

Energy is the essence of chemistry

It determines which reaction can occur

Reaction either absorbs or releases energy

Total energy E has two contributions

a. Potential energy (PE)

$$E_P = mgh$$

m is mass,

h is height above the earth's surface,

$$g = 9.81 \text{ m/s}^2$$

b. Kinetic energy (KE)

$$E_K = \frac{1}{2}m v^2$$

m is mass,

v is speed

And $E = E_K + E_P$

Law of conservation of energy

Total energy of an isolated body is constant

Thus, can convert PE into KE and vice versa,

Example.

Throw a ball in the air:

- At start, KE is maximum and PE is zero,
- At top height PE is maximum and KE is zero

Isolated system:

cannot exchange energy with its surroundings

Internal energy U:

total kinetic and potential energy of atoms and molecules in the system

U is measure of capacity of object to transfer heat (q) and do work (w)

A large value of U means system can provide a large amount q and w.

e.g. Fuel releases U as q, which is transferred to the surroundings

Thermodynamics:

study of energy changes in groups of atoms and molecules

Thermochemistry:

measure heat released or absorbed by a chemical reaction

Definitions

System:

group of atoms and molecules under study

Surroundings:

everything outside the system

Usually limited to material in contact with the system,

e.g. a water bath surrounding the container holding the system.

Open system:

exchanges matter and energy with surroundings

Closed system:

heat q and work w exchanged with surroundings

exchanges energy but not matter with surroundings

Isolated system:

no exchange of energy and matter.

In this course, the open system will not be considered, i.e. no matter transfer.

Heat transfer

Measured by temperature change in the system and surroundings.

Example

System = hot steel block

Surroundings = water bath

Drop block into bath:

- T of block decreases
- T of bath increases,

Thus, heat released by block and heat absorbed by bath.

U of block decreases

i.e. energy removed from system and given to surroundings

Work w :

Object is moved against an opposing force.

Example

System:

Nitrogen gas in cylinder having a piston with a metal block of mass m on top.

If m is raised by height h , system has done work

$$w = mgh$$

The gas has expanded against the opposing force of the mass

The system has done work and lost energy,
 U of system has decreased

The force of the mass can be considered as an opposing pressure.

Later, w will be expressed as $P \cdot \Delta V$

In which P is the opposing pressure and ΔV is the volume change of the gas.

Internal energy U of a system is the sum of:

KE (motion) of the molecules

and

PE (attraction and repulsion between molecules)

Effect of q on ΔU

$$\Delta U = q$$

q can be

(+) (heat transferred to the system by the surroundings)

(-) (heat transferred by the system to the surroundings)

(0) (no heat transferred)

Thus, when $q > 0$

U increases, i.e. energy is stored in the system

When both q and w are involved:

$$\Delta U = q + w \quad \text{first law of thermodynamics}$$

Isolated system

cannot exchange heat or work with the surroundings:

$$q = 0, w = 0.$$

Therefore,

$$\Delta U = q + w = 0$$

And $U_{\text{final state}} = U_{\text{initial state}}$

Thus U of an isolated system is constant.

(Alternate statement of first law)

Self Test 6.2A

(Case I)

A system gains 260kJ of energy as heat while doing 500kJ of work. Determine ΔU .

Solution:

q is positive because the system gains energy

w is negative because the system uses internal energy to do work

Therefore, using
$$\begin{aligned}\Delta U &= q + w \\ &= 260\text{kJ} - 500\text{ kJ} \\ &= -240\text{ kJ}\end{aligned}$$

(Case II)

System gains 500 kJ of energy as heat and does 740 kJ of work

Solution:

$$\begin{aligned}\Delta U &= q + w \\ &= 500\text{kJ} - 740\text{kJ} = -240\text{ kJ}\end{aligned}$$

Since,
$$\Delta U = U_{\text{final state}} - U_{\text{initial state}}$$

$$U_{\text{initial state}} + \Delta U = U_{\text{final state}}$$

and
$$U_{\text{final state}} = U_{\text{initial state}} - 240\text{ kJ}$$

Note:

Final state is the same for both Case I and II, but values for q and w change for the two cases.

Thus,

- U is a state function.
 ΔU depends only on the initial and final states and not on the path used.
- q and w are path functions.
Their values depend on the path used.

Expansion work

done when system expands against an external force.

Compression work

done when the system is compressed by an external force.

Can calculate w using

$$w = mgh$$

$$\text{force} = m \cdot g \quad \text{and} \quad \text{distance} = h$$

Instead of $m \cdot g$,

use the external pressure P_{external} .

i.e. force/area.

And instead of distance,

use volume change:

$$\Delta V = V_{\text{final}} - V_{\text{initial}}$$

Then $w = - P_{\text{external}} \cdot \Delta V$

The minus sign means the system loses energy when it expands.

For expansion

$$V_{\text{final}} > V_{\text{initial}}$$

$$\text{and} \quad P_{\text{external}} > 0.$$

Thus w is negative because energy leaves the system,

i.e. U decreases.

SI units

$$\begin{aligned}\Delta V: & \quad \text{m}^3 \\ P_{\text{external}}: & \quad \text{pascals (Pa)} \\ P_{\text{ext}}\Delta V: & \quad 1\text{Pa} \cdot \text{m}^3 = (1\text{kg}/\text{m} \cdot \text{s}^2) \text{m}^3 \\ & \quad = 1\text{kg} \cdot \text{m}^2/\text{s}^2 \\ & \quad = 1\text{J}\end{aligned}$$

If pressure is in atmospheres

$$1 \text{ atm} = 101,325 \text{ Pa}$$

$$\begin{aligned}\text{and } P\Delta V \text{ units: } 1\text{L} \cdot \text{atm} &= 10^{-3}\text{m}^3 \times 101,325 \text{ Pa} \\ &= 101.325\text{J}\end{aligned}$$

Look at Example 6.2 for expansion.

Compression Example.

Calculate w and ΔU when a gas is compressed from 10.0 L to 2.0 L at 15.0 atm.

Solution

$$\begin{aligned}\Delta V &= V_{\text{final}} - V_{\text{initial}} = 2.0 \text{ L} - 10.0 \text{ L} \\ &= -8.0\text{L}\end{aligned}$$

$$\begin{aligned}w &= -P_{\text{external}} \cdot \Delta V \\ &= -(15.0 \text{ atm} \times (-8.0 \text{ L})) \left(\frac{101.325\text{J}}{1\text{L} \cdot \text{atm}} \right) \\ &= 1.2 \times 10^4 \text{ J}\end{aligned}$$

Note: w is positive,

i.e. work is done on the system and U increases.

Thus, $\Delta U = w = 1.2 \times 10^4 \text{ J}$

If a reaction occurs in a container and volume is constant, no work is done

i.e. $w = 0$

and $\Delta U = q$

ΔU equals the heat transferred at constant volume.

The bomb calorimeter measures q at constant volume.

Enthalpy H is a very useful quantity

If both q and w are involved and the work is done at a constant external pressure

$$\Delta U = q + w$$

$$\Delta U = q - P\Delta V \quad [1]$$

Definition:

At constant P

$$\Delta H = \Delta U + P\Delta V \quad [2]$$

Adding [1] and [2] gives:

$$\Delta H = q$$

Thus ΔH equals the heat transferred at constant pressure.

Self test 6.4B

For a reaction:

50 kJ of heat entered the system at constant pressure;
20 kJ of work was done on the system

Determine ΔH and ΔU .

Solution

Heat at constant pressure equals ΔH , i.e. 50 kJ

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

and

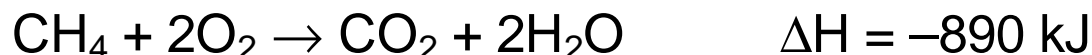
$$\Delta U = \Delta H - P\Delta V$$

$$\Delta U = 50\text{kJ} + 20\text{ kJ} \quad \Delta V < 0 \text{ [negative]}$$

Sign of ΔH :

Exothermic process $\Delta H < 0$
energy leaves the system

Example

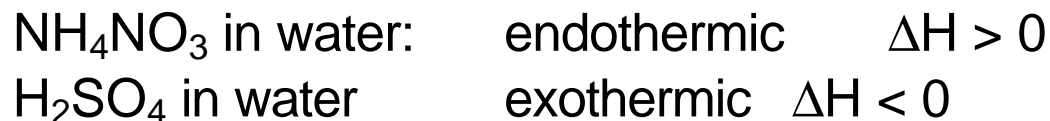


Endothermic process $\Delta H > 0$
energy enters the system

Example



Dissolving a solute in water may be either exothermic or endothermic



To measure heat

measure a temperature change ΔT

Method:

- contact the reaction chamber with water
- measure temperature change in water.
must know the heat capacity of water.

Heat capacity C:

heat needed to raise temperature by 1° K

$$C = \frac{q}{\Delta T} \quad \text{units: J/°K} \quad \text{or} \quad \text{J/°C}$$

q measured either at constant volume or constant pressure

Specific heat capacity C_s

often used because C depends on the amount of material

$$C_s \quad \text{units J/g°K}$$

Thus

$$C = m \times C_s$$

And

$$q = m \times C_s \times \Delta T$$

Self-test 6.5 B

Calculate q if 10.0 g of KClO_3 is raised from 25.0 to 900° C.

$$C_s = 0.8111 \text{ J/g°K}$$

Solution:

$$\begin{aligned} q &= m \times C_s \times \Delta T \\ &= 10.0\text{g} \times (0.8111 \text{ J/g°K}) \times (900 - 25.0) \text{ °K} \\ &= 7.10 \text{ kJ} \end{aligned}$$

Note °C can be used here.

Calorimeter

- Consists of container for system in contact with water
- Heat of process is determined from temperature change of water

Example 6.4

21.0 g of iron at 90.2° C is place in 50.0 g of water at 20.0 C. Calculate C_s of iron if the final temperature is 23.2 C and C_s of water is 4.184 J/g°C.

Solution

- Heat lost by iron = heat gained by water
- Heat lost is negative and heat gained is positive.
- Magnitude is the same.

$$(m \cdot C_s \cdot \Delta T)_{\text{iron}} = - (m \cdot C_s \cdot \Delta T)_{\text{water}}$$

Calculate ΔT

$$\begin{aligned}\Delta T_{\text{iron}} &= T_{\text{final}} - T_{\text{initial}} = 23.2 - 90.2 \\ &= - 67.0^\circ\text{C}\end{aligned}$$

$$\Delta T_{\text{water}} = 23.2 - 20.0 = + 3.2^\circ\text{C}.$$

Calculate C_s

$$\begin{aligned}21.0\text{g} \cdot (C_s)_{\text{iron}} \cdot (- 67.0^\circ\text{C}) &= - 50.0\text{g} \cdot (4.184 \text{ J/g}^\circ\text{C}) \cdot 3.2^\circ\text{C} \\ (C_s)_{\text{iron}} &= + 0.48 \text{ J/g}^\circ\text{C}\end{aligned}$$

Heat capacity of a calorimeter is determined experimentally

Measure $\Delta T_{\text{calorimeter}}$ for a known q_{reaction}

Example 6.5

A known reaction releases 1.78kJ and $\Delta T_{\text{calorimeter}} = +3.65^{\circ}\text{C}$ for an open calorimeter containing 0.100L of aqueous NaCl. Calculate $C_{\text{calorimeter}}$.

Solution:

$$q = C_{\text{cal}} \cdot \Delta T$$

and $C_{\text{cal}} = 1780\text{J}/3.65^{\circ}\text{C} = 487.67\text{J}/^{\circ}\text{C}$

Once C_{cal} is determined q for any reaction can be measure.

Example,

50.0 mL of NaOH is mixed with 50.0 mL of HCl and

$$\Delta T_{\text{cal}} = +1.26^{\circ}\text{C}$$

Calculate heat of reaction

Solution

Note: the volume of solution is still 0.100 L

Also, $\Delta T_{\text{cal}} > 0$ means heat is given to calorimeter.

Thus heat is given up by the reaction,

i.e. $q_{\text{rxn}} < 0$

Or $q_{\text{rxn}} = -q_{\text{cal}}$

Thus, $q_{\text{rxn}} = -C_{\text{cal}} \cdot \Delta T_{\text{cal}}$
 $= -(487.67\text{J}/^{\circ}\text{C}) \times 1.26^{\circ}\text{C}$
 $= -614\text{J}$

Finally does q_{rxn} equal ΔH or ΔU ?

Answer:

$$q_{\text{rxn}} = \Delta H$$

because the calorimeter is open and the pressure is constant at one atm.

Physical change

Enthalpy of vaporization

Liquid \rightarrow vapor

$$\Delta H_{\text{vap}} = H_{\text{vapor}} - H_{\text{liquid}}$$

Process is endothermic, i.e. $\Delta H_{\text{vap}} > 0$

Energy must be given to the molecules to separate them and form gas

Example

For H_2O , $\Delta H_{\text{vap}} = +40.7 \text{ kJ/mol}$ at 100°C

The reverse process is condensation:

vapor \rightarrow liquid,

and $\Delta H = -\Delta H_{\text{vap}}$

heat is given up for $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$

Rule:

If a process is reversed, multiply ΔH by -1 .

i.e. $\Delta H(\text{reverse process}) = -\Delta H(\text{forward process})$

Enthalpy of fusion

Solid \rightarrow liquid

$$\Delta H_{\text{fus}} = H_{\text{liquid}} - H_{\text{solid}}$$

Enthalpy of sublimation

Solid \rightarrow vapor

$$\Delta H_{\text{sub}} = H_{\text{vapor}} - H_{\text{solid}}$$

Table 6.2: units for these ΔH 's: kJ/mol

ΔH values can be added if they are at the same T.

Thus,
$$\Delta H_{\text{sub}} = \Delta H_{\text{vap}} + \Delta H_{\text{fus}}$$

Proof:
$$= (H_{\text{vapor}} - H_{\text{liquid}}) + (H_{\text{liquid}} - H_{\text{solid}})$$
$$= H_{\text{vapor}} - H_{\text{solid}}$$

Heating curve is a graph of heat absorbed as T is increased
(Fig. 6.27)

Example 6.6

79 kJ of heat vaporizes 35.0g of water at 100 C.

Calculate ΔH_{vap}

Solution:

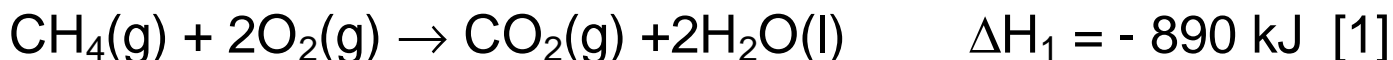
$$\Delta H_{\text{vap}} = q / (\text{moles of } H_2O)$$

$$\text{Mole of } H_2O = 35.0g \times \left(\frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2} \right) = 1.942 \text{ mol}$$

$$\Delta H_{\text{vap}} = 79 \text{ kJ} / 1.94 \text{ mol}$$
$$= 40.6 = 41 \text{ kJ/mol.}$$

Thermochemical Equation

Example



Because $\Delta H < 0$, this reaction is exothermic,
i.e. gives up heat.

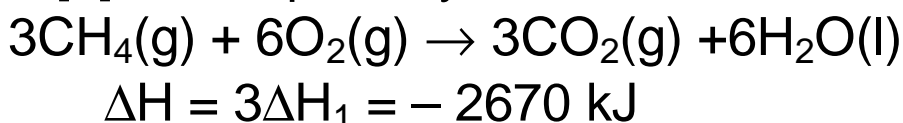
Stoichiometric coefficients are related to the number of moles of reactants and products.

Rule

If the thermochemical equation is multiplied by a number N, ΔH is multiplied by N.

Example

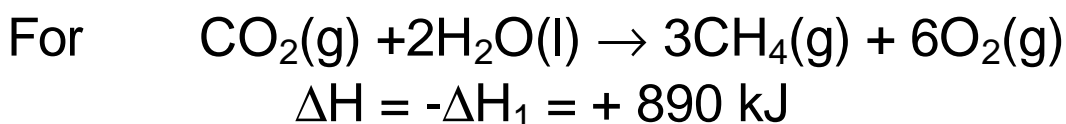
If reaction [1] is multiplied by 3



Rule

If reaction [1] is reversed, multiply ΔH_1 by -1 .

Thus,



Calculating reaction enthalpy, ΔH_r

Units for ΔH_r : kJ/mol

Rule:

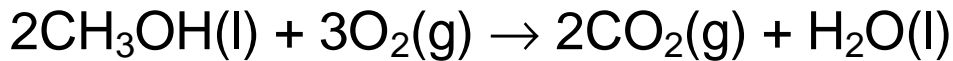
Calculate for stoichiometric coefficient of 1 for key reactant then you can multiply by any number.

Example 6.7

0.515g of CH₃OH burns in excess O₂ in a constant P calorimeter, and T rises by 10.6° K.

$$C_{\text{cal}} = 551 \text{ J/}^\circ\text{C}.$$

Calculate ΔH for:



Solution:

First calculate q_{cal}

$$\begin{aligned} q_{\text{cal}} &= C_{\text{cal}}\Delta T_{\text{cal}} \\ &= (551 \text{ J/}^\circ\text{C}) \times 10.6^\circ\text{C} = 5840.6 \text{ J} \end{aligned}$$

Then calculate q_{rxn}

$$q_{\text{rxn}} = -q_{\text{cal}}$$

Then

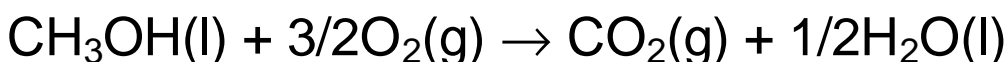
$$\begin{aligned} \Delta H_r &= q_{\text{rxn}} / (\text{no. moles}) \\ \Delta H_r &= -q_{\text{cal}} / (\text{no. moles}) \end{aligned}$$

$$\begin{aligned} \text{moles CH}_3\text{OH} &= 0.515 \text{ g} \times (1 \text{ mol} / 32.04 \text{ g}) \\ &= 0.0161 \text{ mol} \end{aligned}$$

and

$$\begin{aligned} \Delta H_r &= -(5.84 \text{ kJ}) / 0.0161 \text{ mol} \\ &= -363 \text{ kJ/mol} \end{aligned}$$

This result is for



Thus, for $2\text{CH}_3\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

$$\Delta H = 2(-363 \text{ kJ/mol}) = -726 \text{ kJ/mol}$$

Standard Reaction Enthalpy ΔH_r^o
reactants and products in standard states

ΔH depends on physical state of the reactants and products.
Thus, the states must be specified.

Tables in book

data for reactants and products in their standard states,
Standard States

For gases, liquids and solids
pure form at 1 atm. pressure

Example,

standard state for water:

liquid is pure H₂O at 1 atm.

solid is pure H₂O at 1 atm.

For a solution, 1 mol/L of solute,

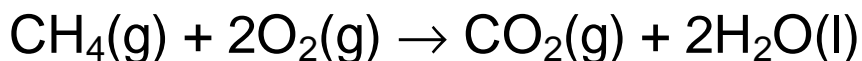
Example

for aqueous solution of HCN

Std State is 1.0 mol/L HCN

Example,

Std State reaction:



$$\Delta H_r^o = -890 \text{ kJ/mol}$$

-Pure CH₄ gas at 1 atm. reacts with pure O₂ gas at 1 atm.
to form:

-pure CO₂ gas and water liquid at 1 atm.

Can have standard state at any temperature

Often thermochemical data are reported at 25°C (298°K)

Hess's Law

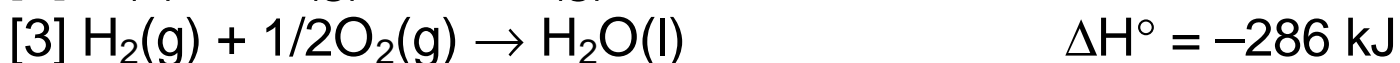
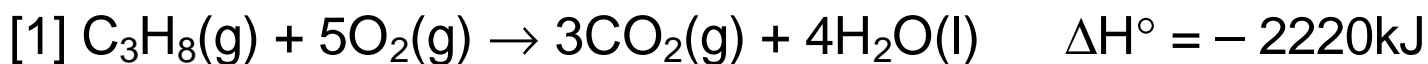
When adding reactions, add their reaction enthalpies to obtain the reaction enthalpy of the final (overall) reaction.

Note: If a reaction is reversed, multiply its ΔH by -1 .

This law is used to calculate ΔH of unknown reaction.

Example 6.8

Calculate ΔH° for $3\text{C(s)} + 4\text{H}_2\text{(g)} \rightarrow \text{C}_3\text{H}_8\text{(g)}$
using the following reactions.



Solution

Note:

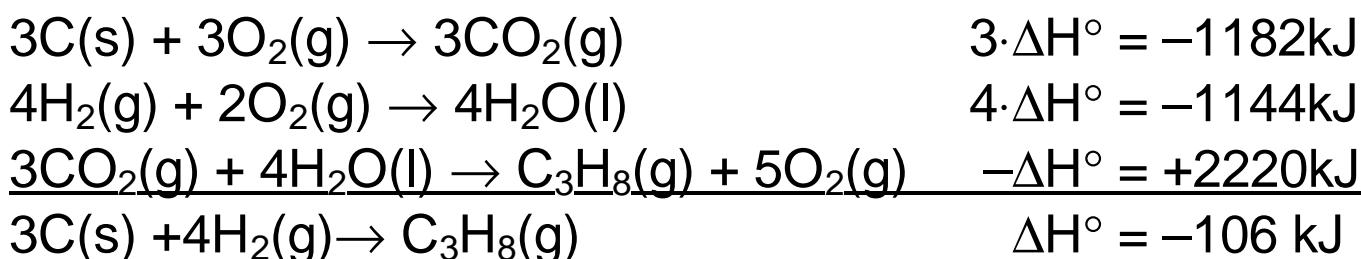
The final reaction has C(s) and $\text{H}_2\text{(g)}$ on the left hand side.

Multiply [2] by 3 and [3] by 4 and add.

However, $\text{C}_3\text{H}_8\text{(g)}$ is on the right hand side.

Reversed [1] and added.

Thus,



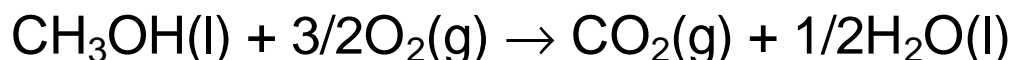
Calculation when reactant is not 1.0 mol.

Example

Calculate the heat for combustion of 10.0g of CH₃OH(l)
at constant pressure if $\Delta H_r^\circ = -363 \text{ kJ/mol}$

Solution:

The combustion reaction is:



$$q = n \times \Delta H_r^\circ$$

Must convert 10.0g to number of moles n.

$$n_{\text{CH}_3\text{OH}} = 10.0\text{g} \cdot (1\text{mol}/32.04\text{g}) = 0.312\text{mol}$$

and

$$\begin{aligned} q &= 0.312\text{mol} \cdot \Delta H_r^\circ \\ &= 0.312\text{mol} \cdot (-363 \text{ kJ/mol}) = -113\text{kJ} \end{aligned}$$

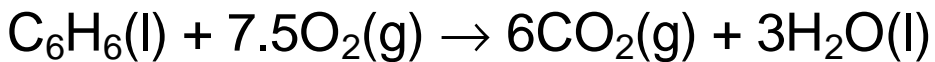
Other examples are given in book starting on page249.

Standard enthalpies of combustion ΔH_c°

Given in Table 6.3. Units: kJ/mol.

Reaction is written for stoichiometric coefficient of 1
for species oxidized.

Example:



$$\Delta H_c^\circ = -3268\text{kJ/mol}$$

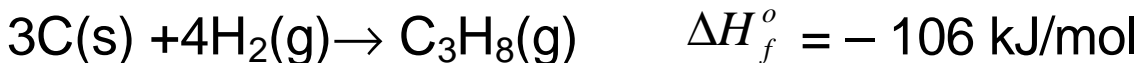
Standard Enthalpy of Formation ΔH_f°

for formation of a chemical from its elements in their most stable form in standard state.

Units: kJ/mol

The reaction is written for stoichiometric coefficient of 1 for this chemical.

Example:



Note:

$$\Delta H_f^\circ = 0 \quad \text{for elements in most stable form.}$$

Thus,

$$\Delta H_f^\circ = 0 \quad \text{for C(s, graphite)}$$

For diamond,



Calculation of ΔH of reaction using ΔH_f°

Rule:

For reaction $aA + bB \rightarrow cC + dD$

$$\Delta H = c\Delta H_f^\circ (C) + d\Delta H_f^\circ (D) - [a\Delta H_f^\circ (A) + b\Delta H_f^\circ (B)]$$

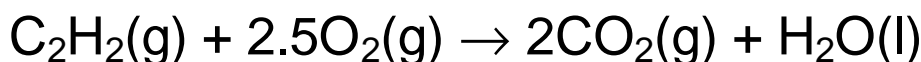
i.e. (products) – (reactants)

Example

Calculate the ΔH_c° for $C_2H_2(g)$ using ΔH_f° values at $25^\circ C$ from Table 6.5.

Solution:

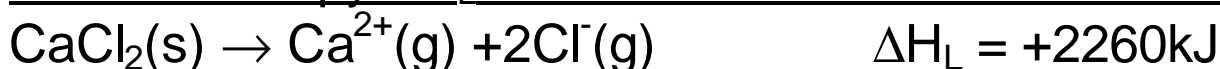
First: Write down the combustion reaction.



Second: use ΔH_f° with appropriate coefficients.

$$\begin{aligned}\Delta H_c^\circ &= \Delta H_f^\circ (H_2O(l)) + 2 \cdot \Delta H_f^\circ (CO_2(g)) - \Delta H_f^\circ (C_2H_2(g)) \\ &= -285.83 \text{kJ/mol} + 2 \cdot (-393.51 \text{kJ/mol}) \\ &\quad - (+226.73 \text{kJ/mol}) \\ &= -1299.5 \text{kJ/mol}\end{aligned}$$

Lattice Enthalpy ΔH_L



ΔH_L cannot be measured directly

Born-Haber Cycle

Thermochemical analysis to calculate ΔH_L

[Uses fact that H is state function.]

$$H_{\text{initial}} = H_{\text{final}} \quad \text{for cycle}$$

Example

Determine ΔH_L for KCl(s).

Reaction is:

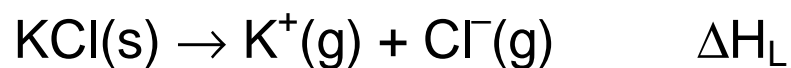
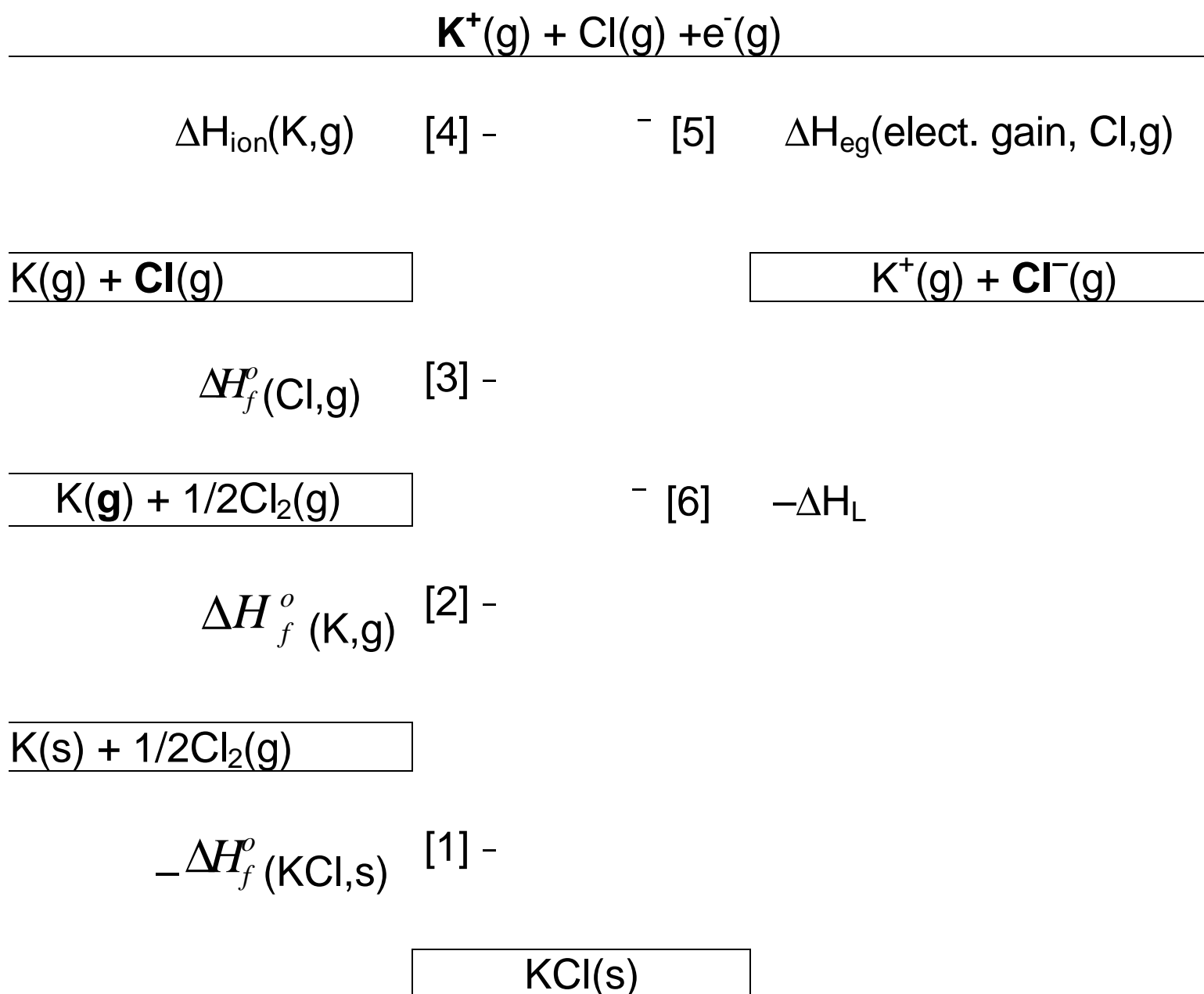


Figure 8.9 Born-Haber Cycle



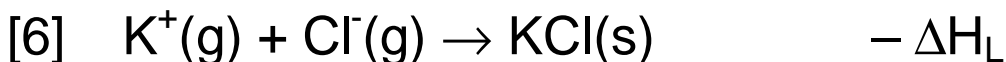
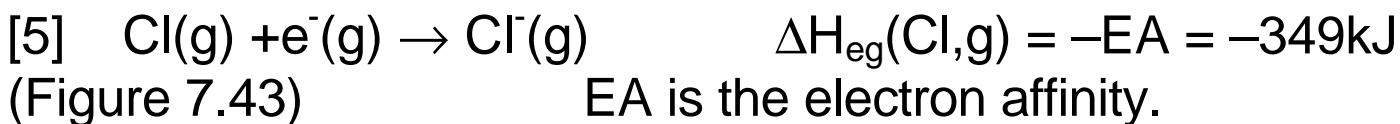
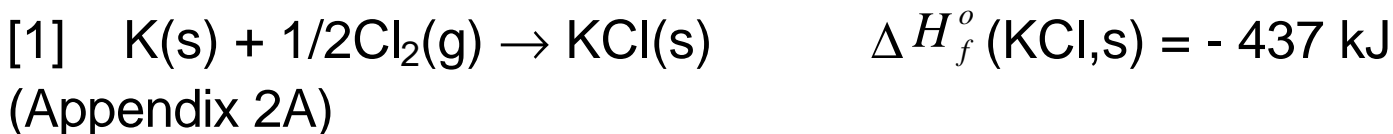
For the cycle, SUM of ΔH 's equals 0.

$$\begin{array}{cccccc}
 [1] & [2] & [3] & [4] & [5] & [6] \\
 -\Delta H_f^\circ(\text{KCl},s) + \Delta H_f^\circ(\text{K},g) + \Delta H_f^\circ(\text{Cl},g) + \Delta H_{\text{ion}}(\text{K},g) + \Delta H_{\text{eg}}(\text{Cl},g) & & & & & \\
 & & & & & -\Delta H_L = 0
 \end{array}$$

Then insert numbers and transpose ΔH_L

$$\begin{array}{ccccccc}
 -(-437) & + & 89 & & 122 & + & 418 & + & (-349) & = & \Delta H_L \\
 & & & & \Delta H_L & & & & & & \\
 & & & & \Delta H_L = 717\text{kJ} & & & & & &
 \end{array}$$

The reaction steps are:



ΔH_L values are in Table 8.1

Ionic Solids

For crystalline solids

- Ions arrange in a regular array
- A negative ion is next to a positive ion.

The strong attraction between these ions causes a high melting and boiling temperature.

Many ionic solids are soluble in water

An electrolyte solution. It conducts electricity

Many are also sparingly soluble in water

Calcium phosphate in bones is very sparingly soluble

Bond Enthalpy ΔH_B

Enthalpy change when a bond is broken in a gaseous molecule

It is an average value.

Averages of many different molecules.

Example



Means N_2 is more stable than two N atoms.

ΔH_B is always positive.

Note:

Bond broken to form neutral atoms
Each atom takes half the bonding electrons

Multiple bond has larger ΔH_B than single bond

$$\Delta H_B(\text{C—C}) = 348\text{kJ}$$

$$\Delta H_B(\text{C}=\text{C}) = 612\text{kJ} \quad 2x\Delta H_B(\text{C—C}) = 696\text{kJ}$$

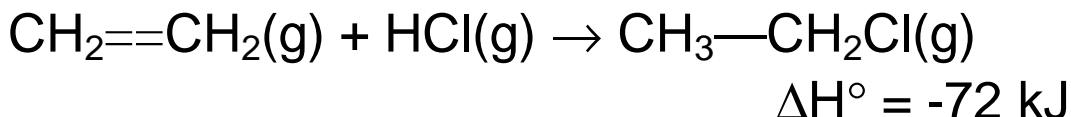
$$\Delta H_B(\text{C}\equiv\text{C}) = 837\text{kJ} \quad 3x\Delta H_B(\text{C—C}) = 1044\text{kJ}$$

Note:

$$\Delta H_B(\text{C}=\text{C}) < 2x\Delta H_B(\text{C—C})$$

Thus replacing a multiple bond by more single bonds gives a more stable molecule.

Example:



The product has a lower enthalpy than the reactants,
i.e. more stable.

Average bond enthalpies can be used to calculate reaction enthalpies,

But the use of ΔH_f° is more accurate.

Reason:

ΔH_B is an average of many compounds

ΔH_f° is specific to each compound in the reaction.

Look at Example 9.5 for how to calculate ΔH° from ΔH_B .

ΔH° tells us the energy involved in a reaction.

It does not tell us if it proceeds spontaneously.

Spontaneous process

Occurs without any external influence, i.e.

- no work done by the surroundings;
- no heat transferred from surrounding to system.

Example:

expansion of a gas at higher pressure P_1 into a container at lower pressure P_2 .

The reverse process is non-spontaneous, i.e.

surroundings must do work on the gas to increase its pressure from P_2 to P_1 .

A spontaneous process need not be fast.

Thermodynamics does not consider time.

For example

Reaction of hydrogen with oxygen is spontaneous.

But they exist together without reaction
a spark is needed.

For a spontaneous change:
energy and matter will be more disordered.

Entropy, S

A measure of the order of the system.

Increase entropy ($\Delta S > 0$),
order decreases, i.e. more disorder.

Increase T

Energy usually increases

More thermal disorder

i.e. an increase in thermal motion of atoms and
molecules—more disorder,

S is larger, i.e. $\Delta S > 0$.

Increase volume of a gas

more locations for the gas—positional disorder,

S is larger, i.e. $\Delta S > 0$.

When solid melts, S is larger

mainly because of thermal disorder.

When liquid vaporizes, S is larger.

mainly because of positional disorder.

Self Test 17.1B.

Does Hg(l) have larger S at -15°C or 0°C ? Why?

Answer:

At 0°C , because of thermal disorder.

S is a state function:

i.e. ΔS depends only on the initial and final states

$$\Delta S = (S_{\text{final}} - S_{\text{initial}}).$$

ΔS does not depend on the path used to get from initial to final state.

Second Law of Thermodynamics

S of an isolated system tends to increase for an irreversible process.

Reversible process:

Can be reversed by an infinitesimal change of a parameter.

Example:

Evaporation of water at 100°C

This process is reversible because we can add or remove a small amount of q

To evaporate a small amount of liquid water to form vapor,

Add a small amount of heat to system.

To condense a small amount of vapor to liquid
Remove a small amount of heat from system.

Book has it wrong: cannot raise or lower T during evaporation.

Calculation of entropy change ΔS .

$$\Delta S = q_{\text{rev}}/T \quad \text{units: J/}^\circ\text{K}$$

q_{rev} is heat transferred reversibly at constant T,
i.e. an infinitesimal amount for each step

T is absolute temperature $^\circ\text{K}$

Cannot use $^\circ\text{C}$

Remember:

q_{rev} can be positive or negative

T is always positive.

Self-Test 17.2B.

Calculate ΔS of a large swimming pool that gives off
240J at 28.0°C .

Solution:

Because pool is large, q is small and T does not change measurably.

$q_{\text{pool}} = -240\text{J}$ because pool gives up heat.

Also this is a reversible q

$$\begin{aligned}\Delta S &= q_{\text{pool}}/T \\ &= -240\text{J}/(273 + 28)^{\circ}\text{K} \\ &= -0.80\text{J}/^{\circ}\text{K}\end{aligned}$$

Entropy of Phase Change

Process is done at constant temperature and is reversible

- Fusion:



- Vaporization



- Sublimation



Self-Test 17.3B

Calculate ΔS_{vap} for NH_3 at its bp.

Table 6.2: $\Delta H_{\text{vap}} = 23.4 \text{ kJ/mol}$ $T_{\text{bp}} = 239.7^{\circ}\text{K}$

Solution

$$\begin{aligned}\Delta S_{\text{vap}} &= \Delta H_{\text{vap}}/T_{\text{bp}} \\ &= (23,400\text{J/mol})/239.7^{\circ}\text{K} \\ &= 97.6\text{J}/^{\circ}\text{K}\cdot\text{mol}\end{aligned}$$

Third Law of Thermodynamics

For a perfect crystal, $S \rightarrow 0$ as $T \rightarrow 0$.

Perfect crystal

All positions in the crystal lattice are occupied.

There is no positional disorder.

At $T = 0^\circ\text{K}$, there is no thermal disorder.

For T above 0°K

Positional and thermal disorder can occur.

And, absolute entropy S is positive.

S increases as T increases

S has been calculated for many chemicals

S_m^o , standard molar entropy at 25°C .

units are (J/K·mol)

(Table 17.1 and Appendix 2A)

S_m^o increases as the number of atoms in the compound increases.

Thus $\text{CaCO}_3(\text{s})$ has larger S_m^o than $\text{CaO}(\text{s})$.

Absolute S cannot be calculated for ions in solution.

Convention, use S of ion relative to S of $\text{H}^+(\text{aq})$.

Thus, ions can have positive or negative values

Examples

$$S_m^{\circ} = +56.5 \text{ J/}^{\circ}\text{K}\cdot\text{mol for Cl}^{-}(\text{aq})$$

$$S_m^{\circ} = -205 \text{ J/}^{\circ}\text{K}\cdot\text{mol for Ce}^{3+}(\text{aq})$$

Remember for ions in water: standard state is 1.0 mol/L

Self-Test 17.4B

Which has the higher S_m° , Pb(s) or Pb(l)? Why?

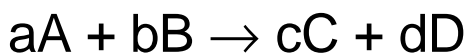
Answer:

Pb(l) because it has more thermal disorder.

Standard reaction entropy ΔS_r°

Calculate using S_m°

Thus for



$$\Delta S_r^{\circ} = c S_m^{\circ}(\text{C}) + d S_m^{\circ}(\text{D}) - [a S_m^{\circ}(\text{A}) + b S_m^{\circ}(\text{B})]$$

In general if the number of gas products is larger than number of gas reactants, $\Delta S_r^{\circ} > 0$.

If opposite occurs, $\Delta S_r^{\circ} < 0$.

Example 17.5:

Calculate ΔS_r° for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

Solution:

$$\begin{aligned}\Delta S_r^\circ &= 2 S_m^\circ (\text{NH}_3) - [S_m^\circ (\text{N}_2) + 3 S_m^\circ (\text{H}_2)] \\ &= -2 \cdot 192.4 - [191.6 + 3 \cdot 130.7] \text{ J/}^\circ\text{K}\cdot\text{mol} \\ &= -198.9 \text{ J/}^\circ\text{K}\cdot\text{mol}\end{aligned}$$

Note the value is negative.

But this reaction is spontaneous!

A spontaneous process requires a positive ΔS .

What is wrong?

Answer:

A positive ΔS occurs for an isolated system. (Second Law of Thermodynamics)

This reaction system is not isolated.

Why?

Answer:

The reactants start at 25°C and the products end at 25°C.

But the reaction is exothermic, i.e. $\Delta H^\circ = -92.22\text{kJ/mol}$.

Therefore

If the system were isolated T would rise

Because the heat would stay in the system,

To keep T constant at 298°K

Heat is transferred to the surroundings,

usually at constant P.

Thus, the real isolated system is reaction system plus the surroundings, and

$$\Delta S_{\text{tot}} = \Delta S_r^{\circ} + \Delta S_{\text{surr}}$$

Calculation of ΔS_{surr}

$$\Delta S_{\text{surr}} = q_{\text{rev}}/T$$

Since the reaction transfers heat to surroundings at constant P,

$$q_{\text{rev}} = -\Delta H^{\circ}, \quad \text{i.e. } q_{\text{rev}} > 0 .$$

Furthermore, the transfer is reversible

i.e. the surroundings is considered very large compared to the heat transferred

and T remains at 298°K.

Then

$$\begin{aligned} \Delta S_{\text{surr}} &= -(-92,220\text{J/mol})/298^{\circ}\text{K} \\ &= +309\text{J}/^{\circ}\text{K}\cdot\text{mol} \end{aligned}$$

And

$$\begin{aligned} \Delta S_{\text{tot}} &= \Delta S_r^{\circ} + \Delta S_{\text{surr}} \\ &= -199 + 309 = +110 \text{ J}/^{\circ}\text{K}\cdot\text{mol} \end{aligned}$$

And $\Delta S_{\text{tot}} > 0$

Means the reaction is spontaneous.

Look at Example 17.6.

It is solved the same way.

But first you must use ΔH_f° to calculate $\Delta H_{\text{sol}}^{\circ}$.

Self-Test 17.6B

A reaction absorbs 71.5kJ of heat from the surroundings at 150°K. Calculate ΔS_{surr} .

Answer:

$$\Delta H = +71.5\text{kJ}$$

because reaction absorbs heat, i.e. endothermic.

For surroundings,

$$q_{\text{rev}} = -\Delta H$$

And

$$\begin{aligned}\Delta S_{\text{surr}} &= -\Delta H/T \\ &= -(71,500\text{J})/150^\circ\text{K} = -477 \text{ J}/^\circ\text{K}\end{aligned}$$

Gibbs Free Energy G

We have shown that at constant T and P:

$$\Delta S_{\text{tot}} = \Delta S_{\text{r}} + \Delta S_{\text{surr}}$$

and

$$\Delta S_{\text{surr}} = -\Delta H/T$$

For any process

$$\Delta S_{\text{tot}} = \Delta S - \Delta H/T$$

in which ΔS is for the system.

And,

$$T\Delta S_{\text{tot}} = T\Delta S - \Delta H$$

It turns out that $\Delta G = -T\Delta S_{\text{tot}}$

And

$$\Delta G = \Delta H - T\Delta S$$

Called free energy because ΔG is the energy free to do work.

Thus ΔG (not ΔH) indicates the work that can be done.

G a state function,

Thus, ΔG depends only on the initial and final states

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

Because $\Delta S_{\text{tot}} > 0$ for a spontaneous process,

$\Delta G < 0$, i.e. it must be negative.

Sign of ΔG

depends on the relative values $T\Delta S$ and ΔH .

Conditions for spontaneous process, i.e. $\Delta G < 0$

Summary of Table 17.3

For an exothermic, $\Delta H < 0$

Two possibilities:

[1] $\Delta S > 0$. Then $-T\Delta S < 0$

and $\Delta G = \Delta H - T\Delta S < 0$ at any T .

The process is spontaneous at all T .

[2] $\Delta S < 0$. Then $-T\Delta S > 0$

$\Delta G < 0$ only if $|T\Delta S| < |\Delta H|$.

Thus, spontaneous process occurs at low T.

If T is increased high enough, can convert from spontaneous to non-spontaneous.

For endothermic, $\Delta H > 0$

Two possibilities.

[3] $\Delta S > 0$.

Then $-T\Delta S < 0$.

$\Delta G < 0$ only if $T\Delta S > \Delta H$.

Spontaneous process occurs at high T.

If T is lowered enough, can convert from spontaneous to non-spontaneous.

[4] $\Delta S < 0$.

Then $-T\Delta S > 0$.

$\Delta G > 0$ at any T.

Process is non-spontaneous at all T.

Thus for [2] and [3], it is possible to raise or lower T to change the sign of ΔG .

This means $\Delta G = 0$ at some value of T for these two cases.

When $\Delta G = 0$, equilibrium

Equilibrium

A reversible process

Occurs at constant T and P

Example

A phase change is an equilibrium process.

Example

Verify $\Delta G = 0$ for freezing water at 273.15°K and 1 atm.

Solution

$$\begin{aligned}\Delta H_{\text{freeze}} &= -\Delta H_{\text{fus}} \\ &= -6.01 \text{ kJ/mol} \qquad \qquad \text{From Table 6.2}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{freeze}} &= -\Delta S_{\text{fus}} \\ &= -21.97 \text{ J/}^\circ\text{K}\cdot\text{mol} \qquad \qquad \text{Using } S_m^\circ\end{aligned}$$

$$\begin{aligned}\Delta G &= \Delta H_{\text{freeze}} - T\Delta S_{\text{freeze}} \\ &= - (6010\text{J/mol}) - 273.15\cdot(-21.97) \text{ J/mol} \\ &= -9 \text{ J/mol} \qquad \text{which is essentially 0.}\end{aligned}$$

The error is in ΔH measurement accuracy.

For this equilibrium

- Water has a decrease in disorder when it freezes
- Surroundings has an increase in disorder
it absorbs heat from the water at constant T.
- The increase equals the decrease, $\Delta S_{\text{tot}} = 0$

An alternate calculation.

Predict T at which a phase change is at equilibrium at 1 atm.

Method: Set $\Delta G = 0$

Example 17.7

Calculate T_{bp} of Na(l) if

$$\Delta S_{vap} = 84.8 \text{ J/}^\circ\text{K}\cdot\text{mol and } \Delta H_{vap} = 98.0 \text{ kJ/mol}$$

Solution:

Must assume ΔS and ΔH are independent of T.

At T_{bp} the pressure is 1 atm. and liquid is in equilibrium with vapor.



Thus $\Delta G = 0$

$$\text{And } 0 = \Delta H_{vap} - T_{bp}\Delta S_{vap}$$

$$\begin{aligned} \text{And } T_{bp} &= \Delta H_{vap}/\Delta S_{vap} \\ &= 98,000\text{J/mol}/(84.8 \text{ J/}^\circ\text{K}\cdot\text{mol}) \\ &= 1,160 \text{ }^\circ\text{K} \\ &= 887 \text{ }^\circ\text{C} \end{aligned}$$

Direction of spontaneous reaction

$\Delta G < 0$, forward (left to right) is spontaneous

$\Delta G = 0$, equilibrium

$\Delta G > 0$, forward is non-spontaneous; reverse reaction is spontaneous

A non-spontaneous reaction can be forced to go by supplying energy from surroundings.

Many non-spontaneous biological reactions are driven by an external energy source.

Standard Free Energy of Reaction ΔG°

It can be calculated thermodynamically in two ways:

[1] Using ΔH° and ΔS° of the reaction.

And $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

In this case, use:

ΔH_f° to calculate ΔH°

and S_m° to calculate ΔS° .

[2] Using ΔG_f° ,

Standard free energy of formation of a compound from its elements in their most stable forms.

Some values in Table 17.4.

Standard states were defined earlier.

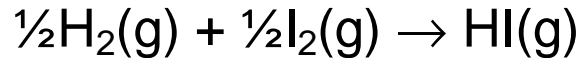
Example Using [1].

Example 17.8

Calculate ΔG_f° of HI(g) at 25.0° C using ΔH_f° and S_m° .

Solution:

The formation reaction is:



Calculate ΔS°

$$\begin{aligned}\Delta S^\circ &= S_m^\circ(\text{HI}) - [\frac{1}{2} S_m^\circ(\text{H}_2) + \frac{1}{2} S_m^\circ(\text{I}_2)] \\ &= 206.59 - [\frac{1}{2} \cdot 130.68 + \frac{1}{2} \cdot 116.14] \quad (\text{J}/^\circ\text{K}\cdot\text{mol}) \\ &= +83.18 \text{ J}/^\circ\text{K}\cdot\text{mol}\end{aligned}$$

Calculate ΔH°

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{HI}) - [\frac{1}{2} \Delta H_f^\circ(\text{H}_2) + \frac{1}{2} \Delta H_f^\circ(\text{I}_2)] \\ &= \Delta H_f^\circ(\text{HI}) = +26.48 \text{ kJ/mol} - [0] \quad (\text{Appendix 2A})\end{aligned}$$

And

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 26,480 \text{ J/mol} - 298^\circ\text{K} \cdot (83.18 \text{ J}/^\circ\text{K}\cdot\text{mol}) \\ &= + 1690 \text{ J/mol}\end{aligned}$$

Method [2]

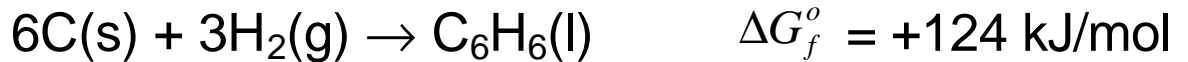
First some information about ΔG_f°

ΔG_f° is a measure of the stability of a compound relative to its elements.

$\Delta G_f^\circ < 0$ (negative):

- Compound more stable than elements.
- Formation is spontaneous.
- Compound is thermodynamically stable

Example

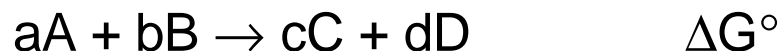


- Benzene is less stable than its elements.
- Reaction is non-spontaneous.
- Benzene is thermodynamically unstable.

But decomposition to its elements is extremely slow,
i.e kinetically stable.

Calculating ΔG° from ΔG_f°

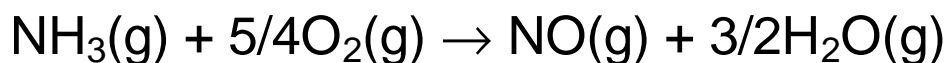
Reaction:



$$\Delta G^\circ = c \Delta G_f^\circ (\text{C}) + d \Delta G_f^\circ (\text{D}) - [a \Delta G_f^\circ (\text{A}) + b \Delta G_f^\circ (\text{B})]$$

Example:

Calculate ΔG° at 25.0°C for the reaction:



Solution:

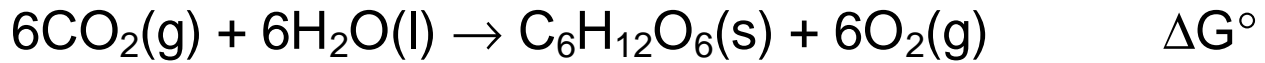
$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ (\text{NO}) + 3/2 \Delta G_f^\circ (\text{H}_2\text{O}) - [\Delta G_f^\circ (\text{NH}_3) + 5/4 \Delta G_f^\circ (\text{O}_2)] \\ &= +86.55 + 1.5 \cdot (-228.57) - [-16.45 + 0] \quad (\text{kJ/mol}) \\ &= -239.9 \text{ kJ/mol.} \end{aligned}$$

Negative sign indicates the reaction is spontaneous,
But NH_3 is kinetically stable.

Look at Example 17.9 and Self-Test 17.12A

Self-Test 17.12 B.

Use ΔG_f° to calculate ΔG° for the reaction:



Solution:

$$\begin{aligned}\Delta G^\circ &= 6\Delta G_f^\circ(\text{O}_2) + \Delta G_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6) - [6\Delta G_f^\circ(\text{CO}_2) + 6\Delta G_f^\circ(\text{H}_2\text{O})] \\ &= 6 \cdot (0) + (-910) - [6 \cdot (-394.4) + 6 \cdot (-120.4)] \\ &= +2179 \text{ kJ/mol} \\ &\text{non-spontaneous} \\ &\text{reverse is spontaneous}\end{aligned}$$

This calculation was made for only one composition of reactants and products,
i.e. pure compounds at 1 atm.

ΔG depends on composition.

The reaction proceeds to a composition at which $\Delta G = 0$.
i.e., the spontaneous reaction proceeds to the equilibrium composition.

Thermodynamics shows:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

R is the gas constant

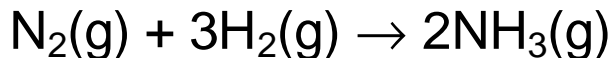
Q is the reaction quotient

Units: (mol/L) for solutes and
(atm.) for gases.

Calculation of ΔG for any pressure or concentration.

Example 17.10

Calculate ΔG for the reaction:



if the partial pressure is 100 atm at 25°C.

Solution:

$$Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{100^2}{100 \times 100^3} \text{ atm}^{-2}$$
$$= 1.00 \times 10^{-4} \quad \text{drop units}$$

Now

$$\Delta G = \Delta G^\circ + RT \ln Q$$

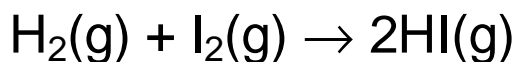
And $\Delta G^\circ = 2x \Delta G_f^\circ (\text{NH}_3) = 2x(-16.45 \text{ kJ/mol})$

And

$$\Delta G^\circ = (-32.90 \text{ kJ/mol}) + 298^\circ\text{K} \cdot 8.314 (\text{J/mol}\cdot\text{K}) \ln(1.00 \cdot 10^{-4})$$
$$= -55.7 \text{ kJ/mol}$$

Self-Test 17.13 A

$\Delta G^\circ = -21.1 \text{ kJ/mol}$ at 500°K for



Calculate ΔG°

if $P_{\text{H}_2} = 1.5 \text{ atm}$; $P_{\text{I}_2} = 0.88 \text{ atm}$; $P_{\text{HI}} = 0.065 \text{ atm}$.

Solution:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = -21.1 \text{ kJ/mol} + 500^\circ\text{K} \cdot 8.314 (\text{J/mol}\cdot\text{K}) \cdot \ln(0.065^2 / 1.5 \cdot 0.88)$$

$$= -45.0 \text{ kJ/mol}$$

spontaneous in forward direction.

This means the reaction goes in direction to decrease reactants.

And $\Delta G \rightarrow 0$ as reaction proceeds.

When $\Delta G = 0$,

$Q = K$ K is the equilibrium constant

Thus $\Delta G = \Delta G^\circ + RT \ln Q$

And $0 = \Delta G^\circ + RT \ln K$

And $\Delta G^\circ = -RT \ln K$

When both gases and solution are involved:

Calculate K using numerical values of:

- partial pressures for gases
- concentrations for solutes

When reaction occurs in solution only: K_c

K_c : equilibrium constant for concentrations only

When reaction occurs in gas only: K_p

K_p : equilibrium constant for pressures only

$K < 1$ when $\Delta G^\circ > 0$

reactants favored at equilibrium

$K > 1$ when $\Delta G^\circ < 0$

products favored at equilibrium

These conditions do not refer to spontaneity.

The reaction is not spontaneous.

It is at equilibrium because $\Delta G = 0!$

Calculation of K using $\Delta G^\circ = -RT \ln K$

When ΔG° values are not given, use 2 steps.

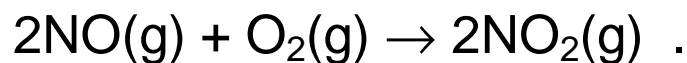
[1] calculate ΔG° using ΔG_f°

[2] calculate K

Example

Self-Test 17.14B

Calculate K_p at 25.0 C for



Solution:

[1] calculate ΔG° .

$$\begin{aligned}\Delta G^\circ &= 2 \Delta G_f^\circ (\text{NO}_2) - [2 \Delta G_f^\circ (\text{NO}) + \Delta G_f^\circ (\text{O}_2)] \\ &= 2 \cdot (+51.31) - [2 \cdot (+86.55) + (0)] \quad (\text{kJ/mol}) \\ &= -70.48 \text{ kJ/mol}\end{aligned}$$

[2] calculate K_p

$$\Delta G^\circ = -RT \cdot \ln K_p$$

$$\ln K_p = -\Delta G^\circ / RT$$

$$= -(-70,480 \text{ J/mol}) / (298^\circ \text{K} \times 8.314 \text{ (J/}^\circ \text{K} \cdot \text{mol)})$$

$$= +28.45$$

$$K_p = \text{antiln}(28.45)$$

$$= 2.26 \times 10^{12}$$

Thus, $K_p \gg 1$
means NO_2 is favored at equilibrium.

Estimating temperature using $K = 1$

Approach:

Using $\Delta G^\circ = -RT \cdot \ln K$

We see $K = 1$ when $\Delta G^\circ = 0$.

Further, we know

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

And $T = \Delta H^\circ / \Delta S^\circ$ When $\Delta G^\circ = 0$

Therefore,

First calculate

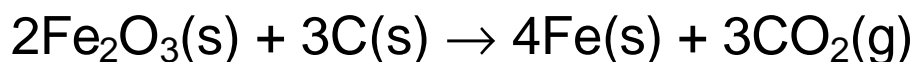
ΔH° using ΔH_f°

and ΔS° using S_m° .

Then calculate T.

Example 17.12

Calculate T at which $K = 1.0$ for the reaction:



Solution:

Calculate ΔH°

$$\begin{aligned}\Delta H^\circ &= 4 \Delta H_f^\circ (\text{Fe}) + 3 \Delta H_f^\circ (\text{CO}_2) - [2 \Delta H_f^\circ (\text{Fe}_2\text{O}_3) + 3 \Delta H_f^\circ (\text{C})] \\ &= 4 \cdot (0) + 3 \cdot (-393.5) - [2 \cdot (-824.2) + 3 \cdot (0)]\end{aligned}$$

$$=+467.9 \text{ kJ/mol}$$

Calculate ΔS°

$$\begin{aligned}\Delta S^\circ &= 4 S_m^\circ (\text{Fe}) + 3 S_m^\circ (\text{CO}_2) - [2 S_m^\circ (\text{Fe}_2\text{O}_3) + 3 S_m^\circ (\text{C})] \\ &= 4 \times 27.3 + 3 \times 213.7 - [2 \times 87.4 + 3 \times 5.7] \\ &= +558.4 \text{ J/K}\cdot\text{mol}\end{aligned}$$

Calculate T

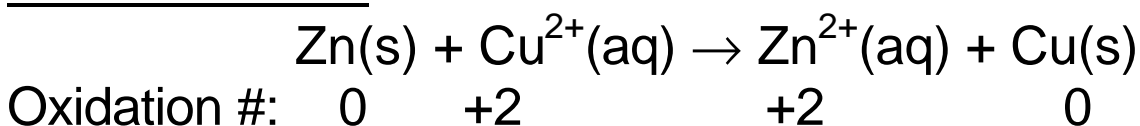
$$\begin{aligned}T &= \Delta H^\circ / \Delta S^\circ \\ &= 467.9 \times 10^3 \text{ (J/mol)} / 558.4 \text{ (J/K}\cdot\text{mol)} \\ &= 838 \text{ K}\end{aligned}$$

REDUCTION/OXIDATION REACTIONS (REDOX)

In Chapter 3 you learned about oxidation numbers and redox reactions.

Review this Chapter if you are rusty.

Redox Reaction



Zn is oxidized

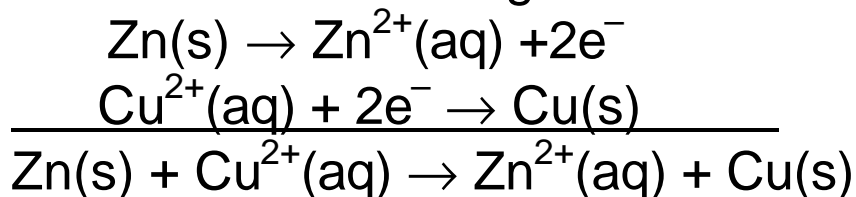


Cu^{2+} is reduced



Redox couples Cu^{2+}/Cu ; and Zn^{2+}/Zn

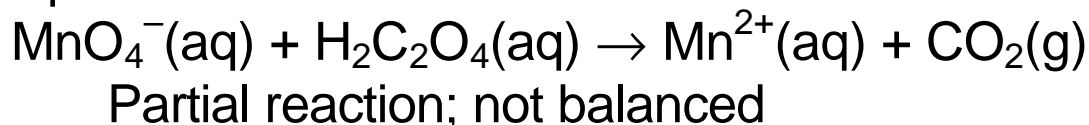
Combine half reactions to give the overall redox reaction.



This is a simple case because redox does not contain H^{+} or OH^{-} .

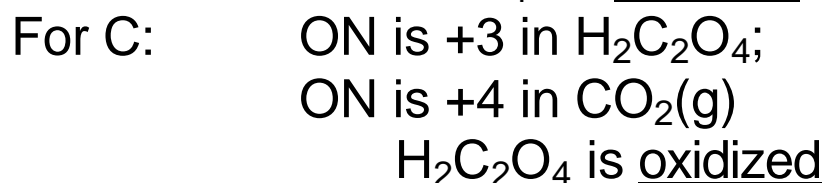
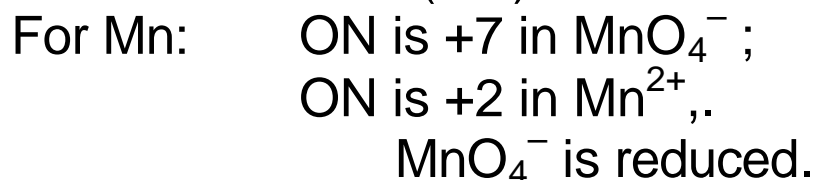
Balancing Method For Acidic Or Basic Solution

Example 18.1 for ACIDIC solution



Method

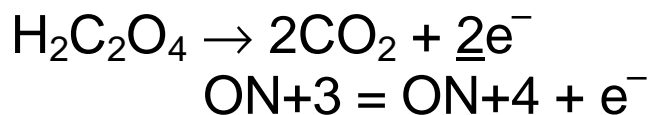
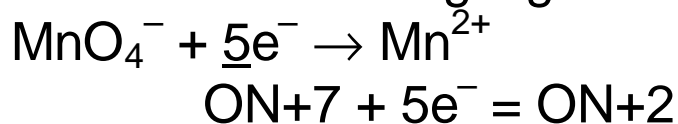
[1] Determine what is reduced and what is oxidized, i.e. oxidation number (ON)



[2] Balance atoms undergoing ON change

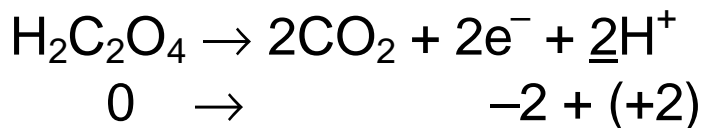
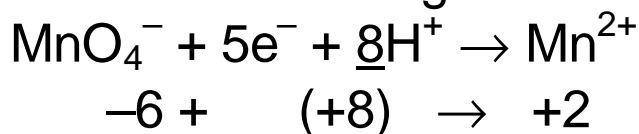


[3] Add e^- to side having higher ON

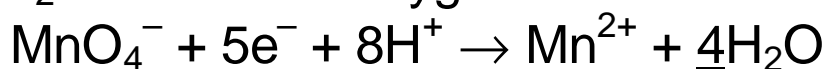


Multiply by 2 for 2C atoms

[4] Add H⁺ to balance charge

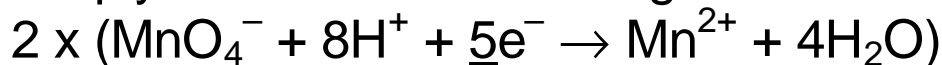


[5] Add H₂O to balance oxygen

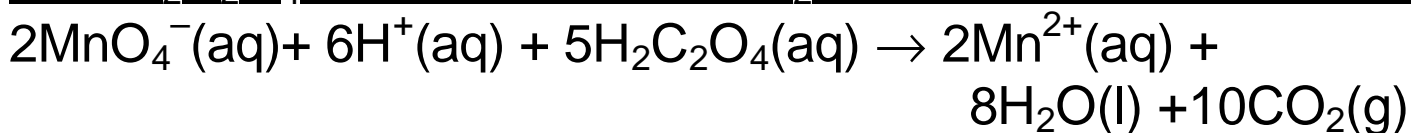
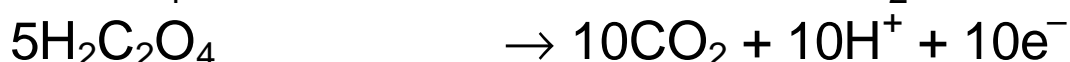
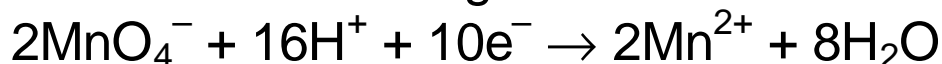


Now half reactions are balanced

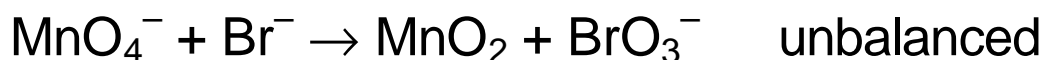
[6] Multiply each half reaction to give same number of e⁻



[7] Add half reactions to give overall redox reaction.



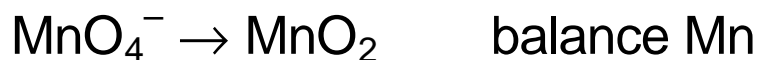
Redox In Basic Solution.



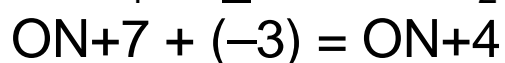
[1] Mn: in MnO₄⁻ ON is +7;
 in MnO₂ ON is +4.

Br: in Br^- ON is -1 ;
 in BrO_3^- ON is $+5$

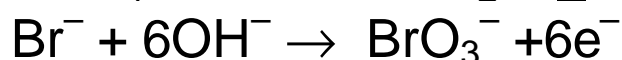
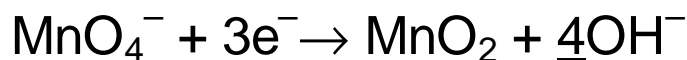
[2] Balance atoms



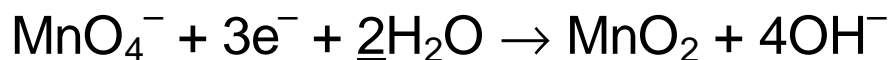
[3] Add e^- to higher ON side



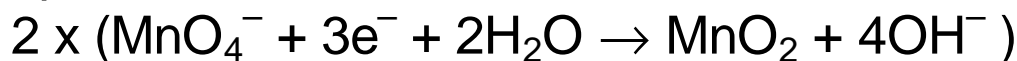
[4] Add OH^- to balance charge



[5] Add H_2O to balance O.

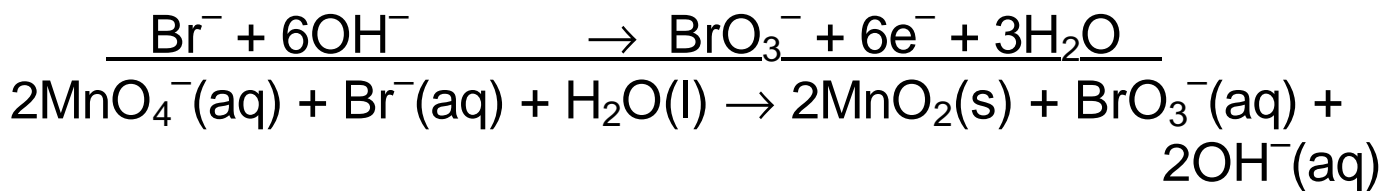


[6] Equalize e^-

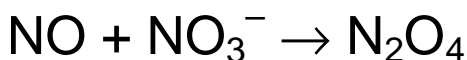


[7] Add half reactions



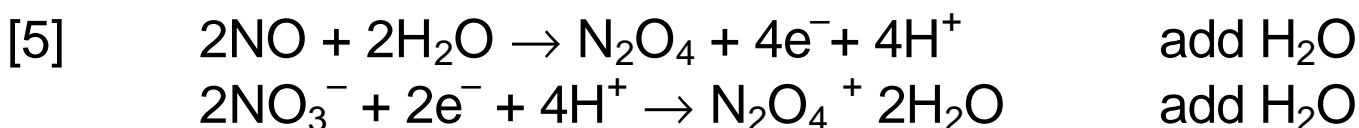
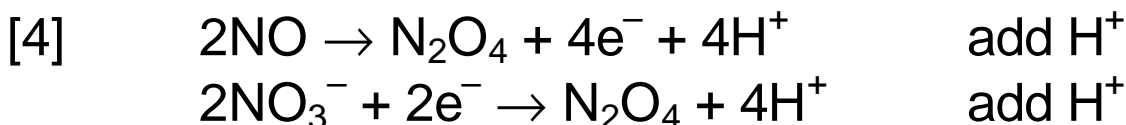
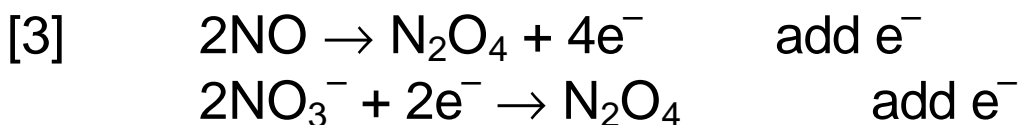
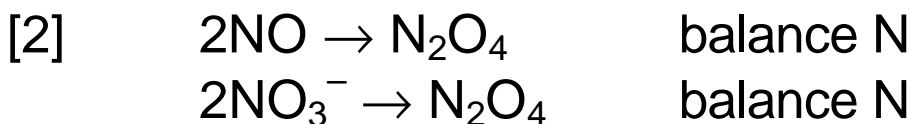


Example Acidic solution

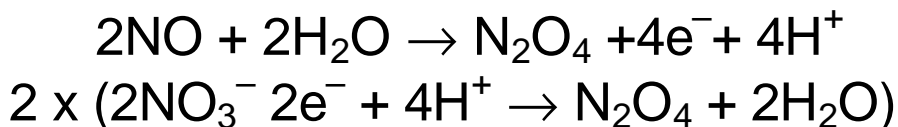


- [1] N: in NO ON is +2;
in N₂O₄ ON is+4
N: in NO₃⁻ ON is +5;
in N₂O₄ ON is+4

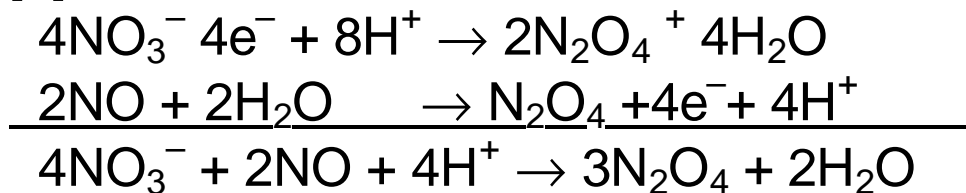
Thus N is both oxidized and reduced.



[6] Equalize e⁻

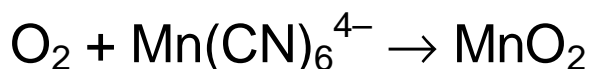


[7] Add half reactions



Often Redox can be balance for acid or base

Example



[1] Mn: ON, +2 \rightarrow +4; oxidation

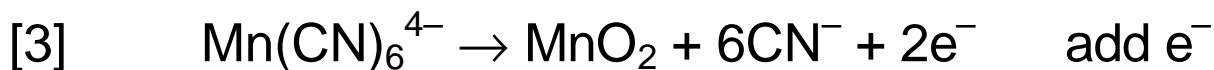
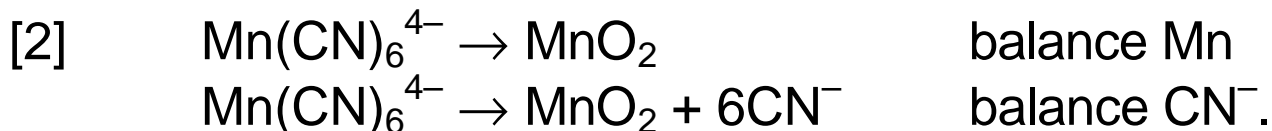
 CN⁻ remains unchanged: not involved

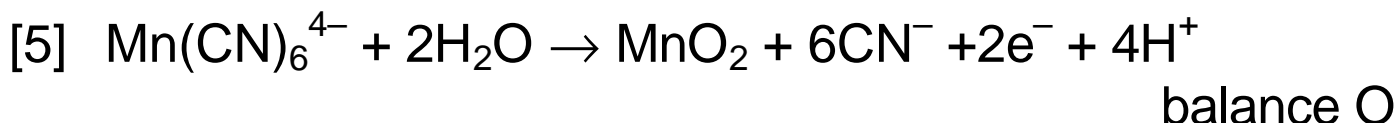
Note:

 O₂ is reduced to H₂O for acid

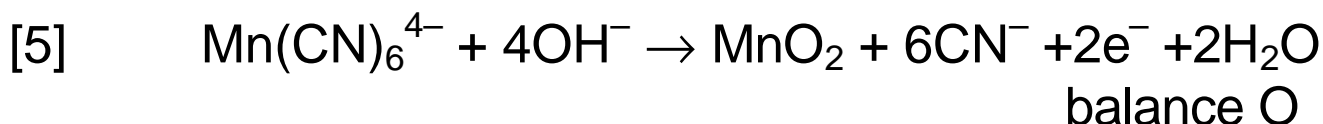
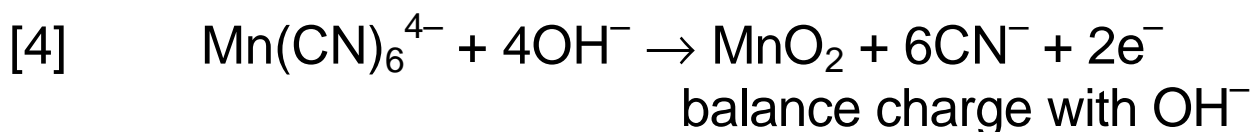
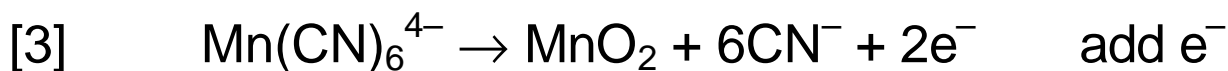
 O₂ is reduced to OH⁻ for base

For Acid





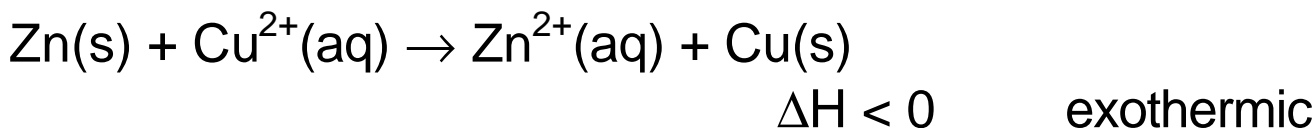
For base



For O₂ in base



Galvanic Cells



But cannot use all of ΔH for work

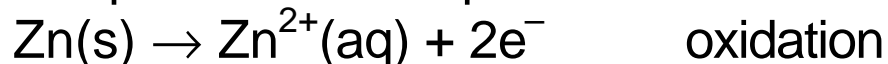
ΔG is the amount of ΔH that can be converted to work

$\Delta G = -212.5 \text{ kJ/mol}$,
amount of work that can be done by this reaction.

To collect ΔG as electrical energy:

Make an electrochemical cell

two compartments to separate the half reactions.



Cell Notation

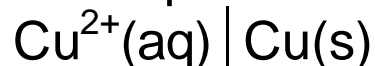
Oxidation compartment



Consists of a Zn rod (electrode) dipped in $\text{Zn}(\text{NO}_3)_2$ solution

Anode compartment

Reduction compartment



Consists of Cu rod (electrode) dipped in $\text{Cu}(\text{NO}_3)_2$ solution

Cathode compartment

Cell Diagram for electrochemical cell



(\parallel) indicates salt bridge

-Isolates the anode from the cathode compartment,

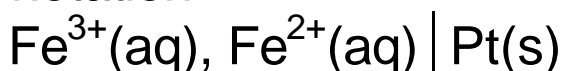
- Prevents Cu^{2+} from reacting directly with Zn to give heat
- At same time it completes the circuit – allows ions to move

For the half reaction $\text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+}$

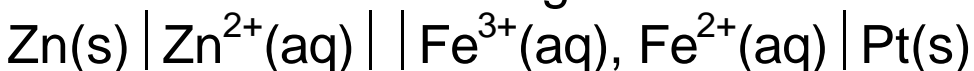
$\text{Fe}(\text{s})$ cannot be used as the electrode

An inert electrode such as Pt is used

Half cell notation

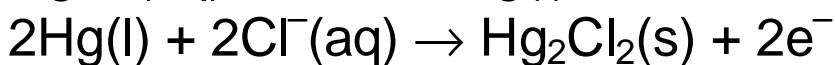
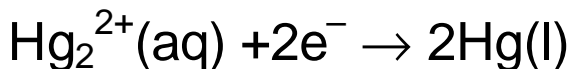


Electrochemical cell diagram



Example 18.3

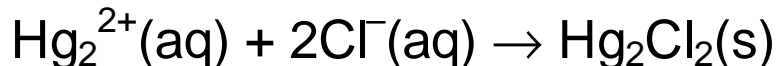
(a) Write the redox reaction resulting from the half reactions



(b) Write the cell diagram

Solution:

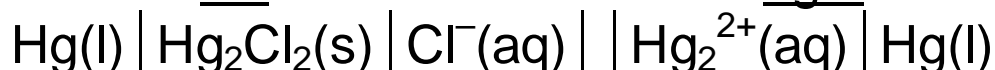
(a) Since number of e^{-} is same for both half reactions, add:



Note: this is not a redox; it is a precipitation.

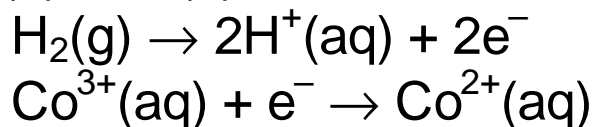
(b) Use half reactions to write cell diagram

oxidation on left and reduction on the right

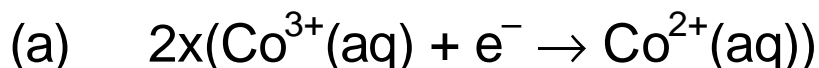


Self-Test 18.5A

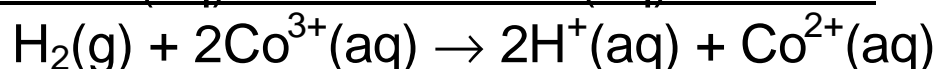
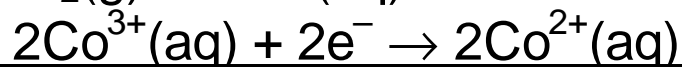
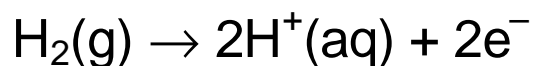
Repeat (a) and (b) for



Solution:



and add:



(b) Both anode and cathode compartments need an inert electrode;

Use Pt(s)



Example 18.5

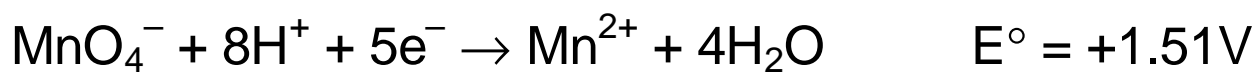
Can KMnO_4 oxidize Fe(II) to Fe(III) in acid at standard state?

Solution:

K^+ is a spectator ion and is ignored

From Table 18.1

Reduction half reactions



Yes. Because $E^\circ(\text{MnO}_4^-) > E^\circ(\text{Fe}^{3+})$

Self-Test 18.7B

Can $\text{Cl}_2(\text{g})$ oxidize $\text{H}_2\text{O}(\text{l})$ to $\text{O}_2(\text{g})$ in base.

Solution

Table 18.1



Yes. Because Cl_2 has larger E° .

Spontaneous direction of Redox.

Recall: Tables give reduction half reactions

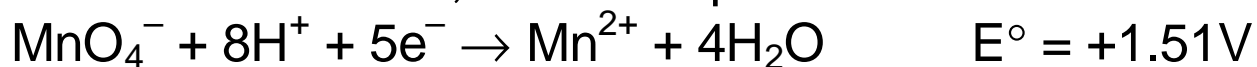
Rule:

Reverse half reaction having smaller E°

Then add half reactions

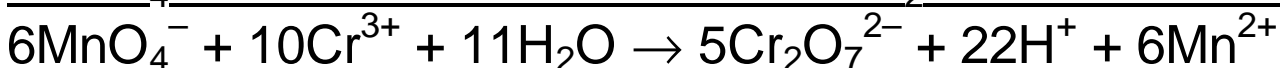
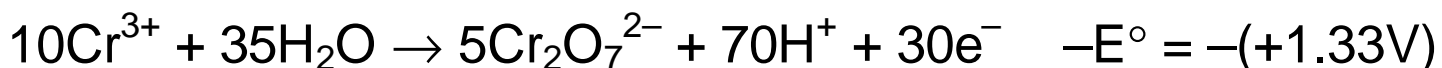
Example 18.6

Given the half reactions, write the spontaneous redox.



Solution:

Cr half reaction is reversed because E° is smaller.



$$E^\circ = 1.51 - 1.33 = +0.18\text{V}$$

Cell diagram:



Calculation of ΔG° for a cell

Example 18.7

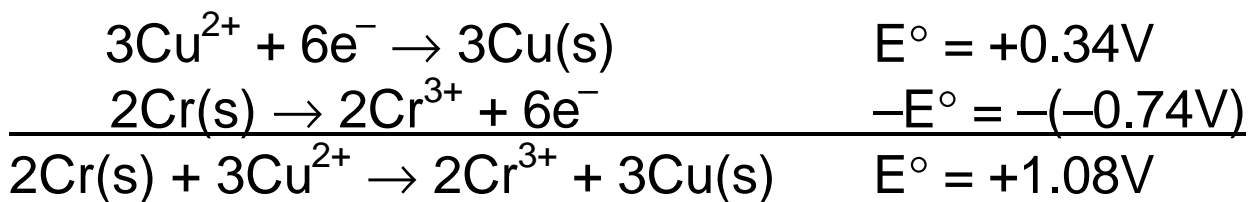
Calculate ΔG° for $\text{Cr(s)} \mid \text{Cr}^{3+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)}$

Solution:

First write half reaction from Appendix 2B



Second add half reactions and E° s



Third, calculate ΔG°

$$\begin{aligned}
 \Delta G^{\circ} &= -nFE^{\circ} \\
 &= -6 \times 96,500 (\text{C/mol}) \cdot 1.08\text{V} \\
 &= -625,000 \text{ C} \cdot \text{V/mol} && \text{C} \cdot \text{V} = \text{J} \\
 &= -625 \text{ kJ/mol}
 \end{aligned}$$

Spontaneous i.e. $\Delta G^{\circ} < 0$

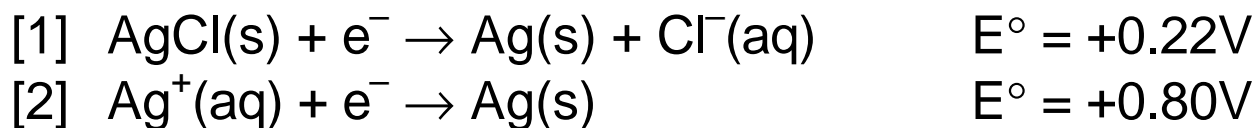
Example 18.8

Calculate solubility product K_{sp} at 25°C for
 $\text{AgCl(s)} \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$

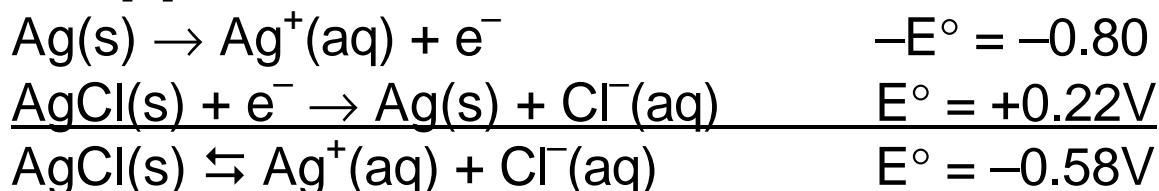
$$K_{\text{sp}} = [\text{Ag}^{+}][\text{Cl}^{-}]$$

Solution:

From Appendix 2B



Reverse [2] and add



$$\begin{aligned}\ln K_{sp} &= nFE^{\circ}/RT \\ &= (1) \times 96500 (\text{C/mol}) \times (-0.58 \text{V}) / [8.314 (\text{J/mol} \cdot \text{K}) \times 298 \text{K}] \\ &= -22.59 \quad \text{units cancel} \\ K_{sp} &= 1.54 \cdot 10^{-10}\end{aligned}$$

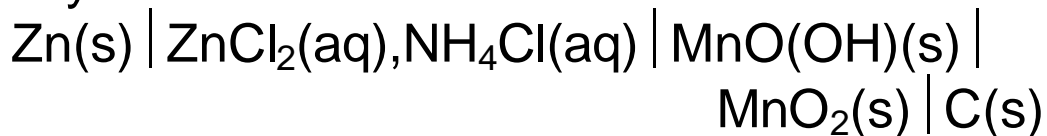
Batteries are galvanic cells

Primary cell

cannot be recharged

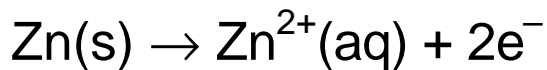
Example

Dry Cell



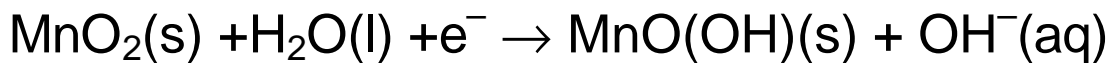
$$E = 1.5 \text{ V}$$

Anode



and $\text{NH}_3(\text{aq})$ coordinates with Zn^{2+}

Cathode



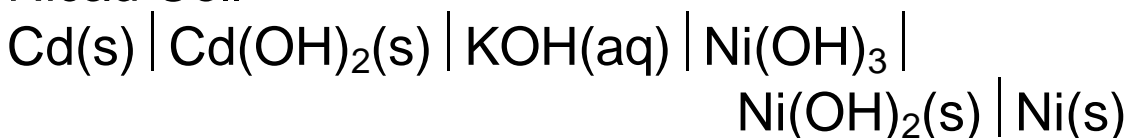
and NH_4Cl reacts with OH^{-}

Figure 18.17

Secondary Cell

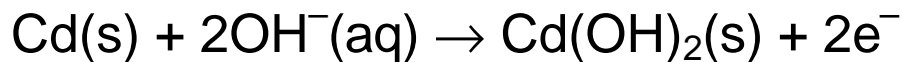
Can be recharged many times

Nicad Cell

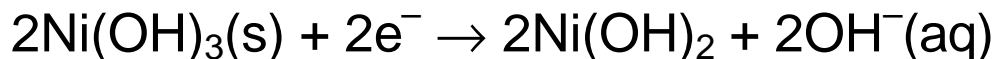


$$E = 1.25\text{V}$$

Anode



Cathode



Fuel cells are primary cells

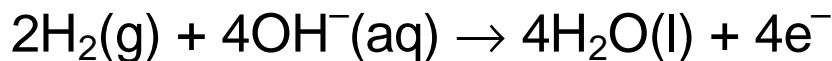
Usually gaseous reactants are used

Hydrogen or hydrocarbon at anode

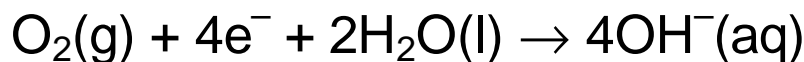
Oxygen at the cathode

Example is the space shuttle alkali fuel cell

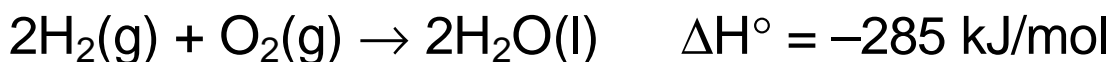
Anode



Cathode



Net reaction



Advantage: a high percentage of ΔH° is
converted to electricity.

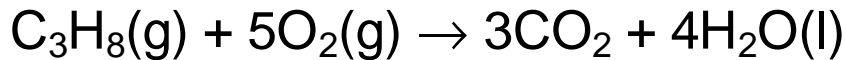
In power plants using combustion,

only about 30% of the heat is converted into electricity.

Example 18.10

Predict E° of fuel cell that uses propane

Reaction is:



Solution

First, determine ΔG°

$$\begin{aligned}\Delta G^\circ &= 4\Delta G_f^\circ(\text{H}_2\text{O}) + 3\Delta G_f^\circ(\text{CO}_2) - \Delta G_f^\circ(\text{C}_3\text{H}_8) \\ &= 4 \cdot (-237.13) + 3 \cdot (-394.36) - (-23.49) \\ &= -2108 \text{ kJ/mol}\end{aligned}$$

Next calculate E°

To determine n , use O_2 half reaction.



$$\begin{aligned}\text{Now } \Delta G^\circ &= -nFE^\circ \\ E^\circ &= -\Delta G^\circ/nF \\ &= -(-2108\text{kJ/mol})/(20 \times 96,500\text{C/mol}) \\ &= +1.093 \text{ V}\end{aligned}$$

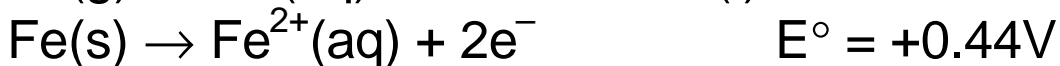
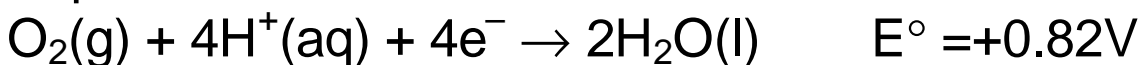
Corrosion

Oxidation of a metal

steel in cars, bridge girders, ships.

Usually involves water and oxygen

At pH 7



Since the sum of E's is positive,
corrosion is spontaneous.

It occurs more quickly when NaCl is present because water becomes more conductive.

Additional O₂ oxidizes Fe²⁺ to Fe₂O₃(s)

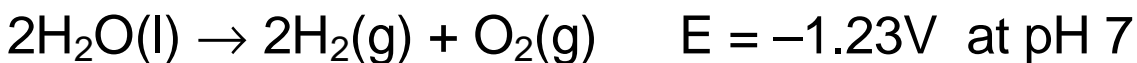
Electrolysis external voltage applied
Very important in industry

Examples

[1] Refine metals such as Cu and Ni



[2] Produce H₂(g) from water.



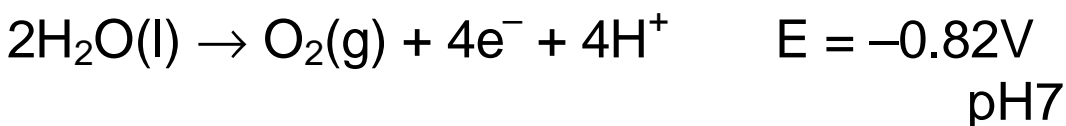
But an external voltage of 1.8 V must be applied to form H₂(g).

Extra 0.6V is an overpotential

Cathode



Anode



To increase the current in electrolysis an inert electrolyte must be in the solution.

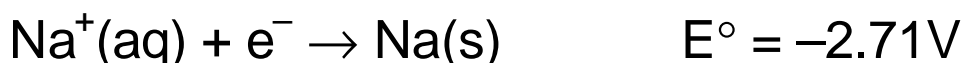
Question:

Is NaCl a suitable electrolyte for water electrolysis?

Solution:

Compare half cell potentials.

Cathode



Anode



Thus NaCl is a suitable electrolyte because:

[1] Reduction of H^+ requires 0.42V

compared to 2.71V for reduction of Na^+

[2] Oxidation of O in H_2O requires 0.82 V

compared to 1.36 V for Cl^- oxidation.

Note: This reasoning ignores overpotentials.

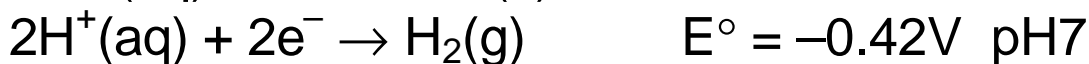
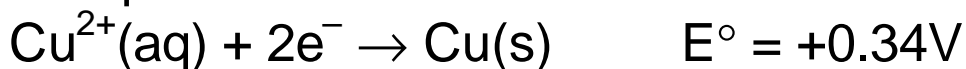
Can $\text{Cu}(\text{NO}_3)_2$ be used to electroplate Cu metal in water?

Solution:

Ions are $\text{Cu}^{2+}(\text{aq})$ and $\text{NO}_3^-(\text{aq})$ at pH7

These ions carry current in solution.

Two possibilities at cathode



Cu^{+} reduction occurs because it has higher E°

At anode

O_2 is formed because NO_3^{-} cannot be oxidized.

A similar answer applies to Self-Test 18.14A

Look at Example 18.11 also.

Self-Test 18.14B is similar to NaCl above.

Mass and moles of product of electrolysis.

a. Must know the number of coulombs passed.

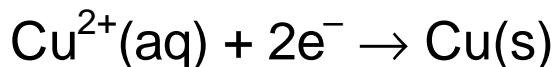
Recall: $1\text{mol e}^{-} = 96,500\text{C}$

b. Must know half reaction to relate moles of product to moles of e^{-} .

Example

Calculate number of moles of $\text{Cu}(\text{s})$ formed if 4mol e^{-} is supplied.

Answer



Thus, 1.0mole Cu gives 2moles e^{-}

And $n_{\text{Cu}} = (4 \text{ mol } e^-)(1 \text{ mol Cu})/(2 \text{ mol } e^-)$
 $= 2 \text{ mol Cu}$

Number of coulombs passed; Coul

$$\text{Coul} = I \cdot t$$

I is current in ampere (A)

$$1 \text{ A} = 1 \text{ C/s}$$

Example

Calculate Coul if $I = 2 \text{ A}$, is passed for 2 min.

Solution:

$$\begin{aligned} \text{Coul} &= I \cdot t \\ &= (2 \text{ C/s}) \cdot (2 \text{ min}) \cdot (60 \text{ s/min}) \\ &= 240 \text{ C} \end{aligned}$$

Calculate number of moles e^-

$$\begin{aligned} n &= \text{Coul}/F = 240\text{C}/(96500 \text{ C/mol}) \\ &= 2.5 \cdot 10^{-3} \text{ mol} \end{aligned}$$

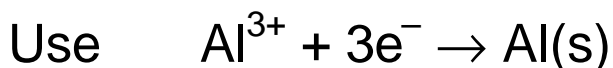
Thus, $n = I \cdot t/F$

This equation can be used to calculate n, I, or t

Example 18.12

Calculate mass of Al(s) produced by electrolysis of Al_2O_3 for 24 hours if

$$I = 1.00 \cdot 10^5 \text{ A.}$$



Solution

[1] Calculate n_e

$$n_e = I \cdot t / F$$

$$n_e =$$

$$(1.00 \cdot 10^5 \text{C/s}) \cdot (24 \text{hr})(3600 \text{s/hr}) / (96500 \text{C/mol})$$

$$n_e = 8.95 \cdot 10^4 \text{ mol}$$

[2] Calculate n_{Al}

$$\begin{aligned} n_{\text{Al}} &= n_e (1 \text{ mol Al}) / (3 \text{ mol e}^-) \\ &= 2.98 \cdot 10^4 \text{ mol} \end{aligned}$$

[3] Calculate m_{Al}

$$\begin{aligned} m_{\text{Al}} &= n_{\text{Al}} \cdot M_{\text{Al}} \\ &= (2.98 \cdot 10^4 \text{ mol}) \cdot (26.98 \text{g/mol}) \\ &= 8.05 \cdot 10^5 \text{ g} \end{aligned}$$

Example 18.13

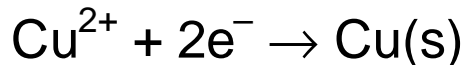
How many seconds are required to deposit 25.0g of Cu(s) if $I = 3.00\text{A}$?

Solution

[1] Moles of Cu

$$\begin{aligned} n_{\text{Cu}} &= m_{\text{Cu}} / M_{\text{Cu}} \\ &= 25.0 \text{g} / (63.5 \text{ g/mol}) \\ &= 0.394 \text{ mol} \end{aligned}$$

[2] Moles of e^-



$$\text{Thus, } n_e = 2n_{\text{Cu}}$$

$$= 2 \times (0.394 \text{ mol})$$
$$= 0.788 \text{ mol}$$

[3] Coulombs

$$\text{Coul} = n_e \cdot F$$
$$= (0.788 \text{ mol}) \cdot (96500 \text{ C/mol})$$
$$= 7.60 \cdot 10^4 \text{ C}$$

[4] Time

$$\text{Coul} = I \cdot t$$

And $t = \text{Coul}/I$

$$= (7.60 \cdot 10^4 \text{ C}) / (3.00 \text{ C/s})$$
$$= 2.53 \cdot 10^4 \text{ s}$$

Kinetics (continuation)

Zero order reaction



$$\text{Rate} = k$$

i.e. $\text{Rate} = k[\text{NH}_3]^0$

Determination of order using initial rates.

Example 13.3

Determine order for BrO_3^- using data below

Initial Concentration, mol/L

BrO_3^-	Br^-	H^+	Init. Rate
0.10	0.10	0.10	$1.2 \cdot 10^{-3}$
0.20	0.10	0.10	$2.4 \cdot 10^{-3}$

Solution:

$$\text{Rate} = [\text{BrO}_3^-]^a [\text{Br}^-]^b [\text{H}^+]^c$$

Take ratio of rates

$$\frac{2.4 \cdot 10^{-3}}{1.2 \cdot 10^{-3}} = \frac{[0.20]^a [0.10]^b [0.10]^c}{[0.10]^a [0.10]^b [0.10]^c}$$

$$2 = 2^a \quad \text{and} \quad a = 1$$

Thus, reaction is 1st order in BrO_3^-

Look at the rest of this example on page 578.

More complicated rate laws

$$\text{Rate} = k [\text{SO}_2][\text{SO}_3]^{-1/2}$$

Reaction is

1st order in SO₂

-1/2 order in SO₃

1/2 order overall

Look at Example 13.4

Self-Test 13.5B

Calculate remaining [C₃H₆] after 200s if

$$[\text{C}_3\text{H}_6]_0 = 0.100\text{mol/L}$$

$$\text{and } k = 6.7 \cdot 10^{-4}/\text{s}.$$

Solution

Units 1/s for k means 1st order.

$$\ln([\text{C}_3\text{H}_6]/ [\text{C}_3\text{H}_6]_0) = -kt$$

$$\ln([\text{C}_3\text{H}_6]/ [\text{C}_3\text{H}_6]_0) = -(6.7 \cdot 10^{-4}/\text{s})(200\text{s})$$

$$\ln([\text{C}_3\text{H}_6]/ [\text{C}_3\text{H}_6]_0) = -0.134$$

$$\text{and } [\text{C}_3\text{H}_6]/ [\text{C}_3\text{H}_6]_0 = 0.875$$

$$[\text{C}_3\text{H}_6] = 0.875 \cdot 0.100\text{mol/L}$$

$$= 0.0875\text{mol/L}$$

Look at example 13.5

Uses plotting method to determine k.

Activation energy E_a

Obtained from T dependence of k.

$$\ln k = \ln A - E_a/RT$$

A is the pre-exponential factor

Look at Example 13.7

Shows a graphical method for calculating E_a

You will be expected to know this method.

An alternate method for two data points

Example

<u>Temp °C</u>	<u>k, L/mol·s</u>
35	$2.8 \cdot 10^{-4}$
50	$1.4 \cdot 10^{-3}$

Calculate E_a .

Solution

$$\ln k_1 = \ln A - E_a/RT_1$$

$$\ln k_2 = \ln A - E_a/RT_2$$

$$\ln k_2 - \ln k_1 = - (E_a/R)(1/T_2 - 1/T_1)$$

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

$$E_a = - \frac{8.314(J / K \cdot mol) \ln(1.4 \times 10^{-3} / 2.8 \times 10^{-4})}{(1/323 - 1/308)(1/^\circ K)}$$

$$E_a = 89 \text{ kJ/mol}$$

When comparing T dependence:

Larger E_a means larger increase in k as T increases.

Reason for E_a

Based on collision of reactants

E_a is the minimum collision energy needed to cause reaction.

Called an energy barrier

Reaction profile

Plots energy barrier relative to energies of the reactants and products

Figure 13.21

Activated complex:

Arrangement of bonds of reactants at the top (E_a) of the barrier.

Catalyst

Speeds up reaction by reducing E_a .

It provides an alternate reaction path having lower E_a .

It is not consumed, i.e. its concentration does not change.

Two types of catalysts

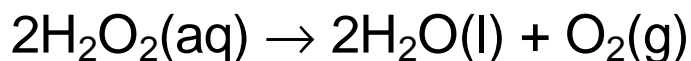
[1] Homogeneous Catalyst

Catalyst is in same phase as reactants

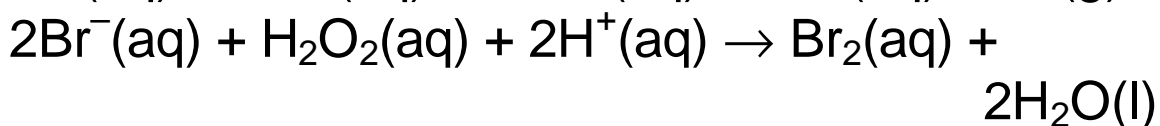
Example

Br_2 is catalyst for decomposition of H_2O_2

Overall reaction:



Details involve two steps:



These two steps are elementary steps.

Adding them gives the overall reaction

When added, the H^+ , Br_2 and Br^- cancel.

Another example: enzymes

- reactant called substrate

- substrate attaches to active site of enzyme

- substrate reacts at active site then leaves.

an inhibitor blocks active site

[2] Heterogeneous Catalyst

Usually a solid in contact with either a solution or gas of reactants.

Reactants attach to surface of solid and bonds are weakened.

-Bonds more easily broken

Radical chain reaction

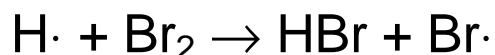
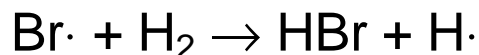
- A radical such as $\text{Br}\cdot$ reacts with a molecule to make another radical such as $\text{H}\cdot$
- Then $\text{H}\cdot$ reacts to form another $\text{Br}\cdot$

Usually has 3 kinds of elementary steps:

[1] Initiation



[2] Propagation



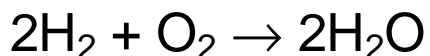
[3] Termination



Some radical reactions have branching steps:

Example:

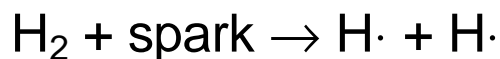
Combustion



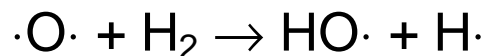
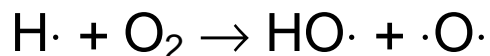
overall reaction

Mechanism

Initiation



Branching



Branching makes 2 radicals from one radical.
Thus, reaction rate increases rapidly.
Boom!