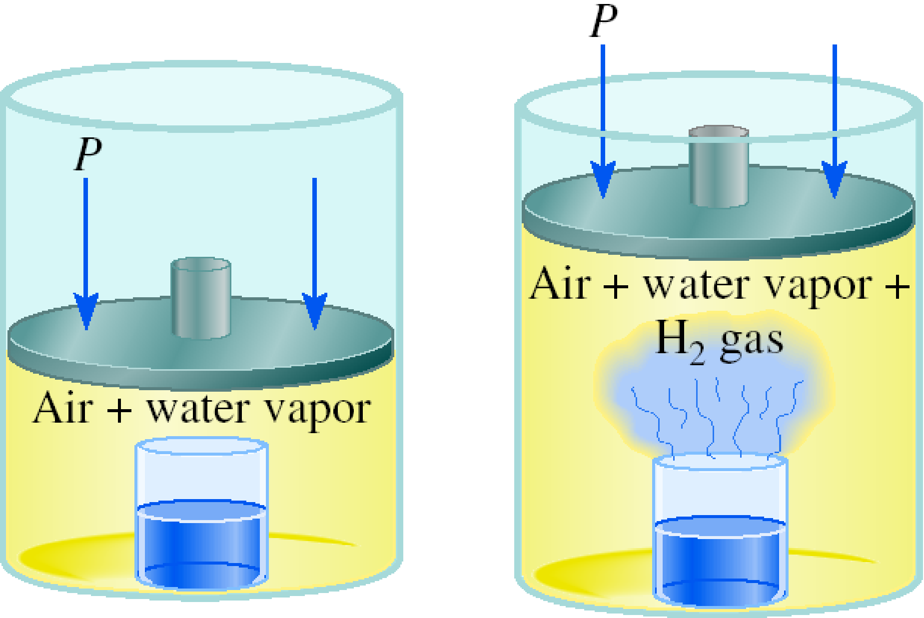
$$2\mathrm{Na}(s) + 2\mathrm{H_2O}(l) \longrightarrow 2\mathrm{NaOH}(aq) + \mathrm{H_2}(g) \quad \Delta H = -367.5\ \mathrm{kJ/mol}$$

$\Delta E = \Delta H - P\Delta V$ At 25 ^{o}C, 1 mole H_2 = 24.5 L at 1 atm

$P\Delta V = 1\ \mathrm{atm} \times 24.5\ \mathrm{L} = 2.5\ \mathrm{kJ}$

$\Delta E = -367.5\ \mathrm{kJ/mol} - 2.5\ \mathrm{kJ/mol} = -370.0\ \mathrm{kJ/mol}$

ΔH is less than ΔE, as some of energy used to do gas expansion work



For reactions that do not involve gases, ΔV is usually very small and so ΔE is practically the same as ΔH

Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta H = 6.01\ \text{kJ/mol}$$

- If you reverse a reaction, the sign of ΔH changes

$$H_2O\ (l) \longrightarrow H_2O\ (s) \qquad \Delta H = -6.01\ \text{kJ/mol}$$

- If you multiply both sides of the equation by a factor *n*, then ΔH must change by the same factor *n*.

$$2H_2O\ (s) \longrightarrow 2H_2O\ (l) \qquad \Delta H = 2 \times 6.01 = 12.0\ \text{kJ}$$

Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.

$$H_2O\,(s) \longrightarrow H_2O\,(l) \qquad \Delta H = 6.01 \text{ kJ/mol}$$

$$H_2O\,(l) \longrightarrow H_2O\,(g) \qquad \Delta H = 44.0 \text{ kJ/mol}$$

Example 6.3

Given the thermochemical equation

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \qquad \Delta H = -198.2 \text{ kJ/mol}$$

calculate the heat evolved when 87.9 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3.

Example 6.3

Strategy

The thermochemical equation shows that for every 2 moles of SO_2 reacted, 198.2 kJ of heat are given off (note the negative sign.) Therefore, the conversion factor is

$$\frac{-198.2\ \text{kJ}}{2\ \text{mol}\ SO_2}$$

How many moles of SO_2 are in 87.9 g of SO_2?

What is the conversion factor between grams and moles?

Example 6.3

Solution We need to first calculate the number of moles of SO_2 in 87.9 g of the compound and then find the number of kilojoules produced from the exothermic reaction. The sequence of conversions is as follows:

$$\text{grams of } SO_2 \longrightarrow \text{moles of } SO_2 \longrightarrow \text{kilojoules of heat generated}$$

Therefore, the enthalpy change for this reaction is given by

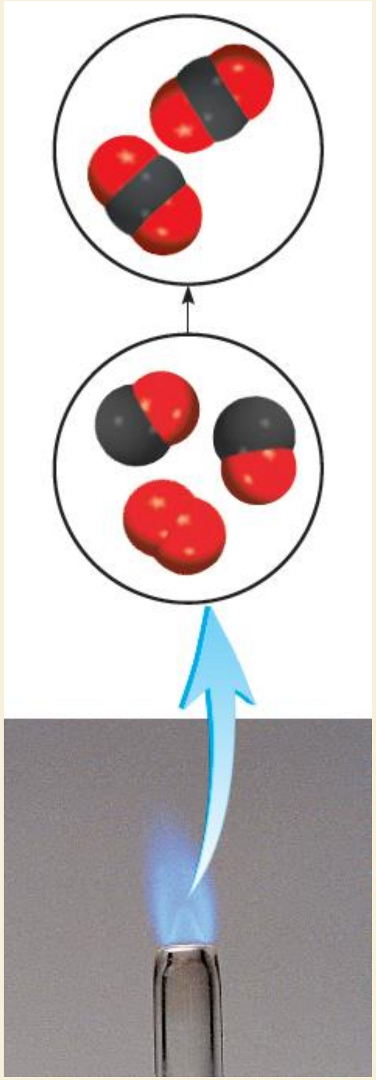
$$\begin{aligned}\Delta H &= 87.9\ \cancel{\text{g } SO_2} \times \frac{1\ \cancel{\text{mol } SO_2}}{64.07\ \cancel{\text{g } SO_2}} \times \frac{-198.2\ \text{kJ}}{2\ \cancel{\text{mol } SO_2}} \\ &= -136\ \text{kJ}\end{aligned}$$

and the heat released to the surroundings is 136 kJ.

Example 6.4

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 atm and 25°C:

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \quad \Delta H = -566.0\ \text{kJ/mol}$$



Carbon monoxide burns in air to form carbon dioxide.

Example 6.4

Strategy

We are given the enthalpy change, ΔH, for the reaction and are asked to calculate the change in internal energy, ΔE.

Therefore, we need Equation (6.10).

What is the change in the number of moles of gases?

Δ *H* is given in kilojoules, so what units should we use for *R*?

Example 6.4

Solution From the chemical equation we see that 3 moles of gases are converted to 2 moles of gases so that

$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases}\\ &= 2 - 3\\ &= -1\end{aligned}$$

Using 8.314 J/K · mol for *R* and *T* = 298 K in Equation (6.10), we write

$$\begin{aligned}\Delta E &= \Delta H - RT\Delta n\\ &= -566.0\ \text{kJ/mol} - (8.314\ \text{J/K}\cdot\text{mol})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)(298\ \text{K})(-1)\\ &= -563.5\ \text{kJ/mol}\end{aligned}$$

The ***specific heat***(***s***) of a substance is the amount of heat (q) required to raise the temperature of **one gram** of the substance by **one degree** Celsius.

The ***heat capacity*** (***C***) of a substance is the amount of heat (q) required to raise the temperature of **a given quantity** (m) of the substance by **one degree** Celsius.

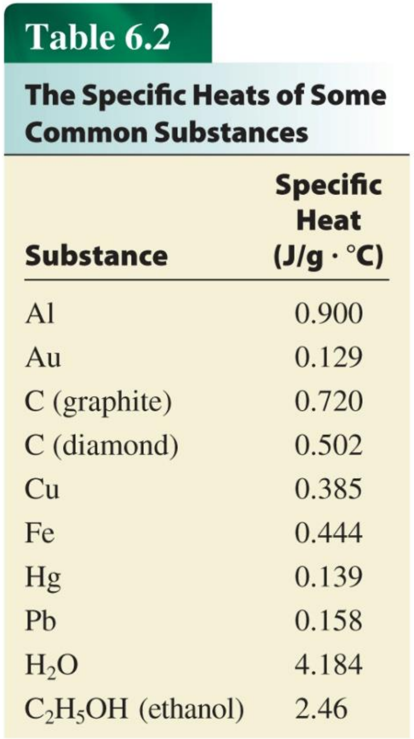


Table 6.2

The Specific Heats of Some Common Substances

Substance	Specific Heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
Pb	0.158
H_2O	4.184
C_2H_5OH (ethanol)	2.46

$$C = m \times s$$

<u>Heat (q) absorbed or released:</u>

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

$$q = C \times \Delta T$$

$$\Delta T = T_{\text{inal}} - T_{\text{initial}}$$

Example 6.5

A 466-g sample of water is heated from 8.50°C to 74.60°C.

Calculate the amount of heat absorbed (in kilojoules) by the water.

Example 6.5

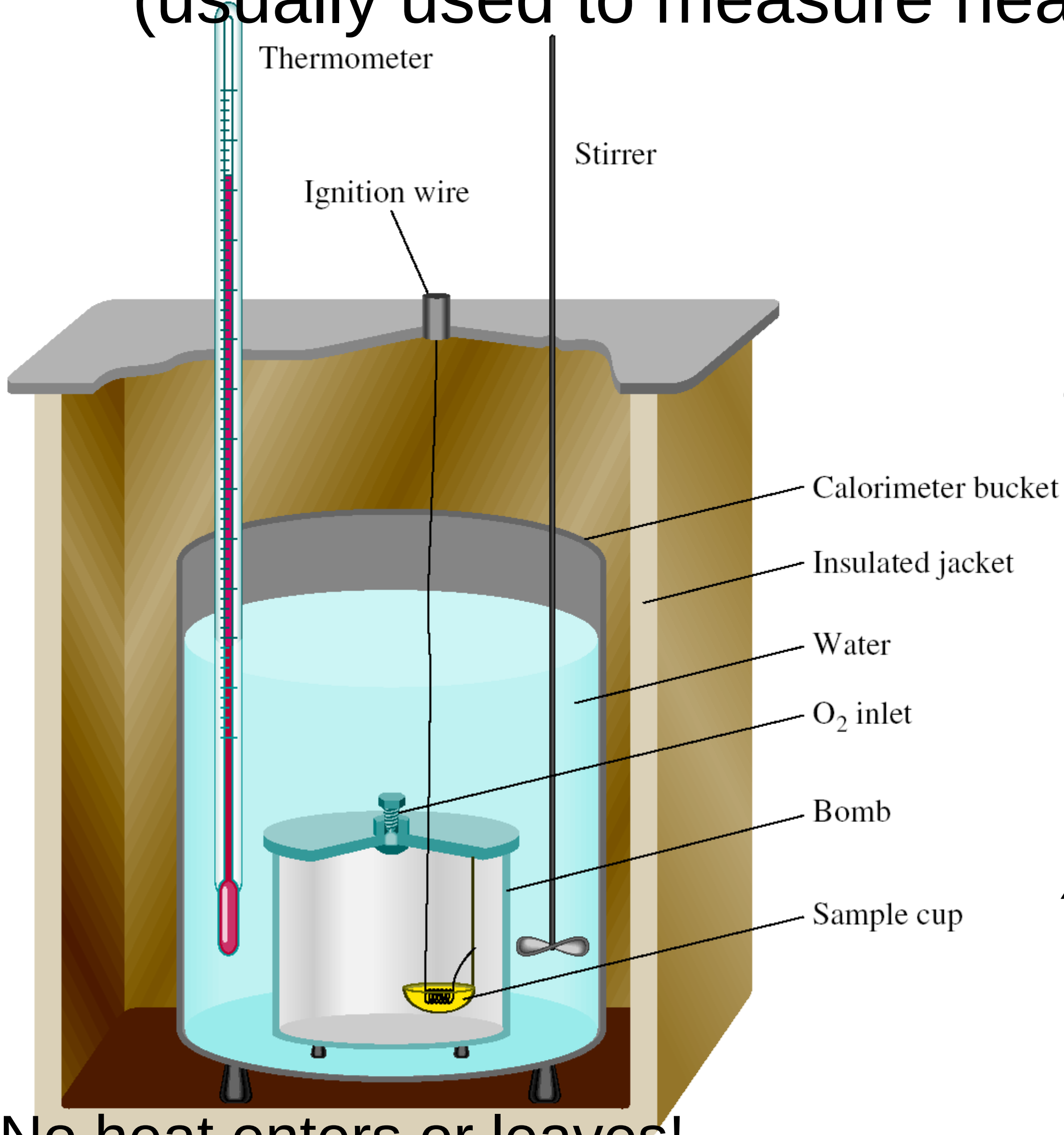
Strategy We know the quantity of water and the specific heat of water. With this information and the temperature rise, we can calculate the amount of heat absorbed (*q*).

Solution Using Equation (6.12), we write

$$
\begin{aligned}
q &= ms\Delta T \\
&= (466\ \text{g})\,(4.184\ \text{J/g}\cdot{}^{\circ}\text{C})\,(74.60^{\circ}\text{C} - 8.50^{\circ}\text{C}) \\
&= 1.29 \times 10^{5}\ \text{J} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \\
&= 129\ \text{kJ}
\end{aligned}
$$

Check The units g and °C cancel, and we are left with the desired unit kJ. Because heat is absorbed by the water from the surroundings, it has a positive sign.

Constant-Volume Calorimetry
(usually used to measure heat of combustion)



$$q_{sys} = q_{cal} + q_{rxn}$$

$$q_{sys} = 0$$

$$q_{rxn} = - q_{cal}$$

$$q_{cal} = C_{cal} \times \Delta T$$

(C_{cal} *comprises both the bomb And the surrounding water)*

Reaction at Constant *V*

$$\Delta H \neq q_{rxn}$$

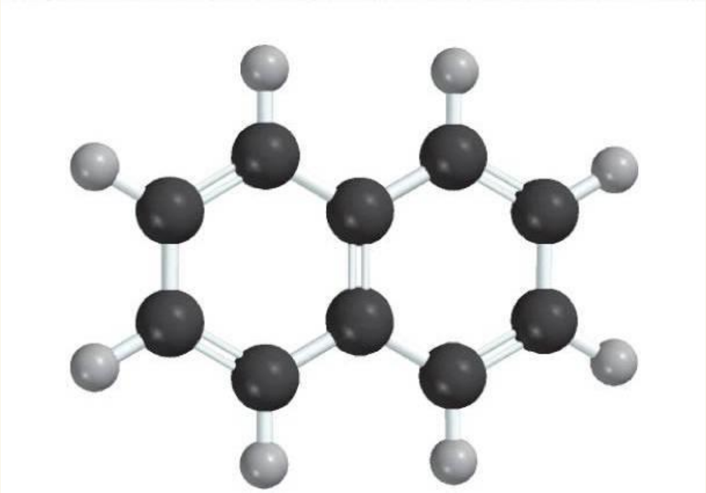
No heat enters or leaves!

Example 6.6

A quantity of 1.435 g of naphthalene ($C_{10}H_8$), a pungent-smelling substance used in moth repellents, was burned in a constant-volume bomb calorimeter.

Consequently, the temperature of the water rose from 20.28°C to 25.95°C.

If the heat capacity of the bomb plus water was 10.17 kJ/°C, calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.



$C_{10}H_8$

Example 6.6

Strategy

Knowing the heat capacity and the temperature rise, how do we calculate the heat absorbed by the calorimeter?

What is the heat generated by the combustion of 1.435 g of naphthalene?

What is the conversion factor between grams and moles of naphthalene?

Example 6.6

Solution The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change.

From Equation (6.16), assuming no heat is lost to the surroundings, we write

$$\begin{aligned} q_{\text{cal}} &= C_{\text{cal}}\Delta t \\ &= (10.17\ \text{kJ}/°\text{C})\ (25.95°\text{C} - 20.28°\text{C}) \\ &= 57.66\ \text{kJ} \end{aligned}$$

Because $q_{\text{sys}} = q_{\text{cal}} + q_{\text{rxn}} = 0$, $q_{\text{cal}} = -q_{\text{rxn}}$. The heat change of the reaction is − 57.66 kJ. This is the heat released by the combustion of 1.435 g of $C_{10}H_8$; therefore, we can write the conversion factor as

$$\frac{-57.66\ \text{kJ}}{1.435\ \text{g}\ C_{10}H_8}$$

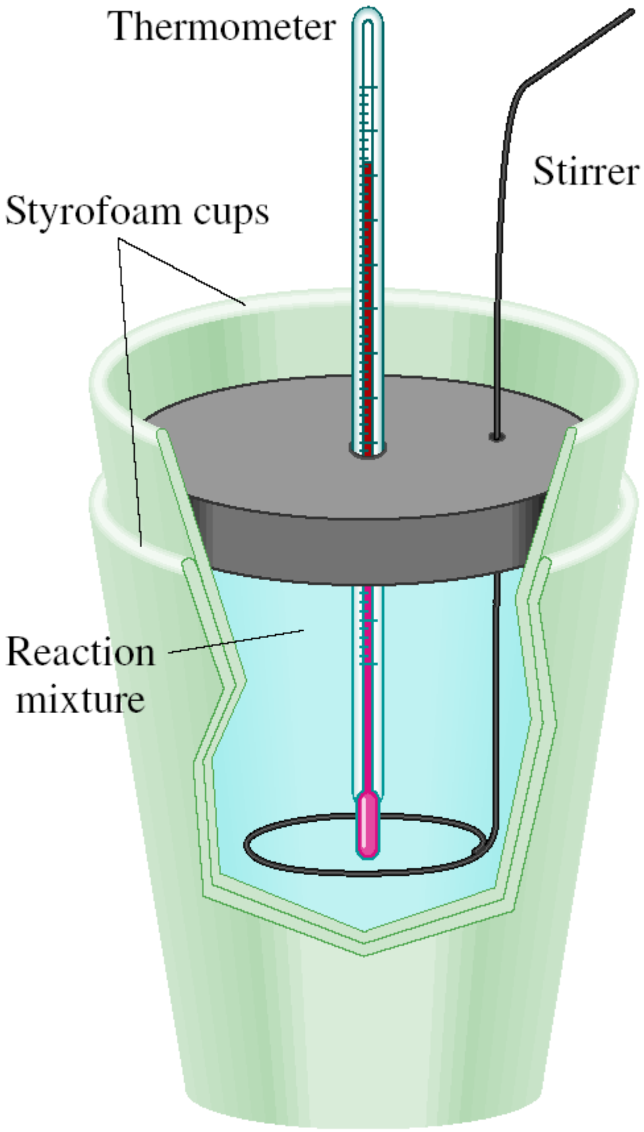
Example 6.6

The molar mass of naphthalene is 128.2 g, so the heat of combustion of 1 mole of naphthalene is

$$\text{molar heat of combustion} = \frac{-57.66\ \text{kJ}}{1.435\ \cancel{\text{g C}_{10}\text{H}_8}} \times \frac{128.2\ \cancel{\text{g C}_{10}\text{H}_8}}{1\ \text{mol C}_{10}\text{H}_8}$$

$$= -5.151 \times 10^{3}\ \text{kJ/mol}$$

Constant-Pressure Calorimetry



$q_{sys} = q_{cal} + q_{rxn}$

$q_{sys} = 0$

$q_{rxn} = -q_{cal}$

$q_{cal} = m \times s \times \Delta T$

$q_{cal} = C_{water} \times \Delta T$

Reaction at Constant *P*

$\Delta H = q_{rxn}$

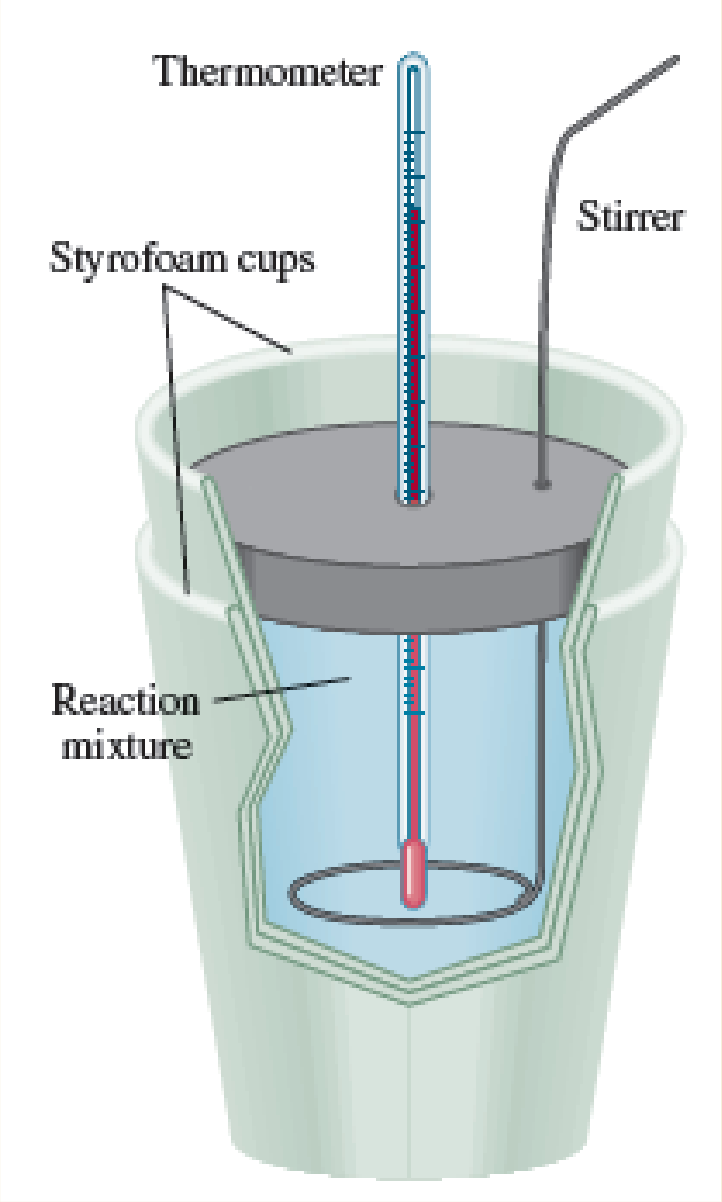
No heat enters or leaves!

Example 6.7

A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water.

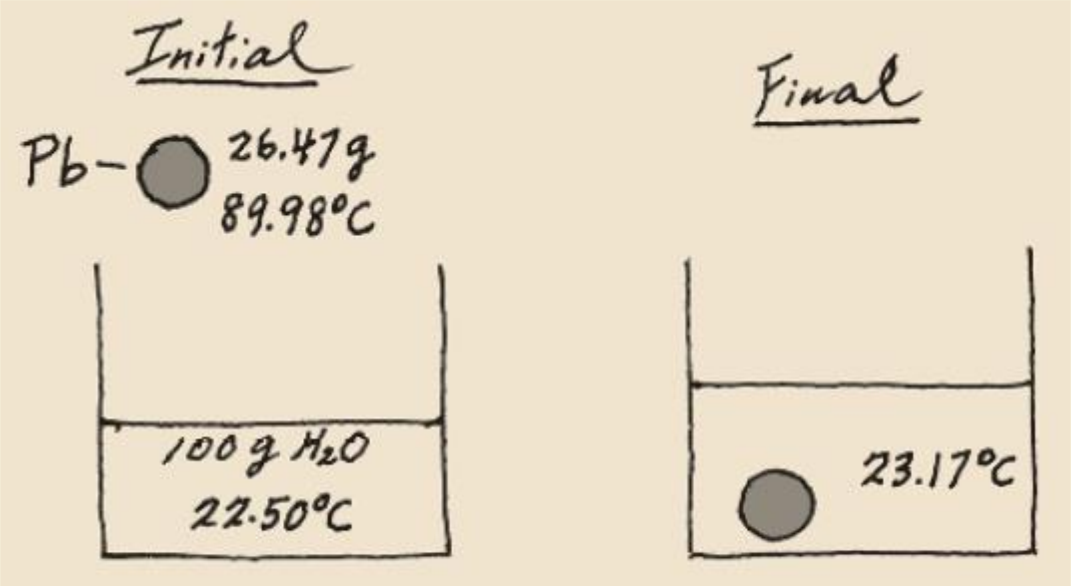
The water temperature rose from 22.50°C to 23.17°C.

What is the specific heat of the lead pellet?



Example 6.7

Strategy A sketch of the initial and final situation is as follows:



We know the masses of water and the lead pellet as well as the initial and final temperatures. Assuming no heat is lost to the surroundings, we can equate the heat lost by the lead pellet to the heat gained by the water. Knowing the specific heat of water, we can then calculate the specific heat of lead.

Example 6.7

Solution Treating the calorimeter as an isolated system (no heat lost to the surroundings), we write

$$q_{\text{Pb}} + q_{\text{H}_2\text{O}} = 0$$

or

$$q_{\text{Pb}} = -q_{\text{H}_2\text{O}}$$

The heat gained by the water is given by

$$q_{\text{H}_2\text{O}} = ms\Delta t$$

where *m* and *s* are the mass and specific heat and

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

Example 6.7

Therefore,

$$q_{H_2O} = (100.0\ \text{g})(4.184\ \text{J/g}\cdot{}^\circ\text{C})\ (23.17^\circ\text{C} - 22.50^\circ\text{C})$$

$$= 280.3\ \text{J}$$

Because the heat lost by the lead pellet is equal to the heat gained by the water, $q_{Pb} = -280.3$ J. Solving for the specific heat of Pb, we write

$$q_{Pb} = ms\Delta t$$

$$-280.3\ \text{J} = (26.47\ \text{g})(s)(23.17^\circ\text{C} - 89.98^\circ\text{C})$$

$$s = 0.158\ \text{J/g}\cdot{}^\circ\text{C}$$

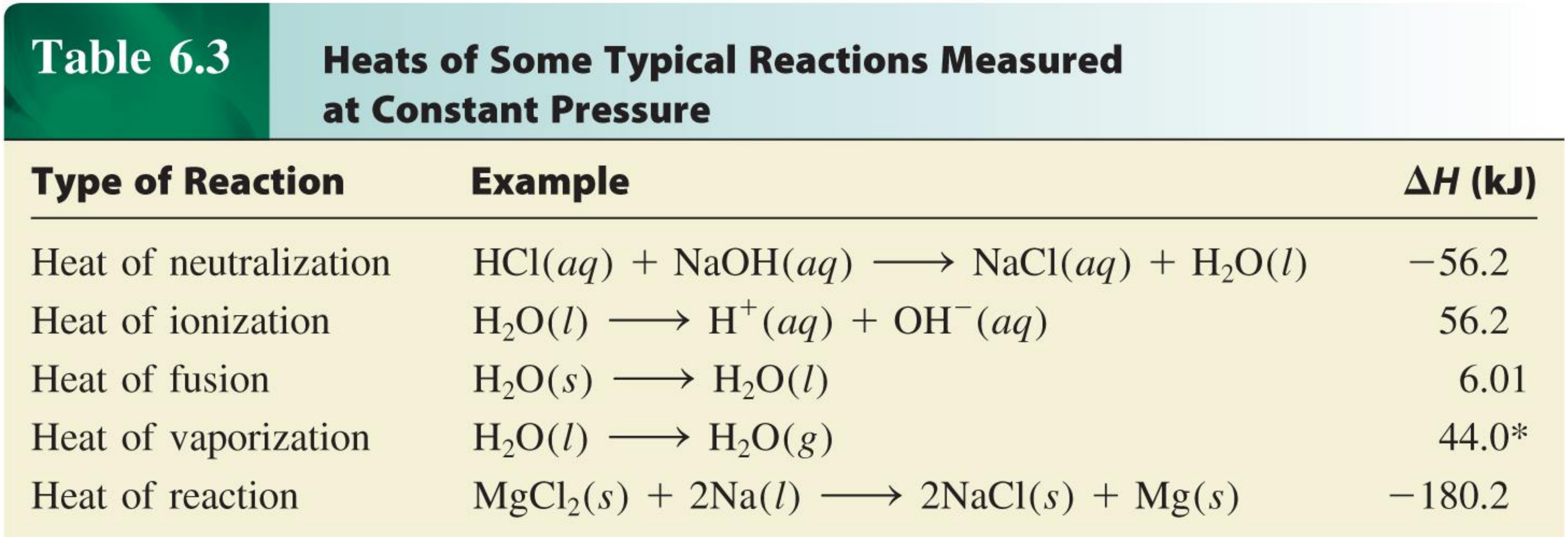


Table 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	−56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	44.0*
Heat of reaction	$MgCl_2(s) + 2Na(l) \longrightarrow 2NaCl(s) + Mg(s)$	−180.2

Example 6.8

A quantity of 1.00×10^2 mL of 0.500 *M* HCl was mixed with 1.00×10^2 mL of 0.500 *M* NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same, 22.50°C, and the final temperature of the mixed solution was 25.86°C. Calculate the heat change for the neutralization reaction on a molar basis:

$$\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 4.184 J/g · °C, respectively).

Example 6.8

Strategy

Because the temperature rose, the neutralization reaction is exothermic.

How do we calculate the heat absorbed by the combined solution?

What is the heat of the reaction?

What is the conversion factor for expressing the heat of reaction on a molar basis?

Example 6.8

Solution Assuming no heat is lost to the surroundings, $q_{sys} = q_{soln} + q_{rxn} = 0$, so $q_{rxn} = -q_{soln}$, where q_{soln} is the heat absorbed by the combined solution. Because the density of the solution is 1.00 g/mL, the mass of a 100-mL solution is 100 g.

Thus,

$$\begin{aligned} q_{soln} &= ms\Delta t \\ &= \left(1.00\times10^2\ \text{g} + 1.00\times10^2\ \text{g}\right)(4.184\ \text{J/g}\cdot{}^\circ\text{C})(25.86^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 2.81\times10^3\ \text{J} \\ &= 2.81\ \text{kJ} \end{aligned}$$

Because $q_{rxn} = -q_{soln}$, $q_{rxn} = -2.81$ kJ.

Example 6.8

From the molarities given, the number of moles of both HCl and NaOH in 1.00 × 10^2 mL solution is

$$\frac{0.500\ \text{mol}}{1\ \text{L}} \times 0.100\ \text{L} = 0.0500\ \text{mol}$$

$$\text{heat of neutralization} = \frac{-2.81\ \text{kJ}}{0.0500\ \text{mol}} = -56.2\ \text{kJ/mol}$$

Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?

Establish an arbitrary scale with the **standard enthalpy of formation** (ΔH_f^0) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH_f^0) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

The standard enthalpy of formation of any element in its most stable form is zero.

ΔH_f^0 (C, graphite) = 0

ΔH_f^0 (O_2) = 0

ΔH_f^0 (C, diamond) = 1.90 kJ/mol

ΔH_f^0 (O_3) = 142 kJ/mol

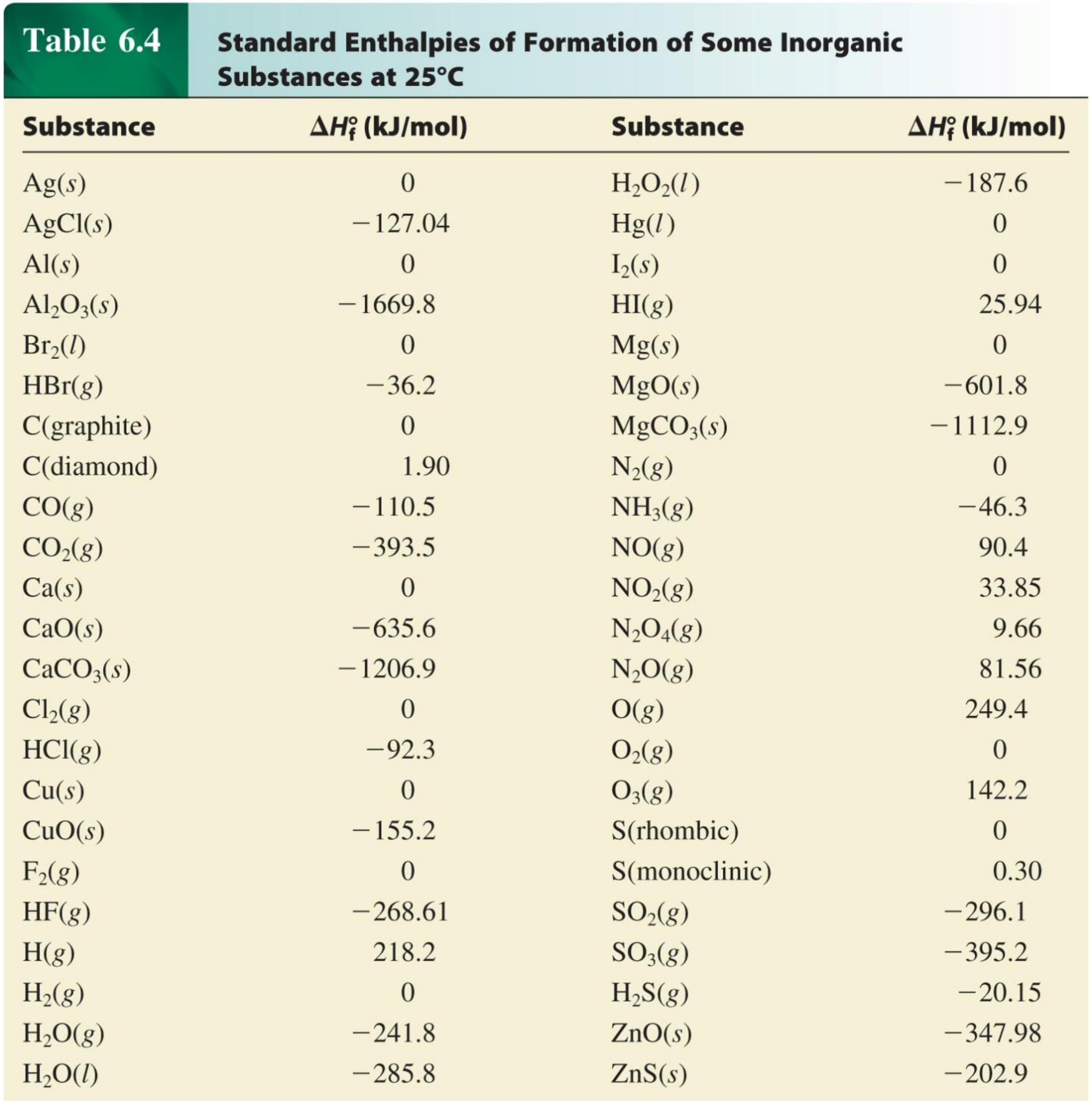


Table 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH°_f (kJ/mol)	Substance	ΔH°_f (kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.04	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	$HI(g)$	25.94
$Br_2(l)$	0	$Mg(s)$	0
$HBr(g)$	−36.2	$MgO(s)$	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
$CO(g)$	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	$NO(g)$	90.4
$Ca(s)$	0	$NO_2(g)$	33.85
$CaO(s)$	−635.6	$N_2O_4(g)$	9.66
$CaCO_3(s)$	−1206.9	$N_2O(g)$	81.56
$Cl_2(g)$	0	$O(g)$	249.4
$HCl(g)$	−92.3	$O_2(g)$	0
$Cu(s)$	0	$O_3(g)$	142.2
$CuO(s)$	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
$HF(g)$	−268.61	$SO_2(g)$	−296.1
$H(g)$	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	$ZnO(s)$	−347.98
$H_2O(l)$	−285.8	$ZnS(s)$	−202.9

The **standard enthalpy of reaction** (ΔH^0_{rxn}) is the enthalpy of a reaction carried out at 1 atm.

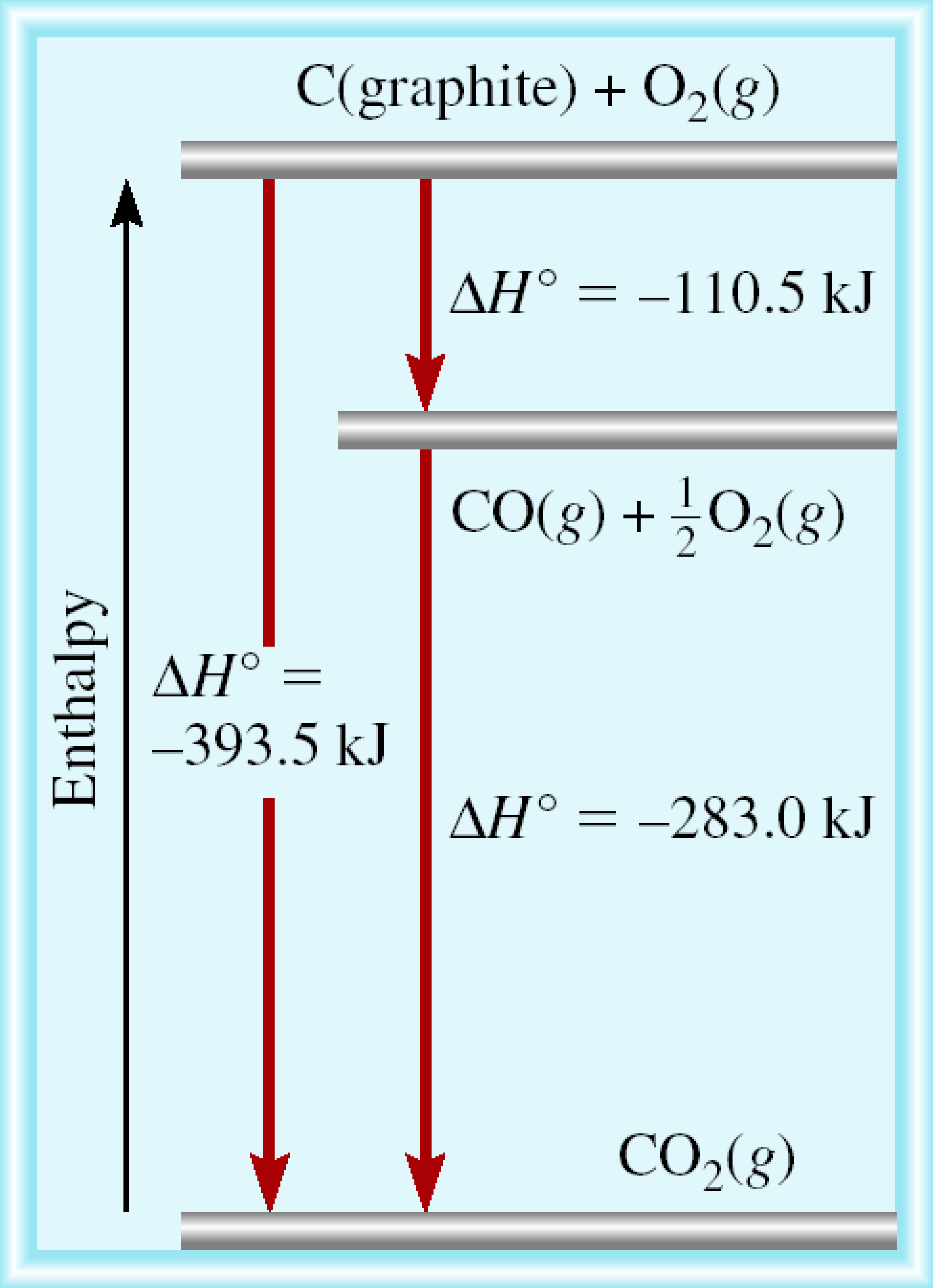
$$aA + bB \longrightarrow cC + dD$$

$$\Delta H^0_{rxn} = [c\Delta H^0_f(C) + d\Delta H^0_f(D)] - [a\Delta H^0_f(A) + b\Delta H^0_f(B)]$$

$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f(\text{products}) - \Sigma m\Delta H^0_f(\text{reactants})$$

Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)



$C\ (\text{graphite}) + 1/2O_2\ (g) \longrightarrow CO\ (g)$

$CO\ (g) + 1/2O_2\ (g) \longrightarrow CO_2\ (g)$

$C\ (\text{graphite}) + O_2\ (g) \longrightarrow CO_2\ (g)$

Example 6.9

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:

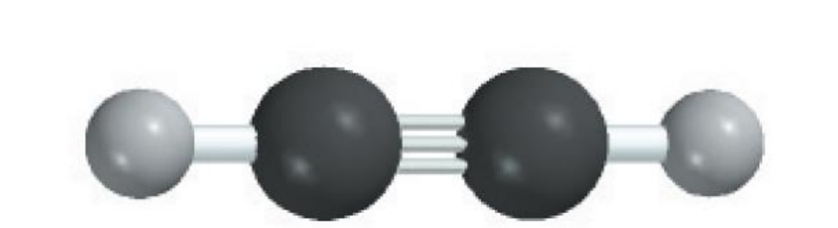
$$2\text{C(graphite)} + \text{H}_2(g) \longrightarrow \text{C}_2\text{H}_2(g)$$

The equations for each step and the corresponding enthalpy changes are

$$\text{(a)}\quad \text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \qquad \Delta H^\circ_{\text{rxn}} = -393.5\ \text{kJ/mol}$$

$$\text{(b)}\quad \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l) \qquad \Delta H^\circ_{\text{rxn}} = -285.8\ \text{kJ/mol}$$

$$\text{(c)}\quad 2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \qquad \Delta H^\circ_{\text{rxn}} = -2598.8\ \text{kJ/mol}$$



C_2H_2

Example 6.9

Strategy Our goal here is to calculate the enthalpy change for the formation of C_2H_2 from its elements C and H_2. The reaction does not occur directly, however, so we must use an indirect route using the information given by Equations (a), (b), and (c).

Solution Looking at the synthesis of C_2H_2, we need 2 moles of graphite as reactant. So we multiply Equation (a) by 2 to get

$$\text{(d)}\quad 2\text{C(graphite)} + 2\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) \qquad \Delta H^\circ_{\text{rxn}} = 2(-393.5\ \text{kJ/mol})$$

$$= -787.0\ \text{kJ/mol}$$

Next, we need 1 mole of H_2 as a reactant and this is provided by Equation (b). Last, we need 1 mole of C_2H_2 as a product.

Example 6.9

Equation (c) has 2 moles of C_2H_2 as a reactant so we need to reverse the equation and divide it by 2:

$$\text{(e)}\quad 2CO_2(g) + H_2O(l) \longrightarrow C_2H_2(g) + \frac{5}{2}O_2(g) \qquad \Delta H^\circ_{rxn} = \frac{1}{2}(2598.8\ \text{kJ/mol})$$

$$= 1299.4\ \text{kJ/mol}$$

Adding Equations (d), (b), and (e) together, we get

$$2C(\text{graphite}) + 2O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H^\circ_{rxn} = -787.0\ \text{kJ/mol}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ_{rxn} = -285.8\ \text{kJ/mol}$$

$$2CO_2(g) + H_2O(l) \longrightarrow C_2H_2(g) + \frac{5}{2}O_2(g) \qquad \Delta H^\circ_{rxn} = 1299.4\ \text{kJ/mol}$$

$$2C(\text{graphite}) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H^\circ_{rxn} = 226.6\ \text{kJ/mol}$$

Example 6.9

Therefore,

$$\Delta H_f^\circ = 226.6 \text{ kJ/mol}$$

This value means that when 1 mole of C_2H_2 is synthesized from 2 moles of C(graphite) and 1 mole of H_2, 226.6 kJ of heat are absorbed by the reacting system from the surroundings. Thus, this is an endothermic process.

Example 6.10

The thermite reaction involves aluminum and iron(III) oxide

$$2\text{Al}(s) + \text{Fe}_2\text{O}_3(s) \longrightarrow \text{Al}_2\text{O}_3(s) + 2\text{Fe}(l)$$

This reaction is highly exothermic and the liquid iron formed is used to weld metals.

Calculate the heat released in kilojoules per gram of Al reacted with Fe_2O_3. The ΔH_f° for Fe(l) is 12.40 kJ/mol.

The molten iron formed in a thermite reaction is run down into a mold between the ends of two railroad rails. On cooling, the rails are welded together.

Example 6.10

Strategy

The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants.

The enthalpy of each species (reactant or product) is given by its stoichiometric coefficient times the standard enthalpy of formation of the species.

Example 6.10

Solution Using the given ΔH_f° value for Fe(*l*) and other ΔH_f° values in Appendix 3 and Equation (6.18), we write

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \left[\Delta H_f^\circ(\text{Al}_2\text{O}_3) + 2\Delta H_f^\circ(\text{Fe})\right] - \left[2\Delta H_f^\circ(\text{Al}) + \Delta H_f^\circ(\text{Fe}_2\text{O}_3)\right] \\ &= [(-1669.8\ \text{kJ/mol}) + 2(12.40\ \ \text{kJ/mol})] - [2(0) + (-822.2\ \text{kJ/mol})] \\ &= -822.8\ \text{kJ/mol}\end{aligned}$$

This is the amount of heat released for two moles of Al reacted. We use the following ratio

$$\frac{-822.8\ \text{kJ}}{2\ \text{mol Al}}$$

to convert to kJ/g Al.

Example 6.10

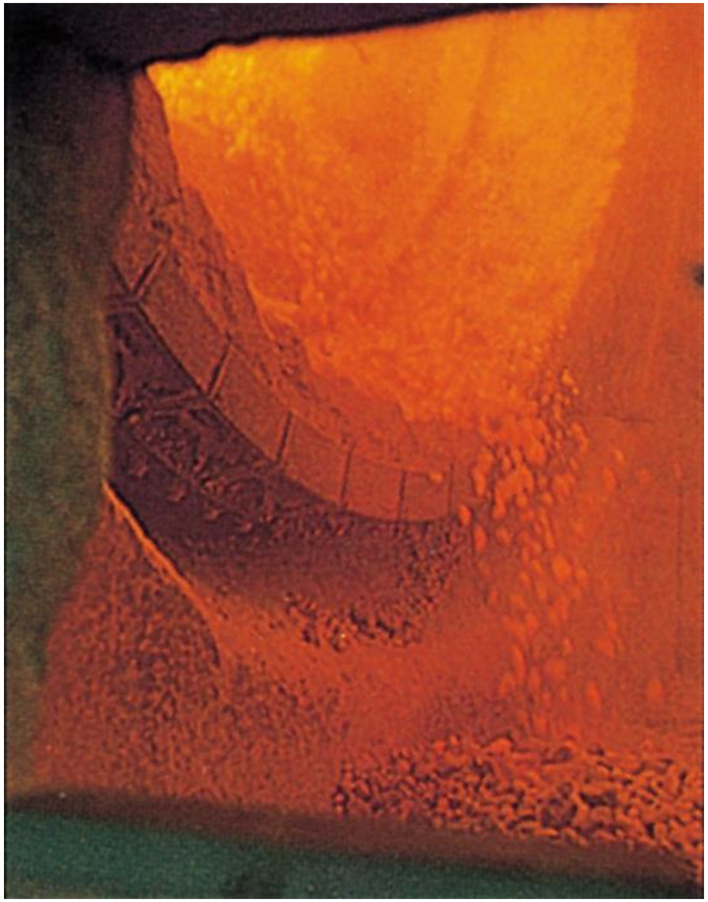
The molar mass of Al is 26.98 g, so

$$\text{heat released per gram of Al} = \frac{-822.8\ \text{kJ}}{2\ \text{mol Al}} \times \frac{1\ \text{mol Al}}{26.98\ \text{g Al}}$$
$$= 15.25\ \text{kJ/g}$$

Check Is the negative sign consistent with the exothermic nature of the reaction? As a quick check, we see that 2 moles of Al weigh about 54 g and give off about 823 kJ of heat when reacted with Fe_2O_3. Therefore, the heat given off per gram of Al reacted is approximately −830 kJ/54 g or −15.4 kJ/g.

Entropy, Free Energy and Equilibrium

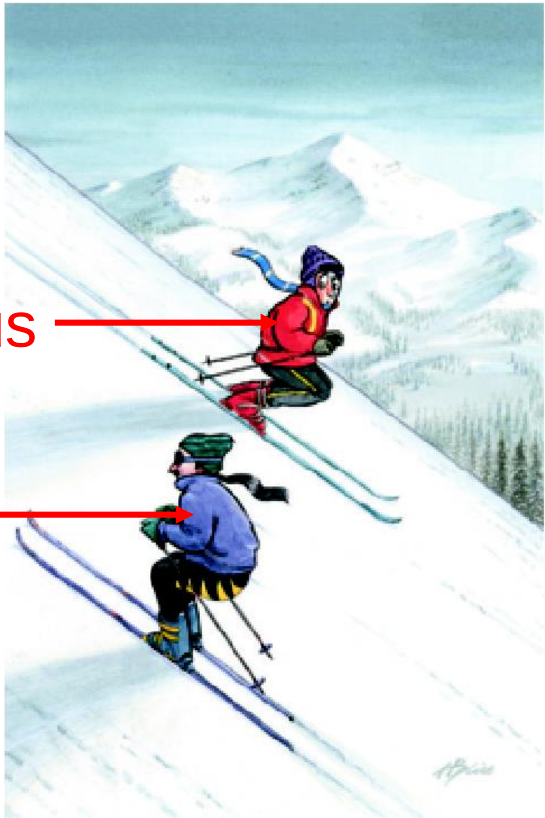
Chapter 17



Spontaneous Physical and Chemical Processes

- A waterfall runs downhill
- A lump of sugar dissolves in a cup of coffee
- At 1 atm, water freezes below 0 ^{o}C and ice melts above 0 ^{o}C
- Heat flows from a hotter object to a colder object
- A gas expands in an evacuated bulb
- Iron exposed to oxygen and

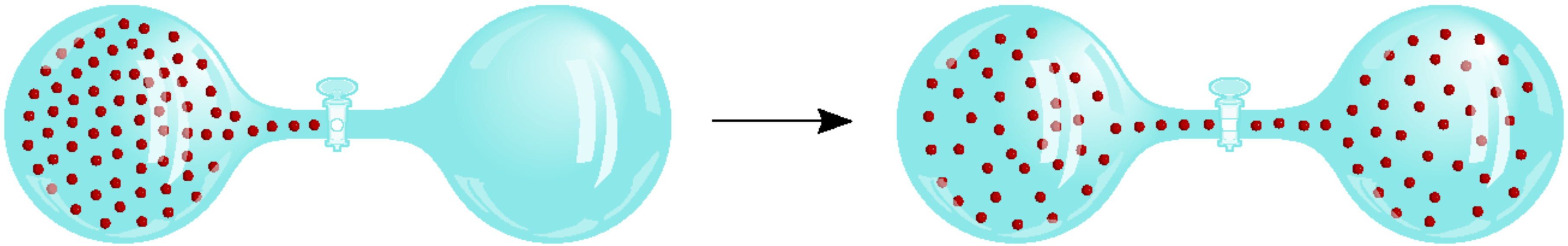
  water forms rust



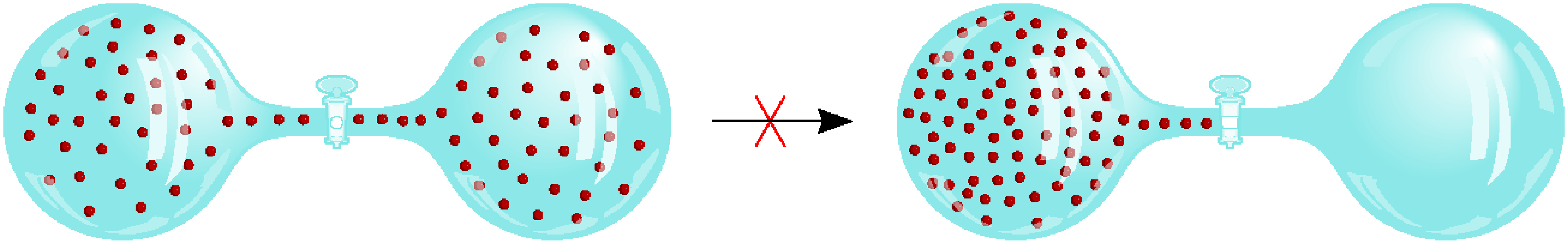
spontaneous

nonspontaneous

spontaneous



nonspontaneous



Does a decrease in enthalpy mean a reaction proceeds spontaneously?

<u>Spontaneous reactions</u>

$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l) \quad \Delta H^0 = -890.4\ \text{kJ/mol}$

$H^+\ (aq) + OH^-\ (aq) \longrightarrow H_2O\ (l) \quad \Delta H^0 = -56.2\ \text{kJ/mol}$

$H_2O\ (s) \longrightarrow H_2O\ (l) \quad \Delta H^0 = 6.01\ \text{kJ/mol}$

$NH_4NO_3\ (s) \xrightarrow{H_2O} NH_4^+(aq) + NO_3^-\ (aq) \quad \Delta H^0 = 25\ \text{kJ/mol}$

Entropy (S) is a measure of the **randomness or disorder** of a system.

order $\uparrow$ $S \downarrow$ disorder $\uparrow$ $S \uparrow$

As entropy is state function $\Delta S = S_f - S_i$

If the change from initial to final results in an increase in randomness

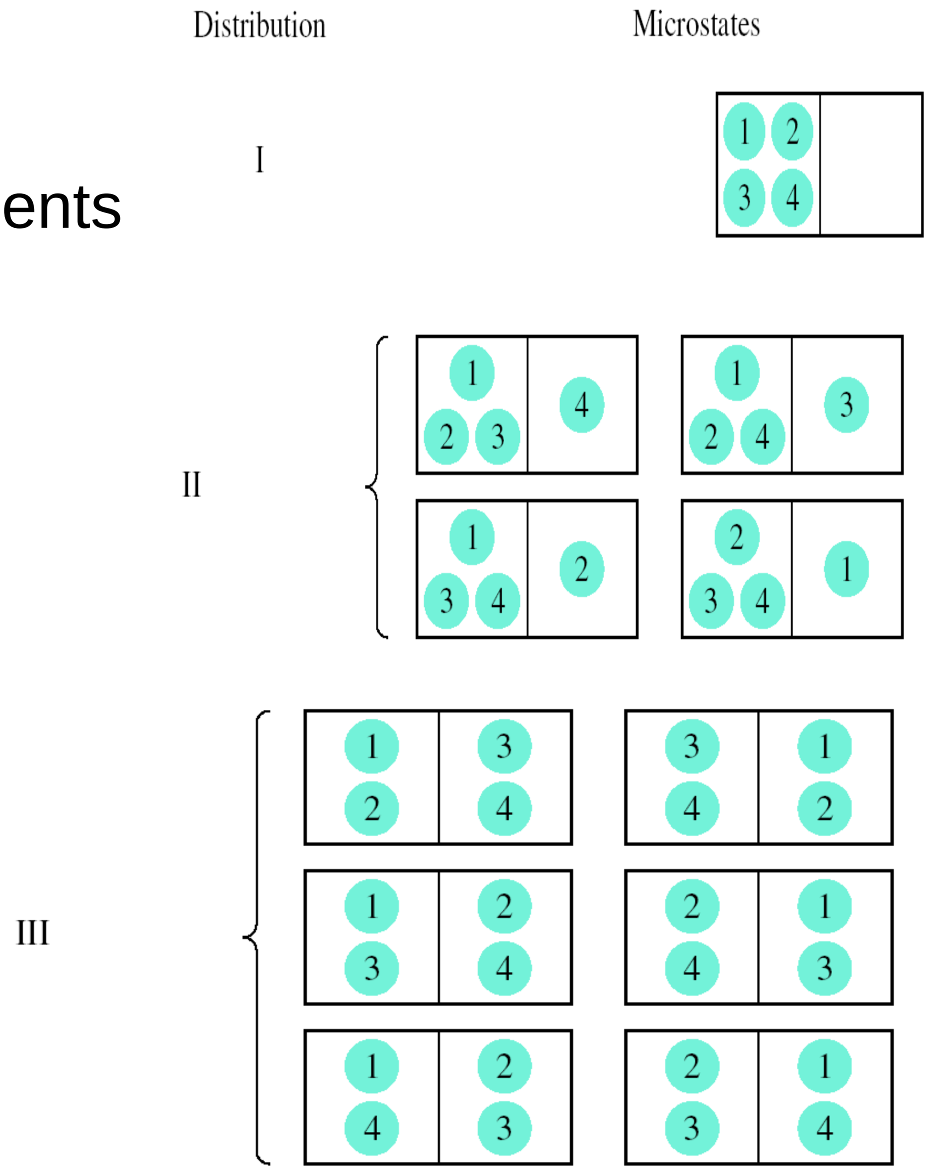
$S_f > S_i$ $\Delta S > 0$

For any substance, the solid state is more ordered than the liquid state and the liquid state is more ordered than gas state.

$$S_{solid} < S_{liquid} \ll S_{gas}$$

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta S > 0$$

Entropy



W = number of microstates
(number of possible arrangements
Of the system)

$$S = k \ln W$$

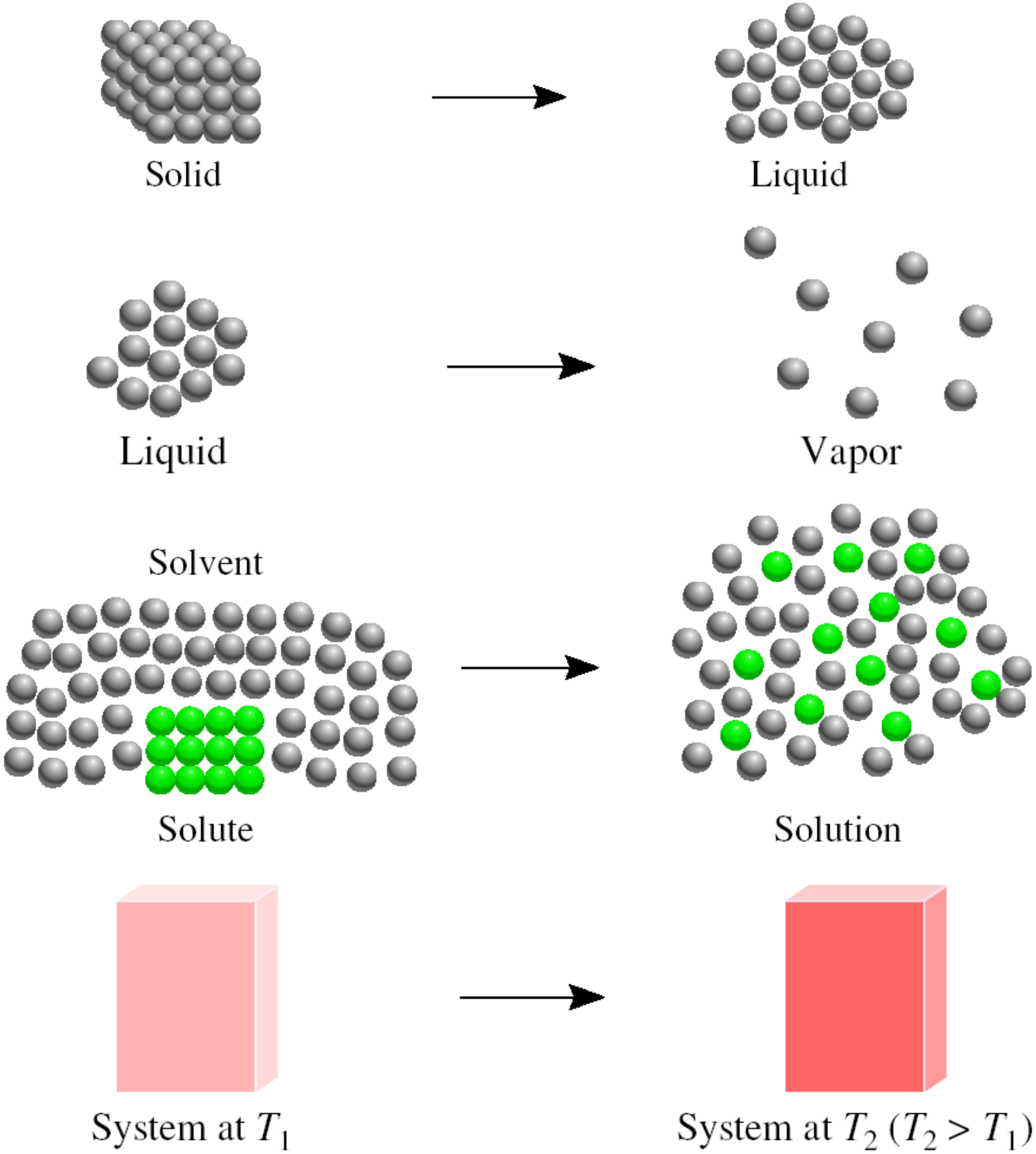
$$\Delta S = S_f - S_i$$

$$\Delta S = k \ln \frac{W_f}{W_i}$$

$W_f > W_i$ then $\Delta S > 0$

$W_f < W_i$ then $\Delta S < 0$

Processes that lead to an increase in entropy ($\Delta S > 0$)



Example: $Br_2(l) \longrightarrow Br_2(g)$

Example: $I_2(s) \longrightarrow I_2(g)$

$\Delta S > 0$

$\Delta S > 0$

Entropy Changes in the System (ΔS_{sys})

When gases are produced (or consumed)

- If a reaction produces more gas molecules than it consumes, $\Delta S^0 > 0$.
- If the total number of gas molecules decrease, $\Delta S^0 < 0$.
- If there is no net change in the total number of gas molecules, then ΔS^0 may be positive or negative BUT ΔS^0 will be a small number.

Example 18.1

Predict whether the entropy change is greater or less than zero for each of the following processes:

(a) freezing ethanol

(b) evaporating a beaker of liquid bromine at room temperature

(c) dissolving glucose in water

(d) cooling nitrogen gas from 80°C to 20°C

Example 18.1

Strategy

To determine the entropy change in each case, we examine whether the number of microstates of the system increases or decreases. The sign of ΔS will be positive if there is an increase in the number of microstates and negative if the number of microstates decreases.

Solution

(a) Upon freezing, the ethanol molecules are held rigid in position. This phase transition reduces the number of microstates and therefore the entropy decreases; that is, $\Delta S < 0$.

Example 18.1

(b) Evaporating bromine increases the number of microstates because the Br_2 molecules can occupy many more positions in nearly empty space. Therefore, $\Delta S > 0$.

(c) Glucose is a nonelectrolyte. The solution process leads to a greater dispersal of matter due to the mixing of glucose and water molecules so we expect $\Delta S > 0$.

(d) The cooling process decreases various molecular motions. This leads to a decrease in microstates and so $\Delta S < 0$.

First Law of Thermodynamics

Energy can be converted from one form to another but energy cannot be created or destroyed.

Second Law of Thermodynamics

The entropy of the **universe** increases in a spontaneous process and remains unchanged in an equilibrium process.

Spontaneous process:
(Irreversible)

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

Equilibrium process:
(Reversible)

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$$

Entropy Changes in the System (ΔS_{sys})

The **standard entropy of reaction** (ΔS^0_{rxn}) is the entropy change for a reaction carried out at 1 atm and 25^{0}C.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta S^0_{rxn} = [\, cS^0(C) + dS^0(D)\,] - [\, aS^0(A) + bS^0(B)\,]$$

$$\Delta S^0_{rxn} = \Sigma nS^0(\text{products}) - \Sigma mS^0(\text{reactants})$$

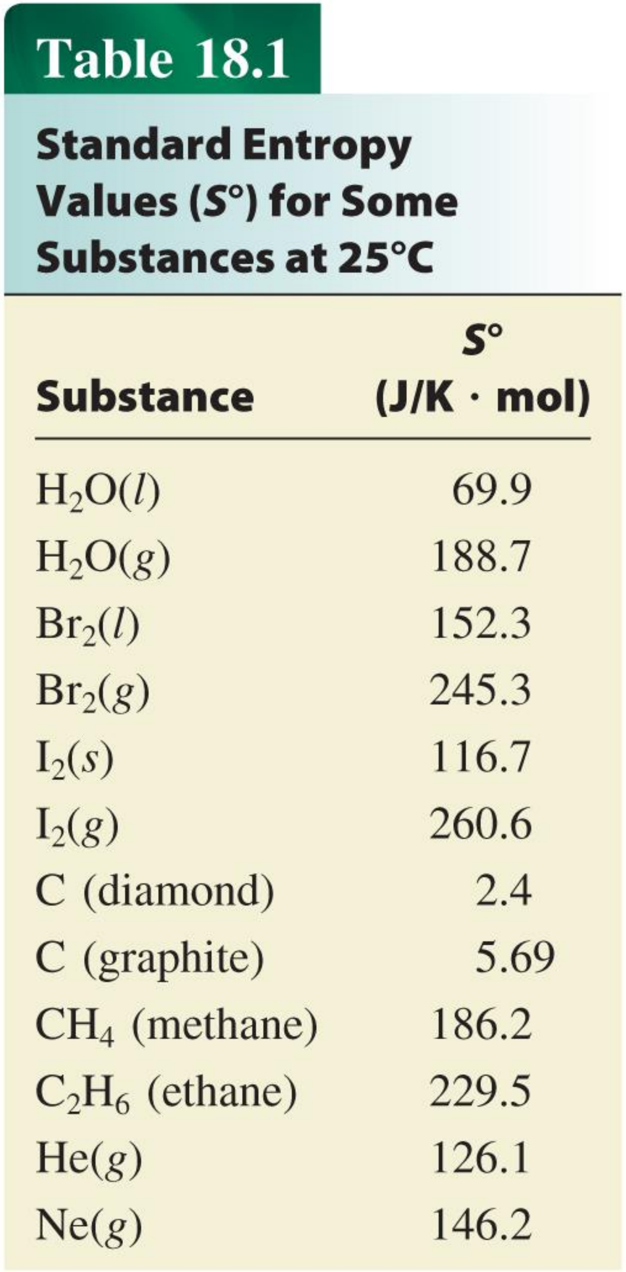


Table 18.1

Standard Entropy Values ($S°$) for Some Substances at 25°C

Substance	$S°$ (J/K · mol)
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.6
C (diamond)	2.4
C (graphite)	5.69
CH_4 (methane)	186.2
C_2H_6 (ethane)	229.5
He(g)	126.1
Ne(g)	146.2

Example 18.2

From the standard entropy values in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C.

(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

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

(c) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

Example 18.2

Strategy

To calculate the standard entropy of a reaction, we look up the standard entropies of reactants and products in Appendix 2 and apply Equation (18.7). As in the calculation of enthalpy of reaction [see Equation (6.18)], the stoichiometric coefficients have no units, so $\Delta S^\circ_{\mathrm{rxn}}$ is expressed in units of J/K·mol.

Example 18.2

Solution

(a) $\Delta S^\circ_{rxn} = [S^\circ(CaO) + S^\circ(CO_2)] - [S^\circ(CaCO_3)]$

$= [(39.8\ J/K\cdot mol) + (213.6\ J/K\cdot mol)] - (92.9\ /K\cdot mol)$

$=$ **160.5 J/K·mol**

Thus, when 1 mole of $CaCO_3$ decomposes to form 1 mole of CaO and 1 mole of gaseous CO_2, there is an increase in entropy equal to 160.5 J/K·mol.

Example 18.2

(b) $\Delta S°_{\text{rxn}} = [2S°(\text{NH}_3)] - [S°(\text{N}_2) + 3S°(\text{H}_2)]$

$= (2)(193\ \text{J/K}\cdot\text{mol}) - [(192\ \text{J/K}\cdot\text{mol}) + (3)(131\ \text{J/K}\cdot\text{mol})]$

$= \mathbf{-199\ J/K\cdot mol}$

This result shows that when 1 mole of gaseous nitrogen reacts with 3 moles of gaseous hydrogen to form 2 moles of gaseous ammonia, there is a decrease in entropy equal to -199 J/K·mol.

Example 18.2

(c) $\Delta S^\circ_{\text{rxn}} = [2S^\circ(\text{HCl})] - [S^\circ(\text{H}_2) + S^\circ(\text{Cl}_2)]$

$= (2)(187\ \text{J/K}\cdot\text{mol}) - [(131\ \text{J/K}\cdot\text{mol}) + (223\ \text{J/K}\cdot\text{mol})]$

$= \mathbf{20\ J/K\cdot mol}$

Thus, the formation of 2 moles of gaseous HCl from 1 mole of gaseous H_2 and 1 mole of gaseous Cl_2 results in a small increase in entropy equal to 20 J/K·mol.

Comment The $\Delta S^\circ_{\text{rxn}}$ values all apply to the system.

Example 18.3

Predict whether the entropy change of the system in each of the following reactions is positive or negative.

(a) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

(b) $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$

(c) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

Example 18.3

Strategy

We are asked to predict, not calculate, the sign of entropy change in the reactions. The factors that lead to an increase in entropy are: (1) a transition from a condensed phase to the vapor phase and (2) a reaction that produces more product molecules than reactant molecules in the same phase. It is also important to compare the relative complexity of the product and reactant molecules. In general, the more complex the molecular structure, the greater the entropy of the compound.

Example 18.3

Solution

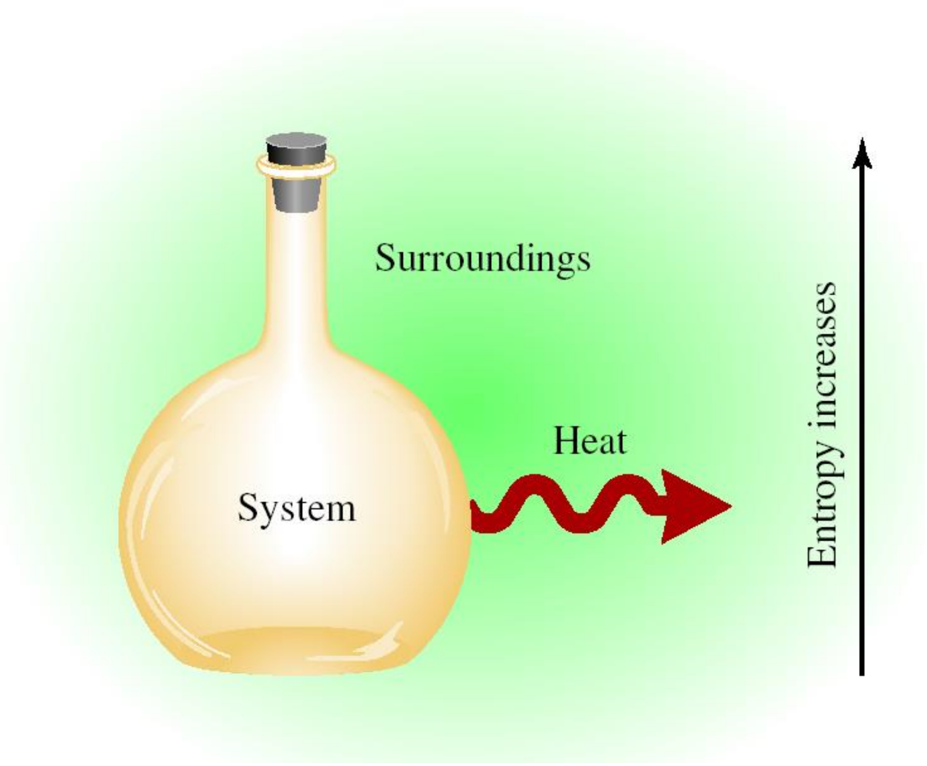
(a) Two reactant molecules combine to form one product molecule. Even though H_2O is a more complex molecule than either H_2 and O_2, the fact that there is a net decrease of one molecule and gases are converted to liquid ensures that the number of microstates will be diminished and hence $\Delta S°$ is negative.

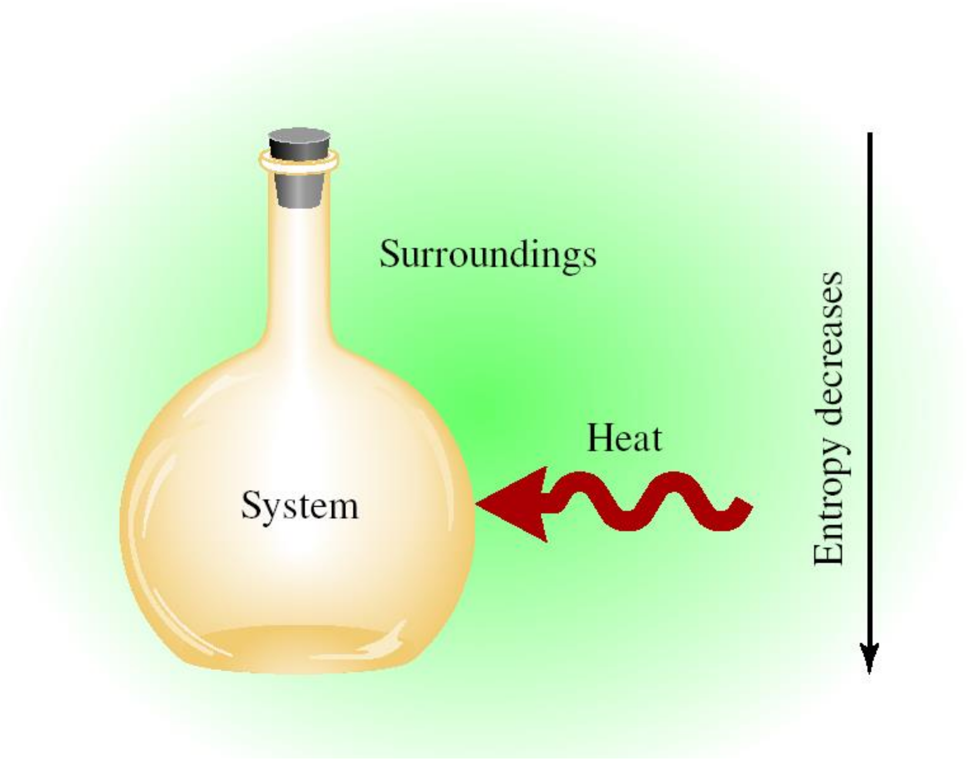
(b) A solid is converted to two gaseous products. Therefore, $\Delta S°$ is positive.

Example 18.3

(c) The same number of molecules is involved in the reactants as in the product. Furthermore, all molecules are diatomic and therefore of similar complexity. As a result, we cannot predict the sign of $\Delta S°$, but we know that the change must be quite small in magnitude.

Entropy Changes in the Surroundings (ΔS_{surr})





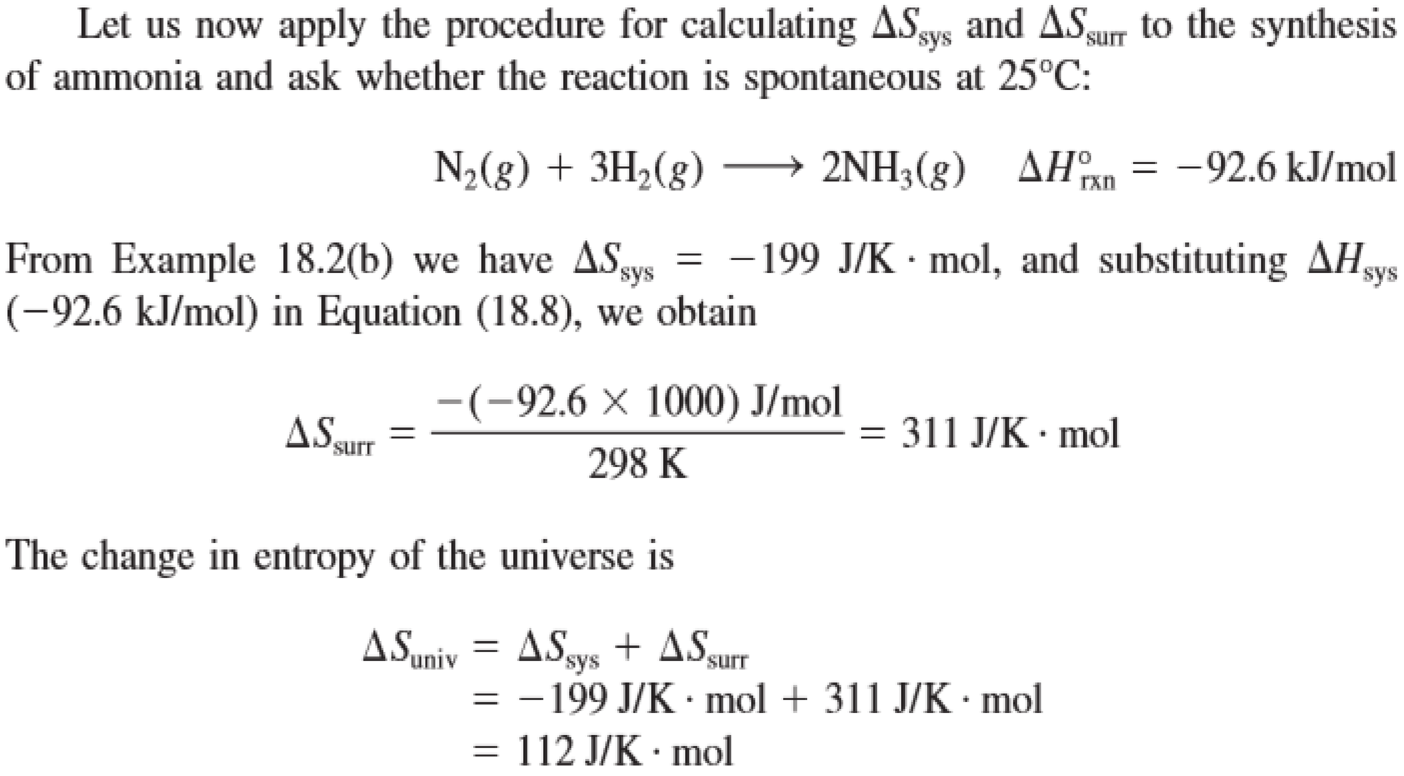
Exothermic Process
$\Delta S_{surr} > 0$

Endothermic Process
$\Delta S_{surr} < 0$

$$\Delta S_{\text{surr}} \propto -\Delta H_{\text{sys}}$$

The minus sign is used because if the process is exothermic, ΔH_{sys} is negative and ΔS_{surr} is a positive quantity, indicating an increase in entropy. On the other hand, for an endothermic process, ΔH_{sys} is positive and the negative sign ensures that the entropy of the surroundings decreases.

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$



Let us now apply the procedure for calculating ΔS_{sys} and ΔS_{surr} to the synthesis of ammonia and ask whether the reaction is spontaneous at 25°C:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \quad \Delta H^\circ_{\text{rxn}} = -92.6\ \text{kJ/mol}$$

From Example 18.2(b) we have $\Delta S_{\text{sys}} = -199\ \text{J/K}\cdot\text{mol}$, and substituting ΔH_{sys} (-92.6 kJ/mol) in Equation (18.8), we obtain

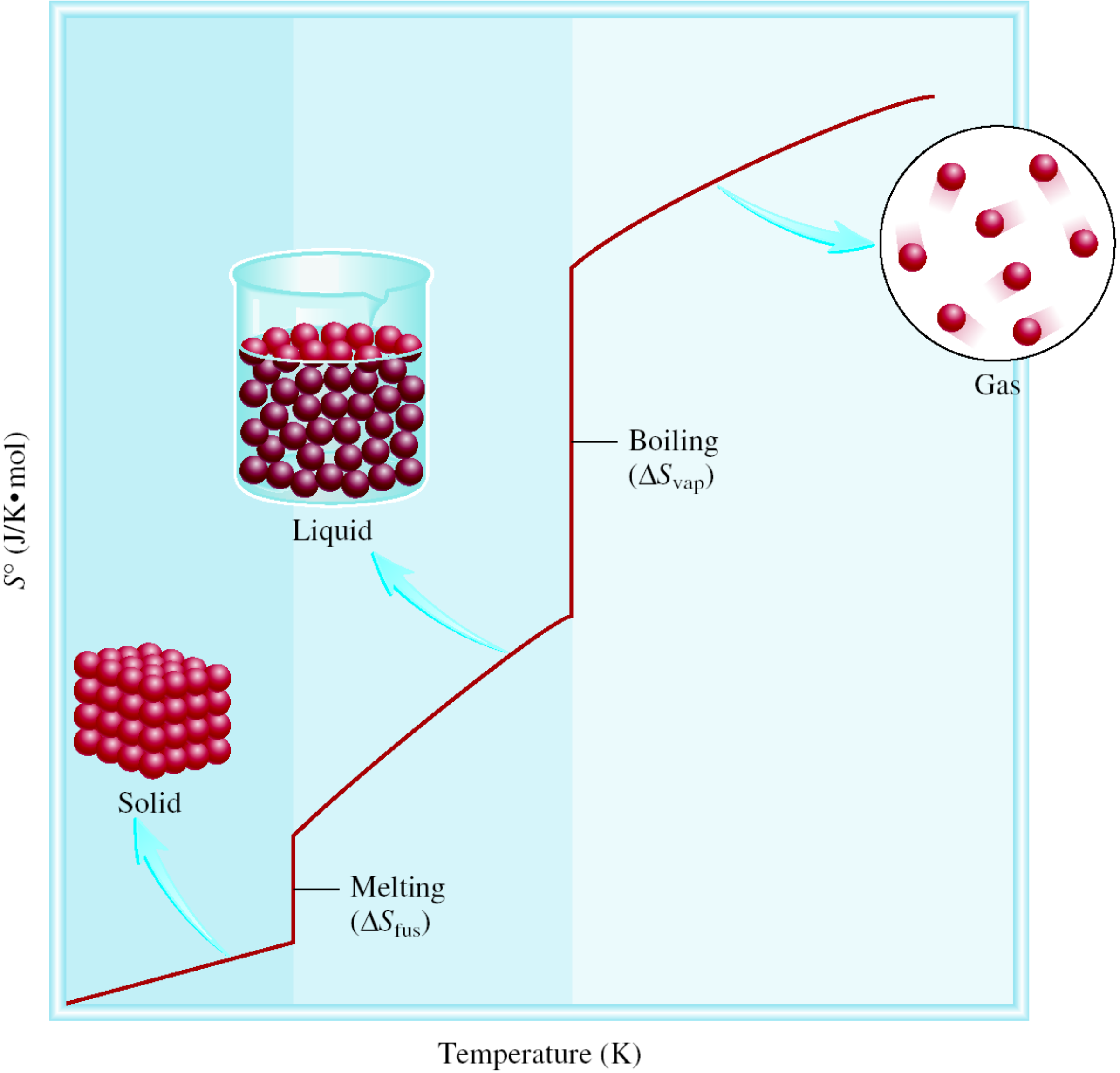
$$\Delta S_{\text{surr}} = \frac{-(-92.6 \times 1000)\ \text{J/mol}}{298\ \text{K}} = 311\ \text{J/K}\cdot\text{mol}$$

The change in entropy of the universe is

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}}\\ &= -199\ \text{J/K}\cdot\text{mol} + 311\ \text{J/K}\cdot\text{mol}\\ &= 112\ \text{J/K}\cdot\text{mol}\end{aligned}$$

Third Law of Thermodynamics

The entropy of a perfect crystalline substance is zero at the absolute zero of temperature (0 kelvin= -273 °C).



$S = k \ln W$

$W = 1$

$S = 0$

Gibbs Free Energy

Spontaneous process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

Equilibrium process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

For a constant temperature and constant pressure process:

Gibbs free energy (G)

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

$\Delta G < 0$ The reaction is spontaneous in the forward direction.

$\Delta G > 0$ The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$\Delta G = 0$ The reaction is at equilibrium.

The ***standard free-energy of reaction (ΔG^0_{rxn})*** is the free-energy change for a reaction when it occurs under standard-state conditions.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G^0_{rxn} = [c\Delta G^0_f(C) + d\Delta G^0_f(D)] - [a\Delta G^0_f(A) + b\Delta G^0_f(B)]$$

$$\Delta G^0_{rxn} = \Sigma n\Delta G^0_f(\text{products}) - \Sigma m\Delta G^0_f(\text{reactants})$$

Standard free energy of formation (ΔG^0_f) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

ΔG^0_f of any element in its stable form is zero.

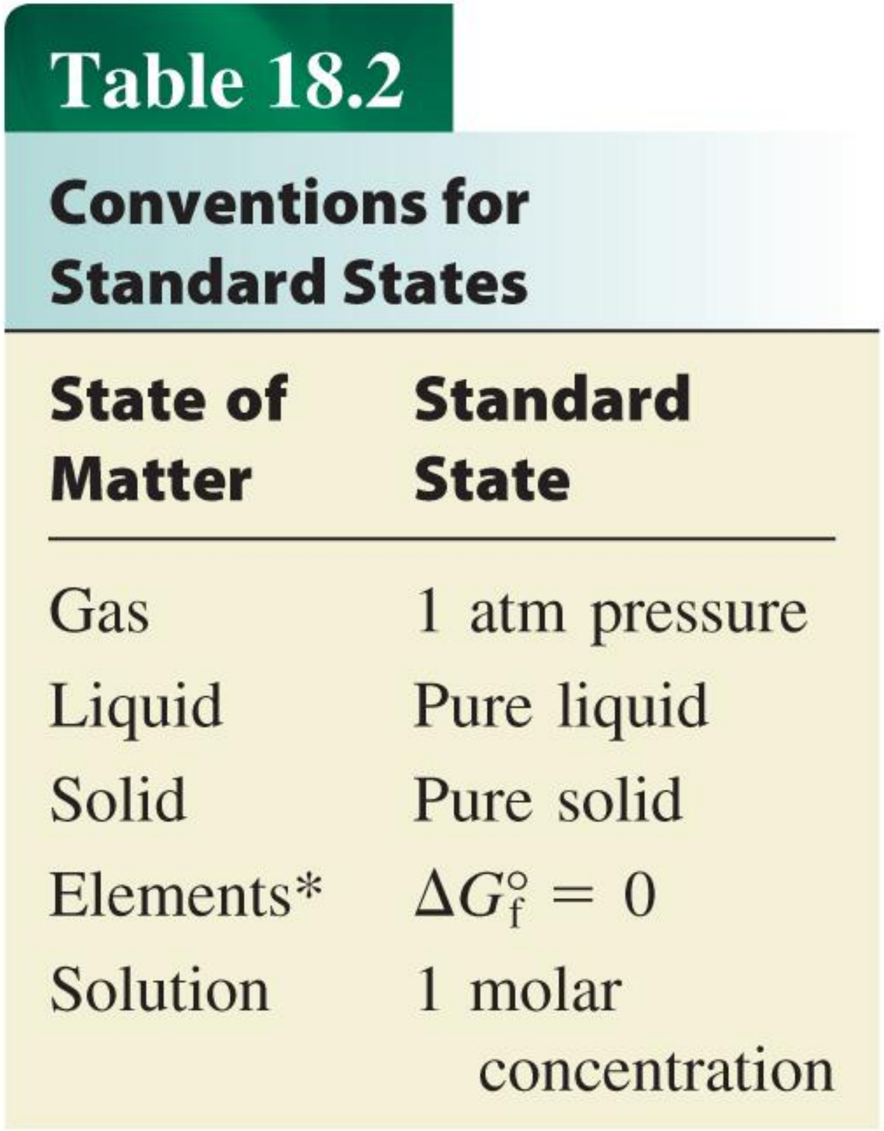


Table 18.2

Conventions for Standard States

State of Matter	Standard State
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure solid
Elements*	$\Delta G_f^\circ = 0$
Solution	1 molar concentration

Example 18.4

Calculate the standard free-energy changes for the following reactions at 25°C.

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

(b) $2MgO(s) \longrightarrow 2Mg(s) + O_2(g)$

Example 18.4

Strategy

To calculate the standard free-energy change of a reaction, we look up the standard free energies of formation of reactants and products in Appendix 2 and apply Equation (18.12). Note that all the stoichiometric coefficients have no units so $\Delta G°_{\text{rxn}}$ is expressed in units of kJ/mol, and $\Delta G°_{\text{f}}$ for O_2 is zero because it is the stable allotropic element at 1 atm and 25°C.

Example 18.4

Solution

(a)According to Equation (18.12), we write

$$\Delta G^\circ_{\mathrm{rxn}} = [\Delta G^\circ_{\mathrm{f}}\,(\mathrm{CO_2}) + 2\Delta G^\circ_{\mathrm{f}}\,(\mathrm{H_2O})] - [\Delta G^\circ_{\mathrm{f}}\,(\mathrm{CH_4}) + 2\Delta G^\circ_{\mathrm{f}}\,(\mathrm{O_2})]$$

We insert the appropriate values from Appendix 2:

$$\Delta G^\circ_{\mathrm{rxn}} = [(-394.4\ \mathrm{kJ/mol}) + (2)(-237.2\ \mathrm{kJ/mol})] - [(-50.8\ \mathrm{kJ/mol}) + (2)\,(0\ \mathrm{kJ/mol})]$$

$$= \mathbf{-818.0\ kJ/mol}$$

Example 18.4

(b) The equation is

$$\Delta G^\circ_{\text{rxn}} = [2\Delta G^\circ_{\text{f}}\ (\text{Mg}) + \Delta G^\circ_{\text{f}}\ (\text{O}_2)] - [2\Delta G^\circ_{\text{f}}\ (\text{MgO})]$$

From data in Appendix 2 we write

$$\Delta G^\circ_{\text{rxn}} = [(2)(0\ \text{kJ/mol}) + (0\ \text{kJ/mol})] - [(2)(-569.6\ \text{kJ/mol})]$$

$$= \mathbf{1139\ kJ/mol}$$

$\Delta G = \Delta H - T\Delta S$

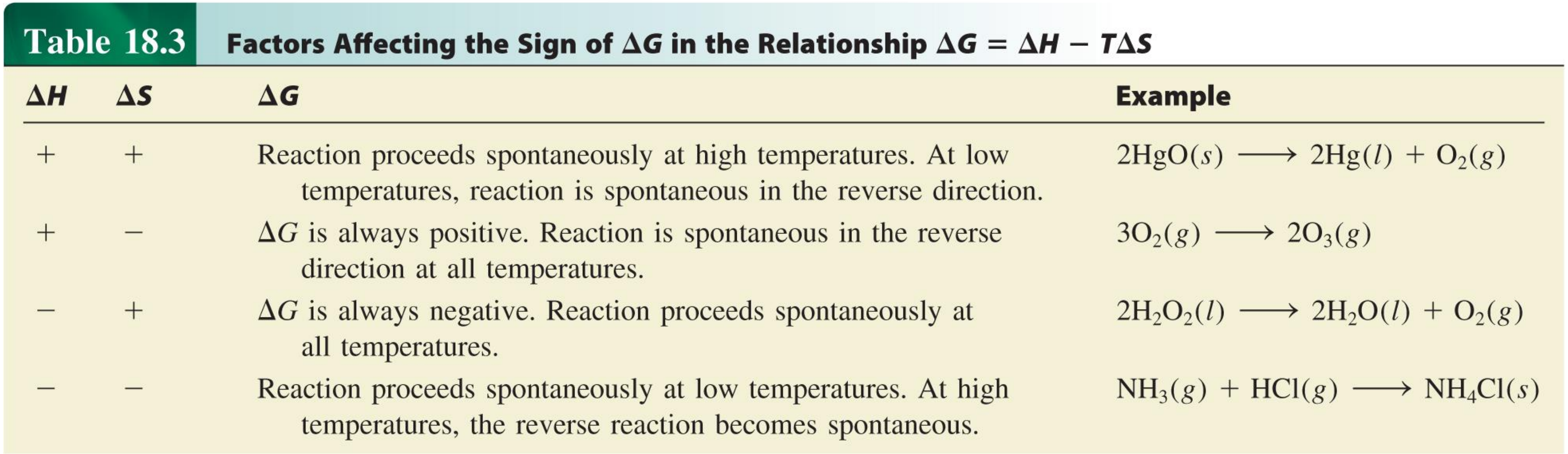


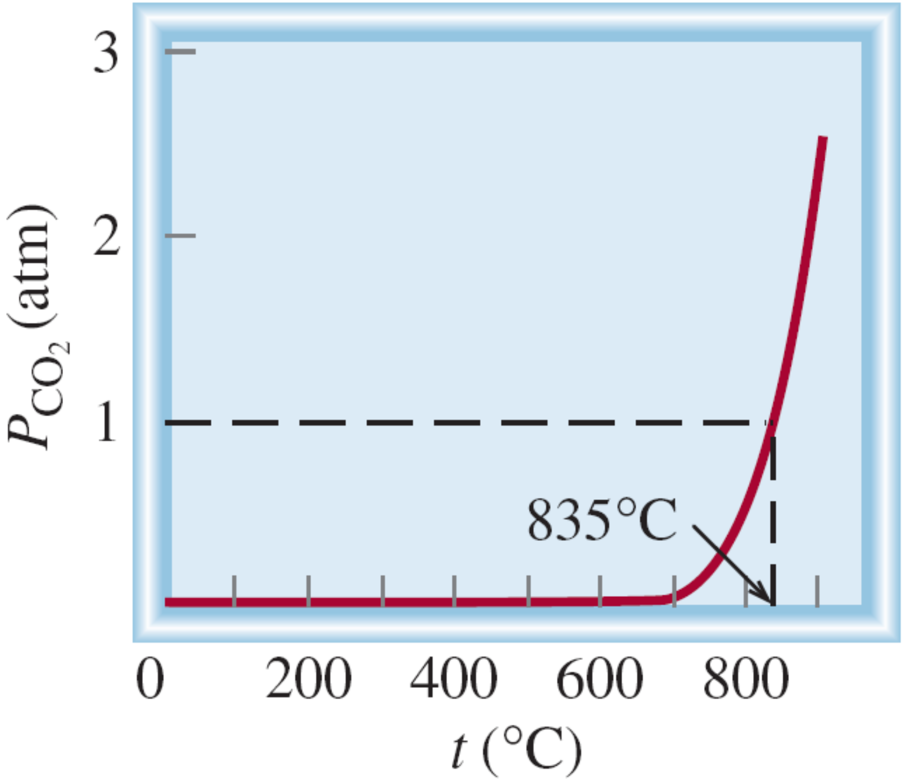
Table 18.3 **Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$**

ΔH	ΔS	ΔG	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$
+	−	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3O_2(g) \longrightarrow 2O_3(g)$
−	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

Temperature and Spontaneity of Chemical Reactions

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

Equilibrium Pressure of CO_2



$\Delta H^0 = 177.8$ kJ/mol

$\Delta S^0 = 160.5$ J/K·mol

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

At 25 °C, $\Delta G^0 = 130.0$ kJ/mol

$\Delta G^0 = 0$ at 835 °C

Gibbs Free Energy and Phase Transitions

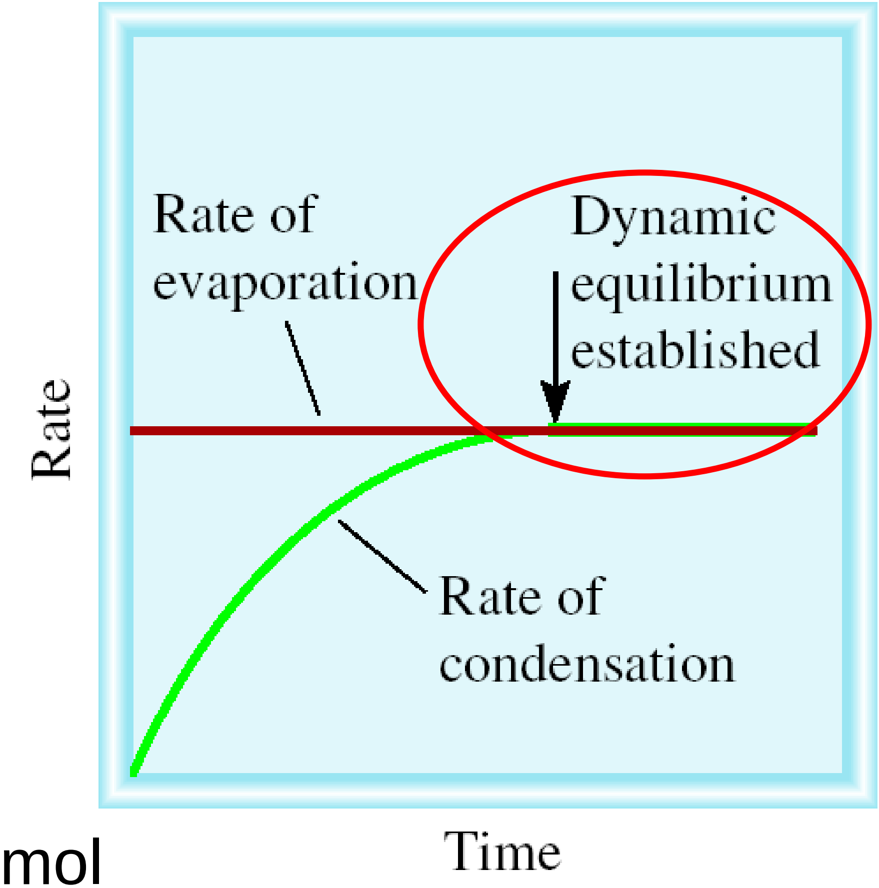
$\Delta G^0 = 0 = \Delta H^0 - T\Delta S^0$

$H_2O\ (l) \rightleftharpoons H_2O\ (g)$

$$\Delta S = \frac{\Delta H}{T} = \frac{40.79\ \text{kJ/mol}}{373\ \text{K}}$$

$= 1.09 \times 10^{-1}$ kJ/K·mol

$= 109$ J/K·mol



Example 18.5

The molar heats of fusion and vaporization of benzene are 10.9 kJ/mol and 31.0 kJ/mol, respectively. Calculate the entropy changes for the solid → liquid and liquid → vapor transitions for benzene. At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.

Example 18.5

Strategy

At the melting point, liquid and solid benzene are at equilibrium, so $\Delta G = 0$. From Equation (18.10) we have $\Delta G = 0 =$

$\Delta H - T\,\Delta S$ or $\Delta S = \Delta H/T$. To calculate the entropy change for the solid benzene → liquid benzene transition, we write

$\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_{\text{f}}$. Here ΔH_{fus} is positive for an endothermic process, so ΔS_{fus} is also positive, as expected for a solid to liquid transition. The same procedure applies to the liquid

benzene → vapor benzene transition. What temperature unit should be used?

Example 18.5

Solution

The entropy change for melting 1 mole of benzene at 5.5°C is

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{f}}}$$

$$= \frac{(10.9 \text{ kJ/mol})(1000 \text{ J/1 kJ})}{(5.5 + 273)\text{K}}$$

$$= \mathbf{39.1\ J / K \cdot mol}$$

Example 18.5

Similarly, the entropy change for boiling 1 mole of benzene at 80.1°C is

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}}$$

$$= \frac{(31.0\ \text{kJ/mol})(1000\ \text{J/1 kJ})}{(80.1 + 273)\text{K}}$$

$$= \mathbf{87.8\ J / K \cdot mol}$$

Check Because vaporization creates more microstates than the melting process, $\Delta S_{\text{vap}} > \Delta S_{\text{fus}}$.

Gibbs Free Energy and Chemical Equilibrium

$$\Delta G = \Delta G^0 + RT \ln Q$$

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature (K)

Q is the reaction quotient

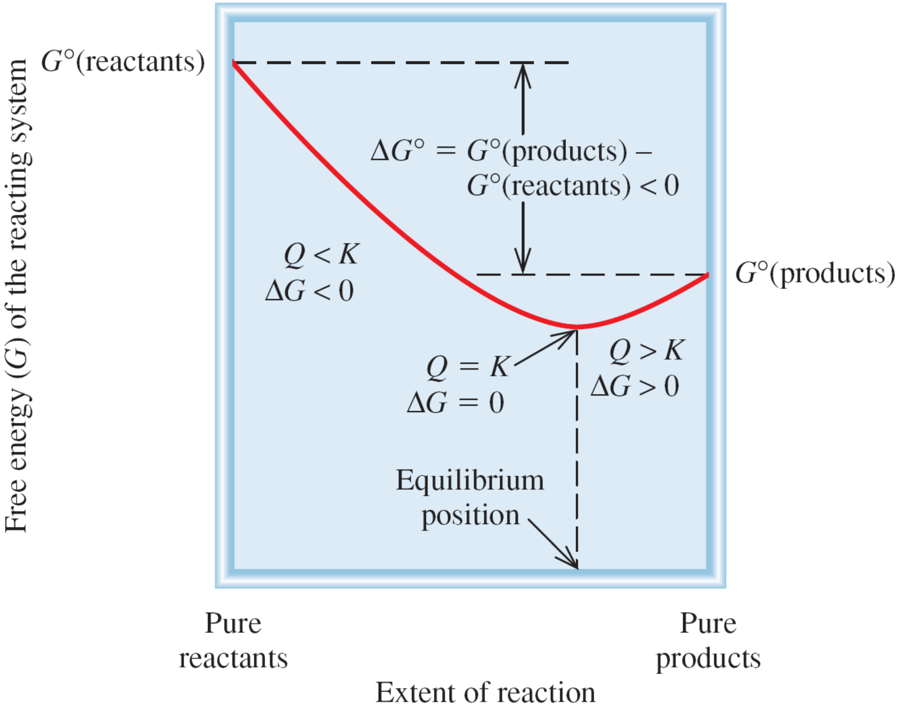
<u>At Equilibrium</u>

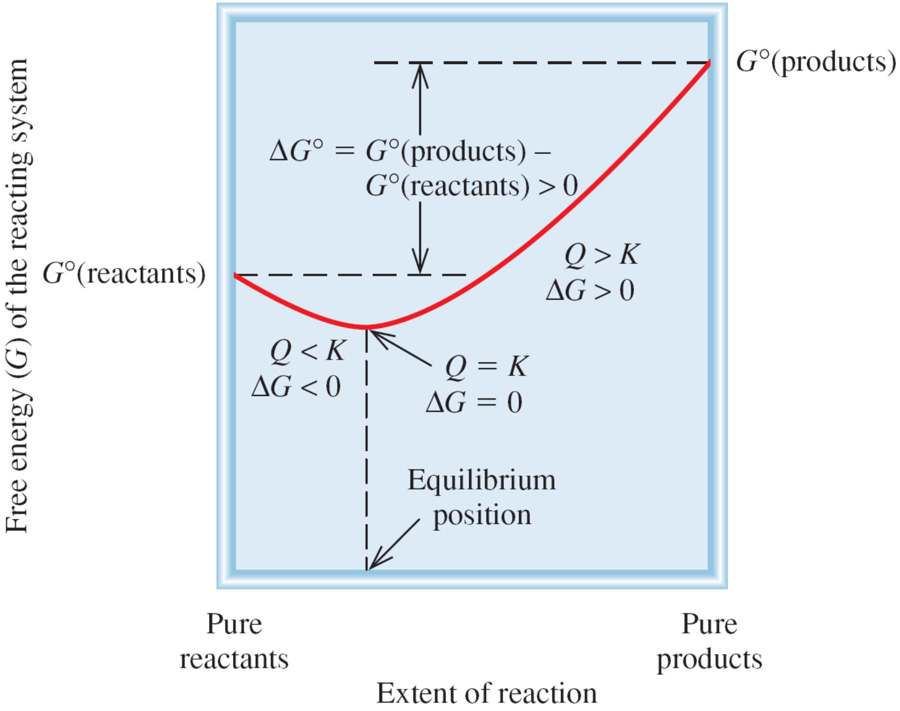
$$\Delta G = 0 \qquad Q = K$$

$$0 = \Delta G^0 + RT \ln K$$

$$\Delta G^0 = - RT \ln K$$

Free Energy Versus Extent of Reaction





$\Delta G^0 < 0$

$\Delta G^0 > 0$

$$\Delta G^0 = - RT \ln K$$

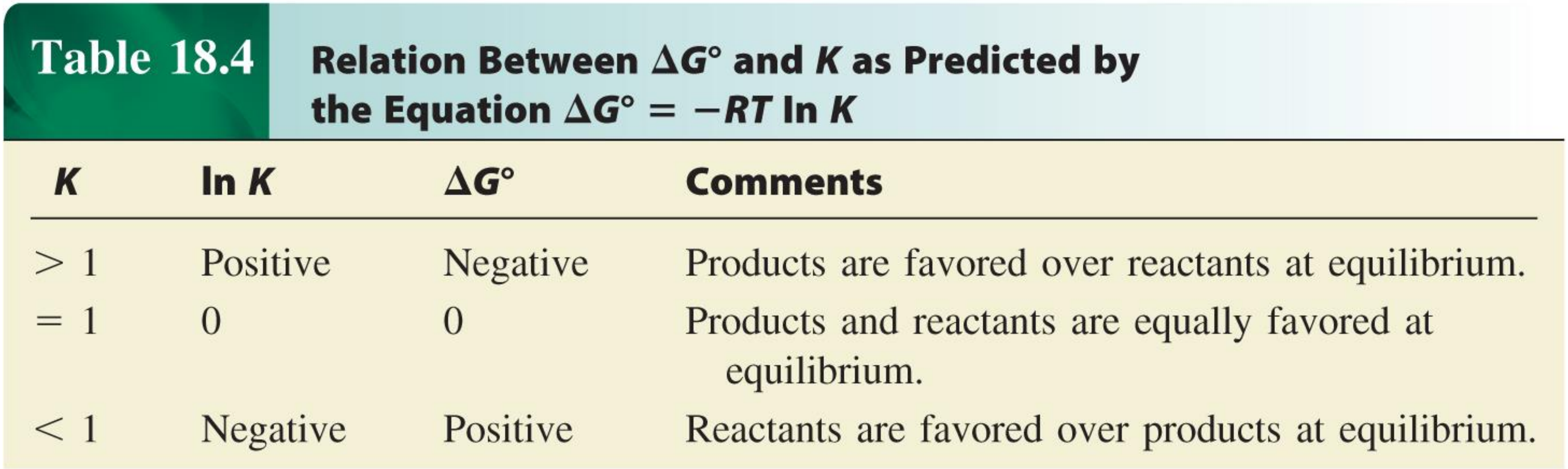


Table 18.4 Relation Between $\Delta G°$ and K as Predicted by the Equation $\Delta G° = -RT \ln K$

K	$\ln K$	$\Delta G°$	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

Example 18.6

Using data listed in Appendix 2, calculate the equilibrium constant (K_P) for the following reaction at 25°C:

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

Example 18.6

Strategy

According to Equation (18.14), the equilibrium constant for the reaction is related to the standard free-energy change; that is, $\Delta G° = -RT \ln K$. Therefore, we first need to calculate $\Delta G°$ by following the procedure in Example 18.4. Then we can calculate K_P. What temperature unit should be used?

Example 18.6

Solution According to Equation (18.12),

$$\Delta G^\circ_{\mathrm{rxn}} = [2\Delta G^\circ_{\mathrm{f}}(\mathrm{H_2}) + \Delta G^\circ_{\mathrm{f}}(\mathrm{O_2})] - [2\Delta G^\circ_{\mathrm{f}}(\mathrm{H_2O})]$$

$$= [(2)(0\ \mathrm{kJ/mol}) + (0\ \mathrm{kJ/mol})] - [(2)(-237.2\ \mathrm{kJ/mol})]$$

$$= \mathbf{474.4\ kJ/mol}$$

Using Equation (18.14)

$$\Delta G^{\mathrm{o}}_{\mathrm{rxn}} = -RT\ln K_{\mathrm{p}}$$

$$474.4\ \mathrm{kJ/mol} \times \frac{1000\ \mathrm{J}}{1\ \mathrm{kJ}} = -(8.314\mathrm{J/K}\cdot\mathrm{mol})(298\ \mathrm{K})\ln K_{\mathrm{p}}$$

$$\ln K_{\mathrm{p}} = -191.5$$

$$K_{\mathrm{p}} = e^{-191.5} = \mathbf{7\times10^{-84}}$$

Example 18.6

Comment

This extremely small equilibrium constant is consistent with the fact that water does not spontaneously decompose into hydrogen and oxygen gases at 25°C. Thus, a large positive $\Delta G°$ favors reactants over products at equilibrium.

Example 18.7

In Chapter 17 we discussed the solubility product of slightly soluble substances. Using the solubility product of silver chloride at 25°C (1.6×10^{-10}), calculate $\Delta G°$ for the process

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

Example 18.7

Strategy

According to Equation (18.14), the equilibrium constant for the reaction is related to standard free-energy change; that is,

$\Delta G° = -RT \ln K$. Because this is a heterogeneous equilibrium, the solubility product (K_{sp}) is the equilibrium constant. We calculate the standard free-energy change from the K_{sp} value of AgCl. What temperature unit should be used?

Example 18.7

Solution The solubility equilibrium for AgCl is

$$\mathrm{AgCl}(s) \rightleftarrows \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

$$K_{\mathrm{sp}} = [\mathrm{Ag}^+][\mathrm{Cl}^-] = 1.6 \times 10^{-10}$$

Using Equation (18.14) we obtain

$$\begin{aligned}\Delta G° &= -(8.314\ \mathrm{J/K{\cdot}mol})\ (298\ \mathrm{K})\ \ln\ (1.6 \times 10^{-10}) \\ &= 5.6 \times 10^{4}\ \mathrm{J/mol} \\ &= \mathbf{56\ kJ/mol}\end{aligned}$$

Check The large, positive Δ*G*° indicates that AgCl is slightly soluble and that the equilibrium lies mostly to the left.

Example 18.8

The equilibrium constant (K_P) for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

is 0.113 at 298 K, which corresponds to a standard free-energy change of 5.40 kJ/mol. In a certain experiment, the initial pressures are $P_{NO_2} = 0.122$ atm and $P_{N_2O_4} = 0.453$ atm. Calculate ΔG for the reaction at these pressures and predict the direction of the net reaction toward equilibrium.

Example 18.8

Strategy

From the information given we see that neither the reactant nor the product is at its standard state of 1 atm. To determine the direction of the net reaction, we need to calculate the free-energy change under nonstandard-state conditions (ΔG) using Equation (18.13) and the given $\Delta G°$ value. Note that the partial pressures are expressed as dimensionless quantities in the reaction quotient Q_P because they are divided by the standard-state value of 1 atm (see Table 18.2).

Example 18.8

Solution Equation (18.13) can be written as

$$\Delta G = \Delta G^{o} + RT \ln Q_{p}$$

$$= \Delta G^{o} + RT \ln \frac{P_{NO_2}^{2}}{P_{N_2O_4}}$$

$$= 5.40 \times 10^{3}\ \text{J/mol} + (8.314\text{J/K} \cdot \text{mol})(298\ \text{K}) \times \ln \frac{(0.122)^{2}}{0.453}$$

$$= 5.40 \times 10^{3}\ \text{J/mol} - 8.46 \times 10^{3}\ \text{J/mol}$$

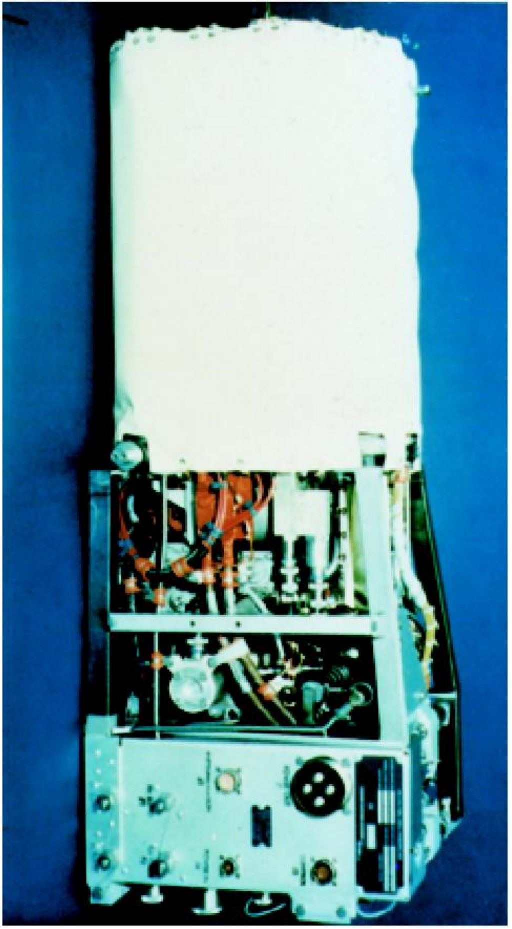
$$= -3.06 \times 10^{3}\text{J/mol} = \mathbf{-3.06 kJ / mol}$$

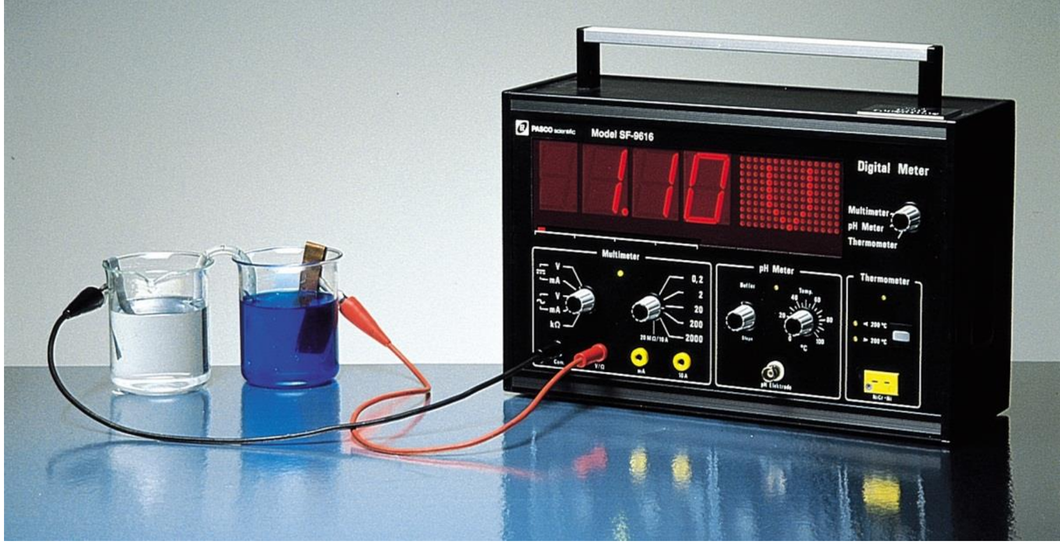
Because Δ*G* < 0, the net reaction proceeds from left to right to reach equilibrium.

Example 18.8

Check

Note that although $\Delta G^\circ > 0$, the reaction can be made to favor product formation initially by having a small concentration (pressure) of the product compared to that of the reactant. Confirm the prediction by showing that $Q_P < K_P$.





Redox Reactions and Electrochemistry

Chapter 19

-***Electrochemistry*** *is the branch of chemistry that deals with the interconversion of electrical energy and chemical energy*

- The conversion between chemical energy and electrical energy is carried out in an ***electrochemical cells***

-***Electrochemical*** processes are oxidation-reduction reactions in which:

- The energy released by a spontaneous reaction is converted to electricity …..Take place in voltaic cell (Galvanic cell)
- Or electrical energy is used to cause a nonspontaneous reaction to occur……Take place in electrolytic cell

Redox reaction $$2\overset{0}{\mathrm{Mg}}\,(s) + \overset{0}{\mathrm{O}_2}\,(g) \longrightarrow 2\overset{2+}{\mathrm{Mg}}\overset{2-}{\mathrm{O}}\,(s)$$

$2Mg \longrightarrow 2Mg^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$O_2 + 4e^- \longrightarrow 2O^{2-}$ ***Reduction*** half-reaction (gain e^-)

-Electrochemistry is the branch of chemistry that deals with the interconversion of electrical energy and chemical energy

-Electrochemical processes are oxidation-reduction reactions (redox reaction) in which:

- the energy released by a spontaneous reaction is converted to electricity or
- Or electrical energy is used to cause a nonspontaneous reaction to occur

$$2\overset{0}{Mg}\,(s) + \overset{0}{O_2}\,(g) \longrightarrow 2\overset{2+}{Mg}\overset{2-}{O}\,(s)$$

$2Mg \longrightarrow 2Mg^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$O_2 + 4e^- \longrightarrow 2O^{2-}$ ***Reduction*** half-reaction (gain e^-)

Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.

$$\text{Na, Be, K, Pb, } H_2\text{, } O_2\text{, } P_4 = 0$$

2. In monatomic ions, the oxidation number is equal to the charge on the ion.

$$Li^+\text{, Li} = +1\text{; } Fe^{3+}\text{, Fe} = +3\text{; } O^{2-}\text{, O} = -2$$

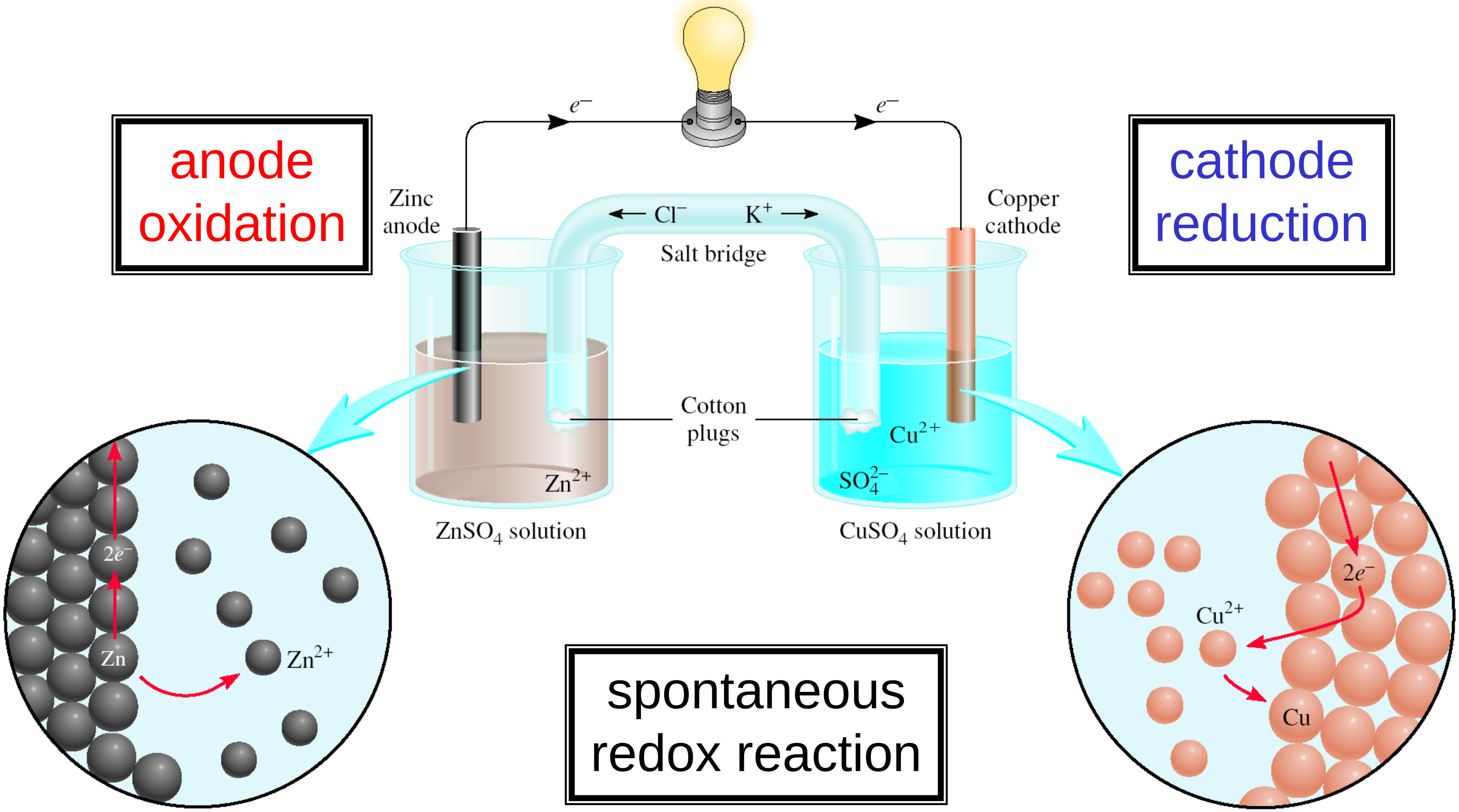
3. The oxidation number of oxygen *is* **usually** –2. In H_2O_2 and O_2^{2-} it is –1.

4. The oxidation number of hydrogen is +1 *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is –1.(ex: NaH, KH…..)

5. Group IA metals are +1, IIA metals are +2 and fluorine is always –1.

6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.

Galvanic Cells



anode
oxidation

cathode
reduction

spontaneous
redox reaction

Zn is oxidized
to Zn^{2+} at anode.

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Net reaction

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

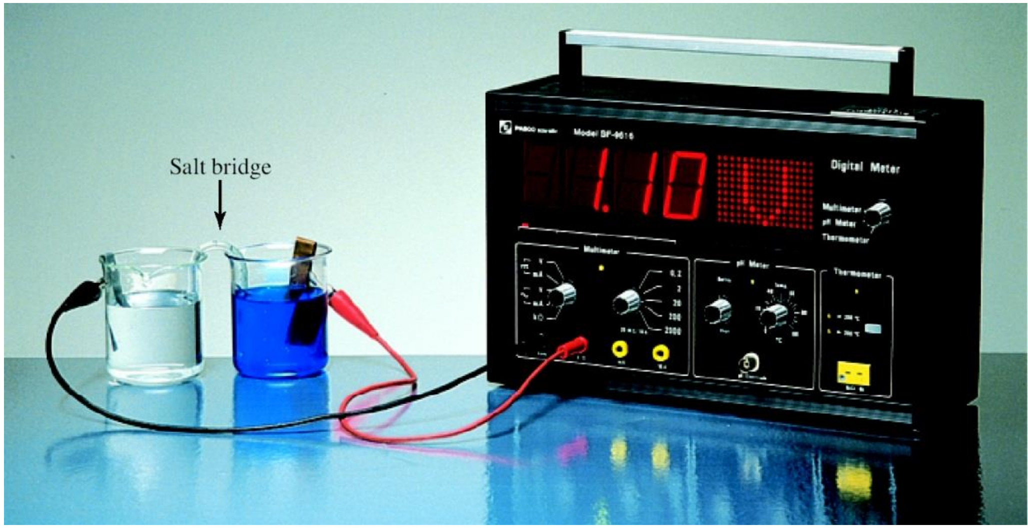
Cu^{2+} is reduced
to Cu at cathode.

$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$

Galvanic Cells

The difference in electrical potential between the anode and cathode is called:

- ***cell voltage***
- ***electromotive force (emf)***
- ***cell potential***



$$\mathrm{Zn}\,(s) + \mathrm{Cu}^{2+}\,(aq) \longrightarrow \mathrm{Cu}\,(s) + \mathrm{Zn}^{2+}\,(aq)$$

$$[\mathrm{Cu}^{2+}] = 1\ M \text{ and } [\mathrm{Zn}^{2+}] = 1\ M$$

Cell Diagram

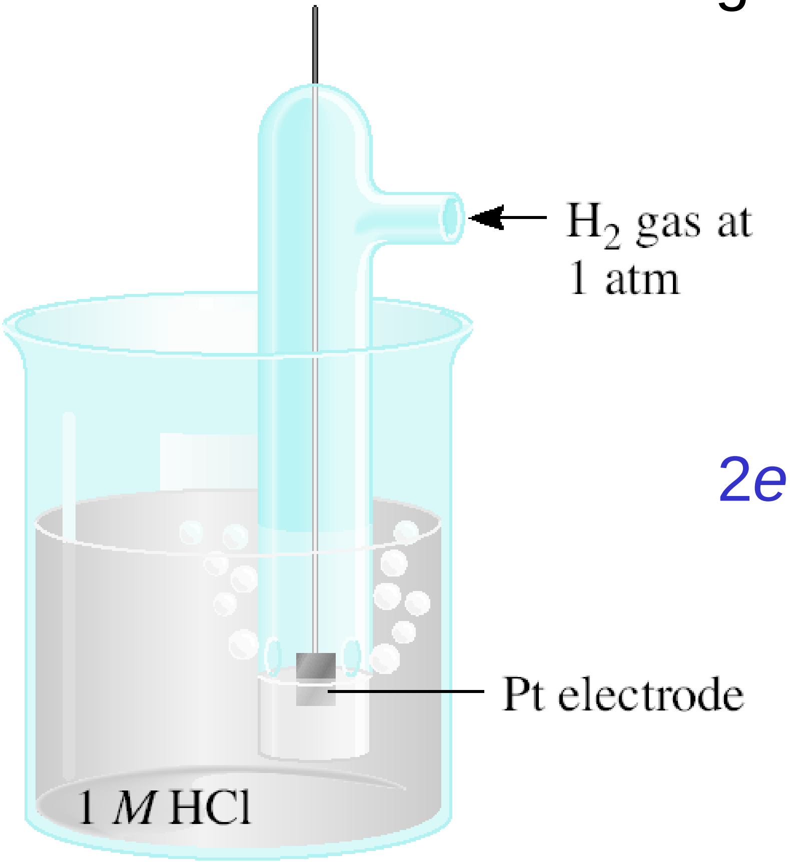
phase boundary

$$\mathrm{Zn}\,(s)\ |\ \mathrm{Zn}^{2+}\,(1\ M)\ ||\ \mathrm{Cu}^{2+}\,(1\ M)\ |\ \mathrm{Cu}\,(s)$$

anode salt bridge cathode

Standard Reduction Potentials

Standard reduction potential (E^0_{red}) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.



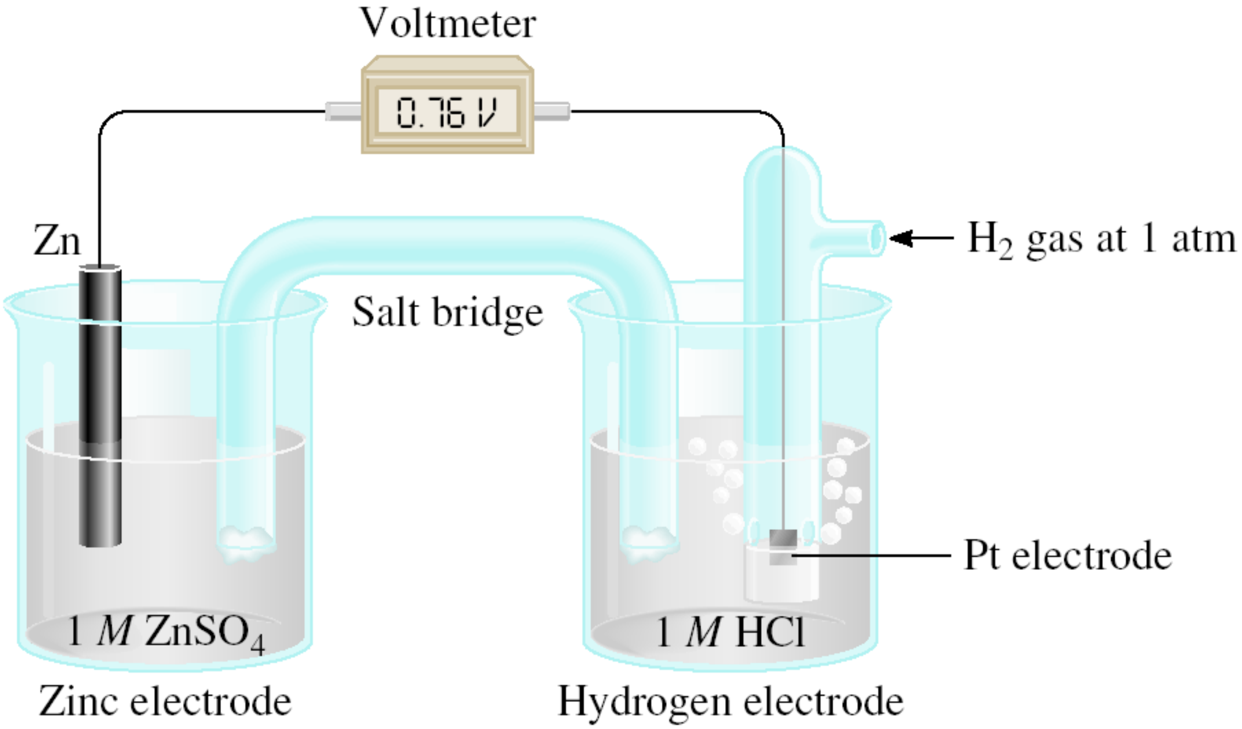
Reduction Reaction

$$2e^- + 2H^+ (1\ M) \longrightarrow H_2\ (1\ atm)$$

$$E^0_{H+/H2} = 0\ V$$

Standard hydrogen electrode (SHE) [Reference electrode]

Standard Reduction Potentials



$$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ H^{+}\ (1\ M)\ |\ H_2\ (1\ atm)\ |\ Pt\ (s)$$

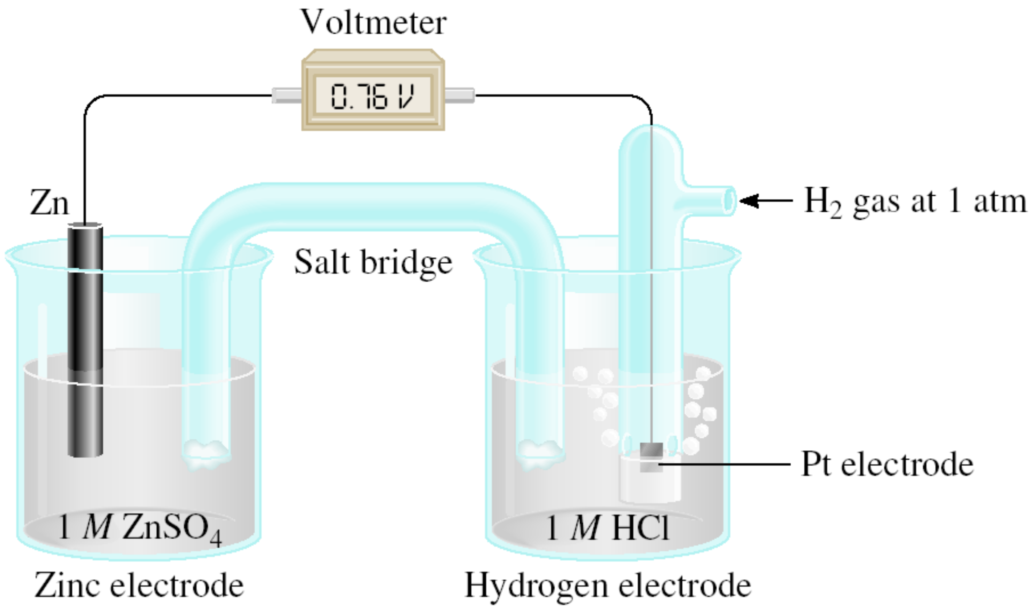
Anode (oxidation): $Zn\ (s) \longrightarrow Zn^{2+}\ (1\ M) + 2e^{-}$

Cathode (reduction): $2e^{-} + 2H^{+}\ (1\ M) \longrightarrow H_2\ (1\ atm)$

$$Zn\ (s) + 2H^{+}\ (1\ M) \longrightarrow Zn^{2+}\ (1\ M) + H_2\ (1\ atm)$$

Standard Reduction Potentials

$$E^0_{\text{cell}} = 0.76\text{ V}$$



Standard emf (E^0_{cell})

$$\boxed{E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}}$$

$$\text{Zn }(s)\mid \text{Zn}^{2+}\text{ (1 }M)\parallel \text{H}^{+}\text{ (1 }M)\mid \text{H}_2\text{ (1 atm)}\mid \text{Pt }(s)$$

$$E^0_{\text{cell}} = E^0_{\text{H}^+/\text{H}_2} - E^0_{\text{Zn}^{2+}/\text{Zn}}$$

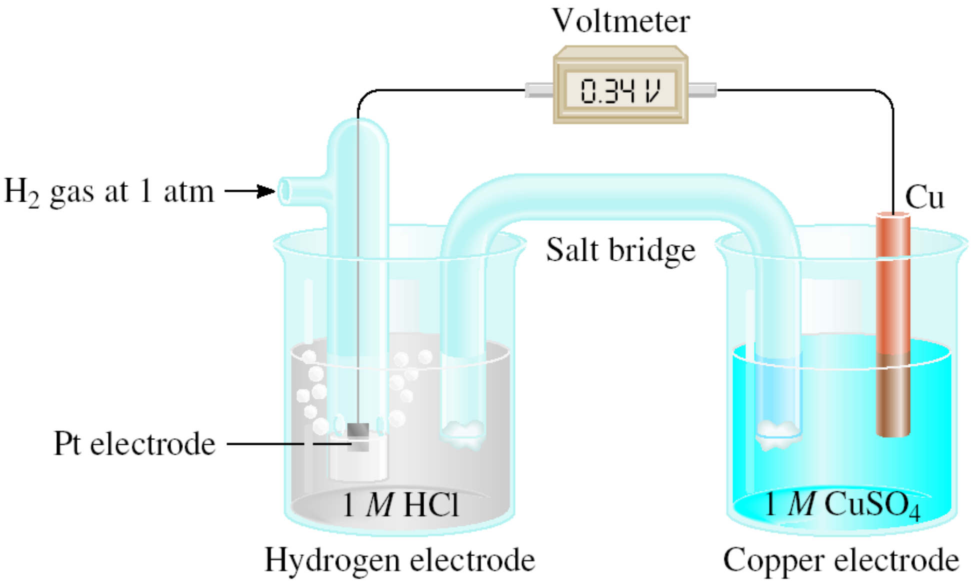
$$0.76\text{ V} = 0 - E^0_{\text{Zn}^{2+}/\text{Zn}}$$

$$E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{ V}$$

$$\text{Zn}^{2+}\text{ (1 }M) + 2e^- \longrightarrow \text{Zn} \qquad E^0 = -0.76\text{ V}$$

Standard Reduction Potentials

$E^0_{cell} = 0.34\ V$



$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{H^+/H_2}$$

$$0.34 = E^0_{Cu^{2+}/Cu} - 0$$

$$E^0_{Cu^{2+}/Cu} = 0.34\ V$$

$Pt\ (s)\ |\ H_2\ (1\ atm)\ |\ H^+\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$

Anode (oxidation): $H_2\ (1\ atm) \longrightarrow 2H^+\ (1\ M) + 2e^-$

Cathode (reduction): $2e^- + Cu^{2+}\ (1\ M) \longrightarrow Cu\ (s)$

$$H_2\ (1\ atm) + Cu^{2+}\ (1\ M) \longrightarrow Cu\ (s) + 2H^+\ (1\ M)$$

For the **Daniell cell** shown in Figure 19.1, we can now write

Anode (oxidation): $Zn(s) \longrightarrow Zn^{2+}(1\ M) + 2e$

Cathode (reduction): $Cu^{2+}(1\ M) + 2e \longrightarrow Cu(s)$

Overall: $Zn(s) + Cu^{2+}(1\ M) \longrightarrow Zn^{2+}(1\ M) + Cu(s)$

The emf of the cell is

$$E°_{cell} = E°_{cathode} - E°_{anod}$$

$$= 0.34 – (- 0.76)$$

$$= 1.1\ V$$

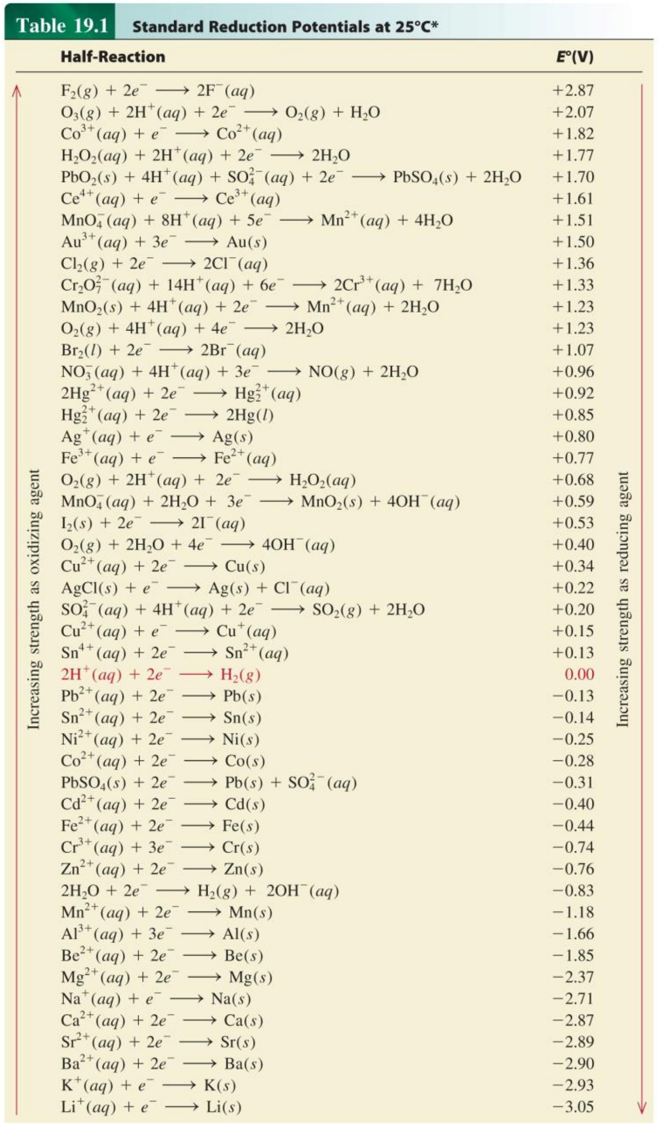


Table 19.1 **Standard Reduction Potentials at 25°C***

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

E^0 is for the reaction as written

-The more positive E^0 the greater the tendency for the substance to be reduced

-The half-cell reactions are reversible

-The sign of E^0 changes when the reaction is reversed

-Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E^0 (as E^0 is intensive property)

-Under standard-state conditions, any species on the left of a given half-cell reaction will react spontaneously with a species that appears on the right of any half-cell reaction located below it in Table 19.1. This principle is sometimes called the diagonal rule

Example 19.2

Predict what will happen if molecular bromine (Br_2) is added to a solution containing NaCl and NaI at 25°C. Assume all species are in their standard states.

Example 19.2

Strategy To predict what redox reaction(s) will take place, we need to compare the standard reduction potentials of Cl_2, Br_2, and I_2 and apply the diagonal rule.

Solution From Table 19.1, we write the standard reduction potentials as follows:

$Cl_2(1\ \text{atm}) + 2e^- \longrightarrow 2Cl^-(1\ M)$ $E° = 1.36\ \text{V}$

$Br_2(l) + 2e^- \longrightarrow 2Br^-(1\ M)$ $E° = 1.07\ \text{V}$

$I_2(s) + 2e^- \longrightarrow 2I^-(1\ M)$ $E° = 0.53\ \text{V}$

Example 19.2

Applying the diagonal rule we see that Br_2 will oxidize I^- but will not oxidize Cl^-. Therefore, the only redox reaction that will occur appreciably under standard-state conditions is

Oxidation: $2I^-(1\ M) \longrightarrow I_2(s) + 2e^-$

Reduction: $Br_2(l) + 2e^- \longrightarrow 2Br^-(1\ M)$

Overall: $2I^-(1\ M) + Br_2(l) \longrightarrow I_2(s) + 2Br^-(1\ M)$

Check We can confirm our conclusion by calculating $E°_{cell}$. Try it. Note that the Na^+ ions are inert and do not enter into the redox reaction.

Example 19.3

A galvanic cell consists of a Mg electrode in a 1.0 *M* $Mg(NO_3)_2$ solution and a Ag electrode in a 1.0 *M* $AgNO_3$ solution. Calculate the standard emf of this cell at 25°C.

Example 19.3

Strategy At first it may not be clear how to assign the electrodes in the galvanic cell. From Table 19.1 we write the standard reduction potentials of Ag and Mg and apply the diagonal rule to determine which is the anode and which is the cathode.

Solution The standard reduction potentials are

$$\mathrm{Ag^+}(1.0\ M) + e^- \longrightarrow \mathrm{Ag}(s) \qquad E° = 0.80\ \mathrm{V}$$

$$\mathrm{Mg^{2+}}(1.0\ M) + 2e^- \longrightarrow \mathrm{Mg}(s) \qquad E° = -2.37\ \mathrm{V}$$

Example 19.3

Applying the diagonal rule, we see that Ag^+ will oxidize Mg:

Anode (oxidation): $Mg(s) \longrightarrow Mg^{2+}(1.0\ M) + 2e^-$

Cathode (reduction): $2Ag^+(1.0\ M) + 2e^- \longrightarrow 2Ag(s)$

Overall: $Mg(s) + 2Ag^+(1.0\ M) \longrightarrow Mg^{2+}(1.0\ M) + 2Ag(s)$

Example 19.3

Note that in order to balance the overall equation we multiplied the reduction of Ag^+ by 2. We can do so because, as an intensive property, *E*° is not affected by this procedure. We find the emf of the cell by using Equation (19.1) and Table 19.1:

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Mg}^{2+}/\text{Mg}} \\ &= 0.80\ \text{V} - (-2.37\ \text{V}) \\ &= \mathbf{3.17\ V} \end{aligned}$$

Check The positive value of *E*° shows that the forward reaction is favored.

Spontaneity of Redox Reactions

$\Delta G = -nFE_{\text{cell}}$ n = number of moles of electrons in reaction

$\Delta G^0 = -nFE^0_{\text{cell}}$ $F = 96{,}500 \dfrac{\text{J}}{\text{V} \cdot \text{mol}} = 96{,}500 \text{ C/mol}$

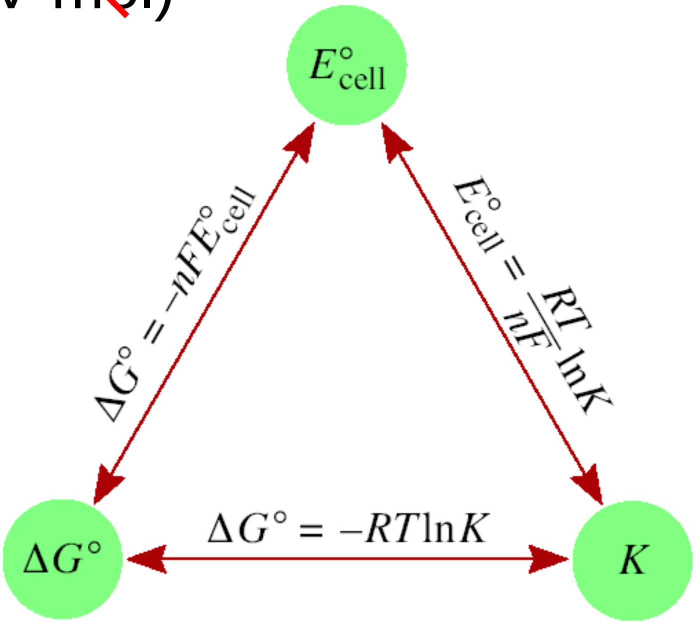
(F) Faraday constant

$\Delta G^0 = -RT \ln K = -nFE^0_{\text{cell}}$

$$E^0_{\text{cell}} = \frac{RT}{nF} \ln K = \frac{(8.314 \cancel{\text{J}}/\cancel{\text{K}}\cdot\cancel{\text{mol}})(298 \cancel{\text{K}})}{n\,(96{,}500 \cancel{\text{J}}/\text{V}\cdot\cancel{\text{mol}})} \ln K$$

$$E^0_{\text{cell}} = \frac{0.0257 \text{ V}}{n} \boxed{\ln} K$$

$$E^0_{\text{cell}} = \frac{0.0592 \text{ V}}{n} \boxed{\log} K$$



Spontaneity of Redox Reactions

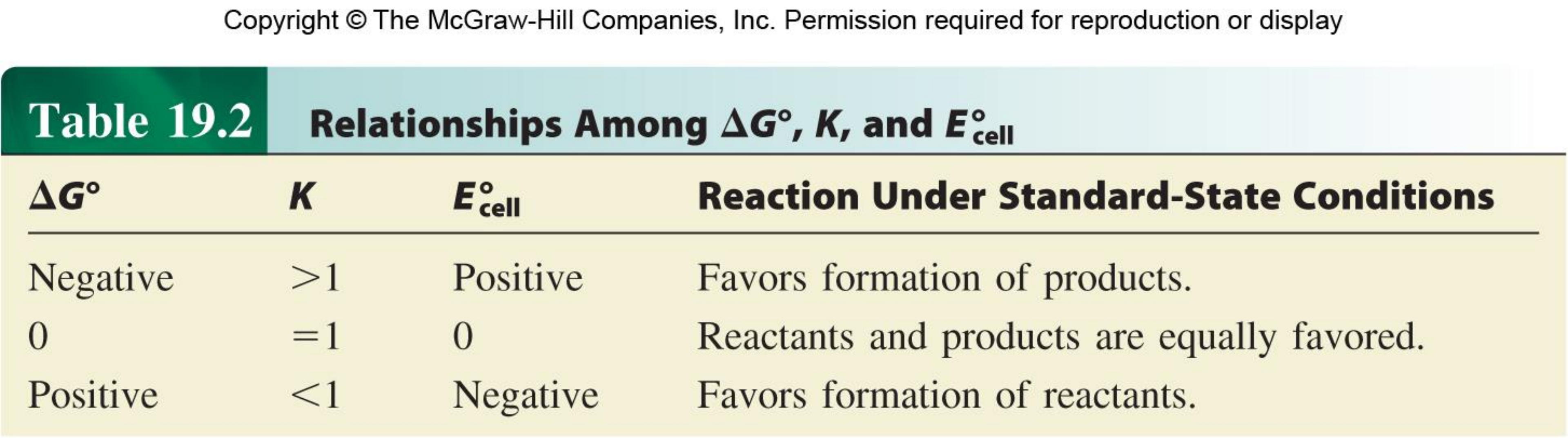


Table 19.2 **Relationships Among $\Delta G°$, K, and $E°_{cell}$**

$\Delta G°$	K	$E°_{cell}$	Reaction Under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

$$\Delta G^0 = -RT \ln K = -nFE^0_{cell}$$

Example 19.4

Calculate the equilibrium constant for the following reaction at 25°C:

$$\mathrm{Sn}(s) + 2\mathrm{Cu}^{2+}(aq) \rightleftharpoons \mathrm{Sn}^{2+}(aq) + 2\mathrm{Cu}^{+}(aq)$$

Example 19.4

Strategy

The relationship between the equilibrium constant K and the standard emf is given by Equation (19.5):

$$E^\circ_{\text{cell}} = (0.0257\ \text{V}/n)\ln K$$

Thus, if we can determine the standard emf, we can calculate the equilibrium constant. We can determine the E°_{cell} of a hypothetical galvanic cell made up of two couples (Sn^{2+}/Sn and Cu^{2+}/Cu^+) from the standard reduction potentials in Table 19.1.

Example 19.4

Solution

The half-cell reactions are

Anode (oxidation): $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$

Cathode (reduction): $2Cu^{2+}(aq) + 2e^- \longrightarrow 2Cu^+(aq)$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= E^\circ_{Cu^{2+}/Cu^+} - E^\circ_{Sn^{2+}/Sn} \\ &= 0.15\ \mathrm{V} - (-0.14\ \mathrm{V}) \\ &= 0.29\ \mathrm{V} \end{aligned}$$

Example 19.4

Equation (19.5) can be written

$$\ln K = \frac{nE^\circ}{0.0257\ \text{V}}$$

In the overall reaction we find *n* = 2. Therefore,

$$\ln K = \frac{(2)(0.29\text{V})}{0.0257\ \text{V}} = 22.6$$

$$K = e^{22.6} = \mathbf{7 \times 10^{9}}$$

Example 19.5

Calculate the standard free-energy change for the following reaction at 25°C:

$$2\text{Au}(s) + 3\text{Ca}^{2+}(1.0\ M) \longrightarrow 2\text{Au}^{3+}(1.0\ M) + 3\text{Ca}(s)$$

Example 19.5

Strategy

The relationship between the standard free energy change and the standard emf of the cell is given by Equation (19.3): $\Delta G° = -nFE°_{\text{cell}}$. Thus, if we can determine $E°_{\text{cell}}$, we can calculate $\Delta G°$. We can determine the $E°_{\text{cell}}$ of a hypothetical galvanic cell made up of two couples (Au^{3+}/Au and Ca^{2+}/Ca) from the standard reduction potentials in Table 19.1.

Example 19.5

Solution

The half-cell reactions are

Anode (oxidation): $2Au(s) \longrightarrow 2Au^{3+}(1.0\ M) + 6e^-$

Cathode (reduction): $3Ca^{2+}(1.0\ M) + 6e^- \longrightarrow 3Ca(s)$

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{Ca^{2+}/Ca} - E^\circ_{Au^{3+}/Au} \\ &= -2.87\ \text{V} - 1.50\ \text{V} \\ &= -4.37\ \text{V} \end{aligned}$$

Example 19.5

Now we use Equation (19.3):

$$\Delta G° = -nFE°$$

The overall reaction shows that n = 6, so

$$G° = -(6)\ (96{,}500\ \text{J/V} \cdot \text{mol})\ (-4.37\ \text{V})$$
$$= 2.53 \times 10^6\ \text{J/mol}$$
$$= \mathbf{2.53 \times 10^3\ kJ/mol}$$

Check The large positive value of $\Delta G°$ tells us that the reaction favors the reactants at equilibrium. The result is consistent with the fact that $E°$ for the galvanic cell is negative.

The Effect of Concentration on Cell Emf

$\Delta G = \Delta G^0 + RT \ln Q$ $\Delta G = -nFE$ $\Delta G^0 = -nFE^0$

$$-nFE = -nFE^0 + RT \ln Q$$

Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln Q$$

At 298 K

$$E = E^0 - \frac{0.0257\ \mathrm{V}}{n} \ln Q \qquad E = E^0 - \frac{0.0592\ \mathrm{V}}{n} \log Q$$

Example 19.6

Predict whether the following reaction would proceed spontaneously as written at 298 K:

$$\mathrm{Co}(s) + \mathrm{Fe}^{2+}(aq) \longrightarrow \mathrm{Co}^{2+}(aq) + \mathrm{Fe}(s)$$

given that $[\mathrm{Co}^{2+}] = 0.15\ M$ and $[\mathrm{Fe}^{2+}] = 0.68\ M$.

Example 19.6

Strategy

Because the reaction is not run under standard-state conditions (concentrations are not 1 *M*), we need Nernst’s equation [Equation (19.8)] to calculate the emf (*E*) of a hypothetical galvanic cell and determine the spontaneity of the reaction. The standard emf (*E*°) can be calculated using the standard reduction potentials in Table 19.1. Remember that solids do not appear in the reaction quotient (*Q*) term in the Nernst equation. Note that 2 moles of electrons are transferred per mole of reaction, that is, $n = 2$.

Example 19.6

Solution

The half-cell reactions are

Anode (oxidation): $\mathrm{Co}(s) \longrightarrow \mathrm{Co}^{2+}(aq) + 2e^-$

Cathode (reduction): $\mathrm{Fe}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Fe}(s)$

$$
\begin{aligned}
E^\circ_{\mathrm{cell}} &= E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}} \\
&= E^\circ_{\mathrm{Fe^{2+}/Fe}} - E^\circ_{\mathrm{Co^{2+}/Co}} \\
&= -0.44\ \mathrm{V} - (-0.28\ \mathrm{V}) \\
&= -0.16\ \mathrm{V}
\end{aligned}
$$

Example 19.6

From Equation (19.8) we write

$$E = E^{\circ} - \frac{0.0257\text{ V}}{n}\ln Q$$

$$= E^{\circ} - \frac{0.0257\text{ V}}{n}\ln\frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]}$$

$$= -0.16\text{ V} - \frac{0.0257\text{ V}}{2}\ln\frac{0.15}{0.68}$$

$$= -0.16\text{ V} + 0.019\text{ V}$$

$$= -0.14\text{ V}$$

Because *E* is negative, the reaction is not spontaneous in the direction written.

Concentration Cells

Galvanic cell from two half-cells composed of the *same* material but differing in ion concentrations.

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(0.10\,M)\,||\,\mathrm{Zn}^{2+}(1.0\,M)\,|\,\mathrm{Zn}(s)$$

$$\begin{array}{lrcl} \text{Oxidation:} & \mathrm{Zn}(s) & \longrightarrow & \mathrm{Zn}^{2+}(0.10\,M) + 2e^- \\ \text{Reduction:} & \mathrm{Zn}^{2+}(1.0\,M) + 2e^- & \longrightarrow & \mathrm{Zn}(s) \\ \hline \text{Overall:} & Zn^{2+}(1.0\,M) & \longrightarrow & \mathrm{Zn}^{2+}(0.10\,M) \end{array}$$

$$E = E^\circ - \frac{0.0257\ \mathrm{V}}{2}\ln\frac{[\mathrm{Zn}^{2+}]_{\mathrm{dil}}}{[\mathrm{Zn}^{2+}]_{\mathrm{conc}}}$$

$$E = 0 - \frac{0.0257\ \mathrm{V}}{2}\ln\frac{0.10}{1.0} = 0.0296\ \mathrm{V}$$