



Aalto University

# CHEM-E6100

## Fundamentals of chemical thermodynamics

*Week 2, Fall 2022*

# Contents

- **Thermochemistry, energy of system (Ch. 2)**
- **1<sup>st</sup> law of thermodynamics**
- **Enthalpy**
- **Specific heat**
- **2<sup>nd</sup> law of thermodynamics (Ch. 3)**
- **Entropy (Ch. 3& 4)**
- **Some practical functions of state (Ch. 5)**

# Learning outcomes for Week 2

- **Be familiar with the concepts of thermochemistry**
- **Understand the relations of heat, work and internal energy in connection to the 1<sup>st</sup> law of thermodynamics**
- **Understand the relations between enthalpy and heat capacity and how they are derived**
- **Understand the relations between entropy and the 2<sup>nd</sup> law of thermodynamics**

# Thermochemistry

- **A branch of chemistry that deals with the interrelation of heat with chemical reaction or physical change of state**
- **Thermochemistry describes and studies the behavior of thermal energy contained/stored by a system in various ‘processes’ and ‘transformations’**
- **It uses the general principle of conservation of mass in substances and processes**
- **No matter is generated or destroyed in the chemical reactions**

# Thermochemistry

- **All energy in thermochemistry can be measured at least in principle**
- **Thus there may be an accounting method for the changes in the energetic state of the entire system**
- **Calculations of**
  - Heat capacity
  - Heat of combustion
  - Heat of formation
  - Enthalpy
  - Entropy
  - Gibbs free energy

# Thermochemistry

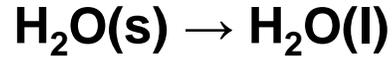
## Background findings in history

- **Lavoisier and Laplace's law (1780): The energy change in any transformation is equal and opposite to the energy change of the reverse process**



- **Hess' law (1840): The energy change in any transformation is the same whether the process happens in one or several steps.**
  - State functions are not dependent on the path.

# Observable examples of Lavoisier and Laplace's law



melting of ice

$$[0 \text{ }^\circ\text{C}, \Delta H^0 = +6000.7 \text{ J}\cdot\text{mol}^{-1}]$$



freezing of water

$$[0 \text{ }^\circ\text{C}, \Delta H^0 = -6000.7 \text{ J}\cdot\text{mol}^{-1}]$$

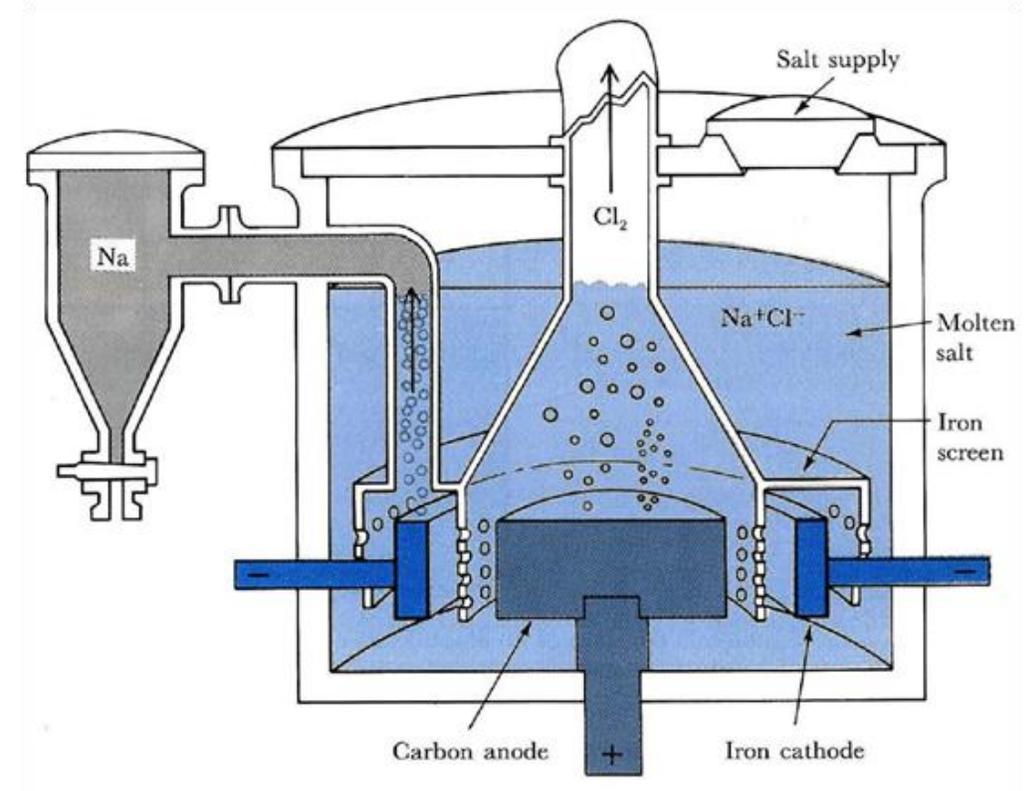
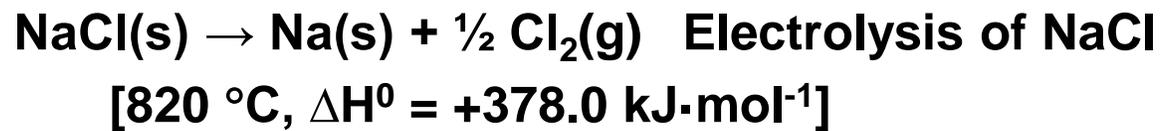
## Phase Change Materials (PCM)

- Used for energy storage
- Heating pads

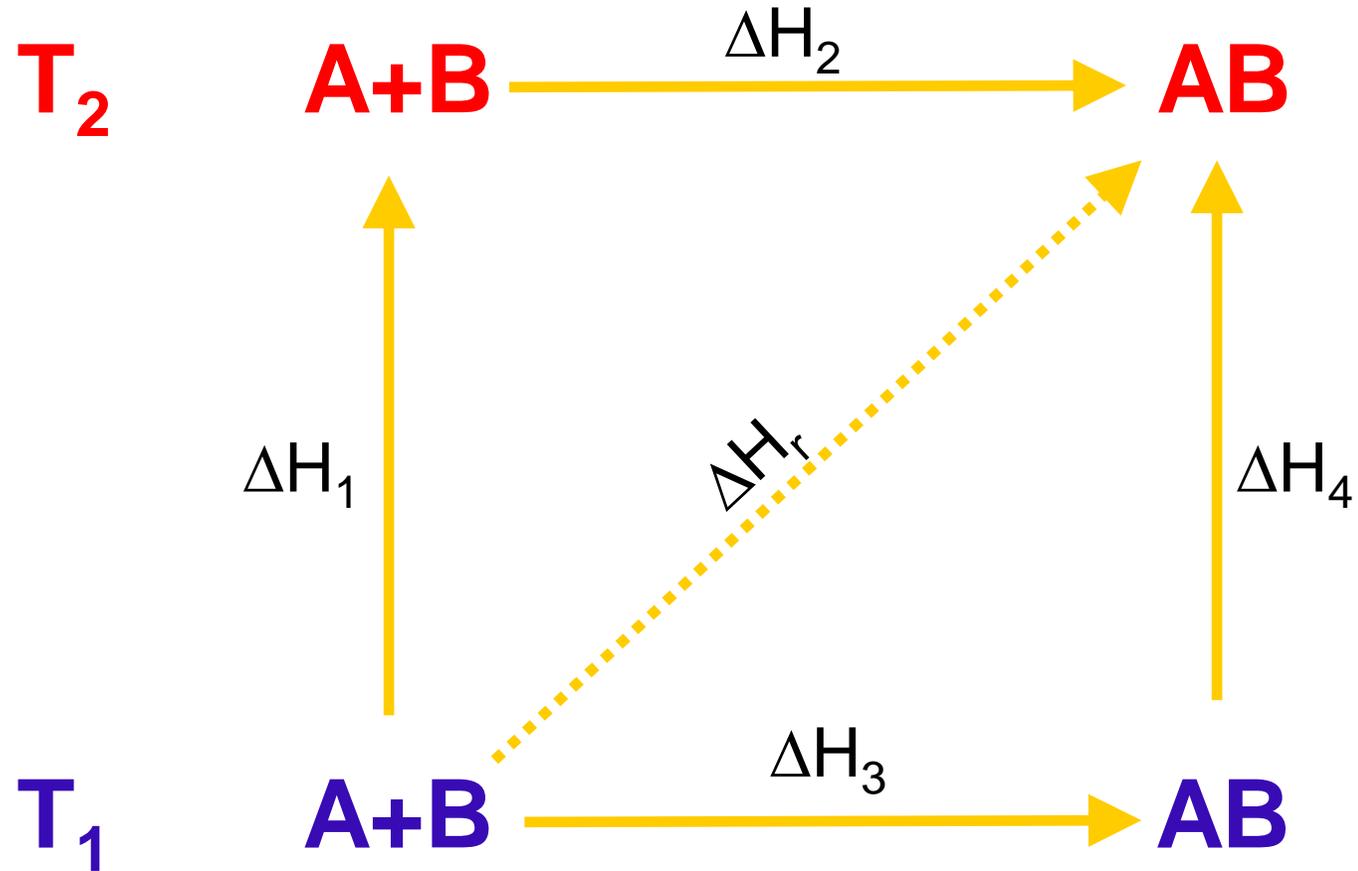


Example of heating pad

# Observable examples of Lavoisier and Laplace's law



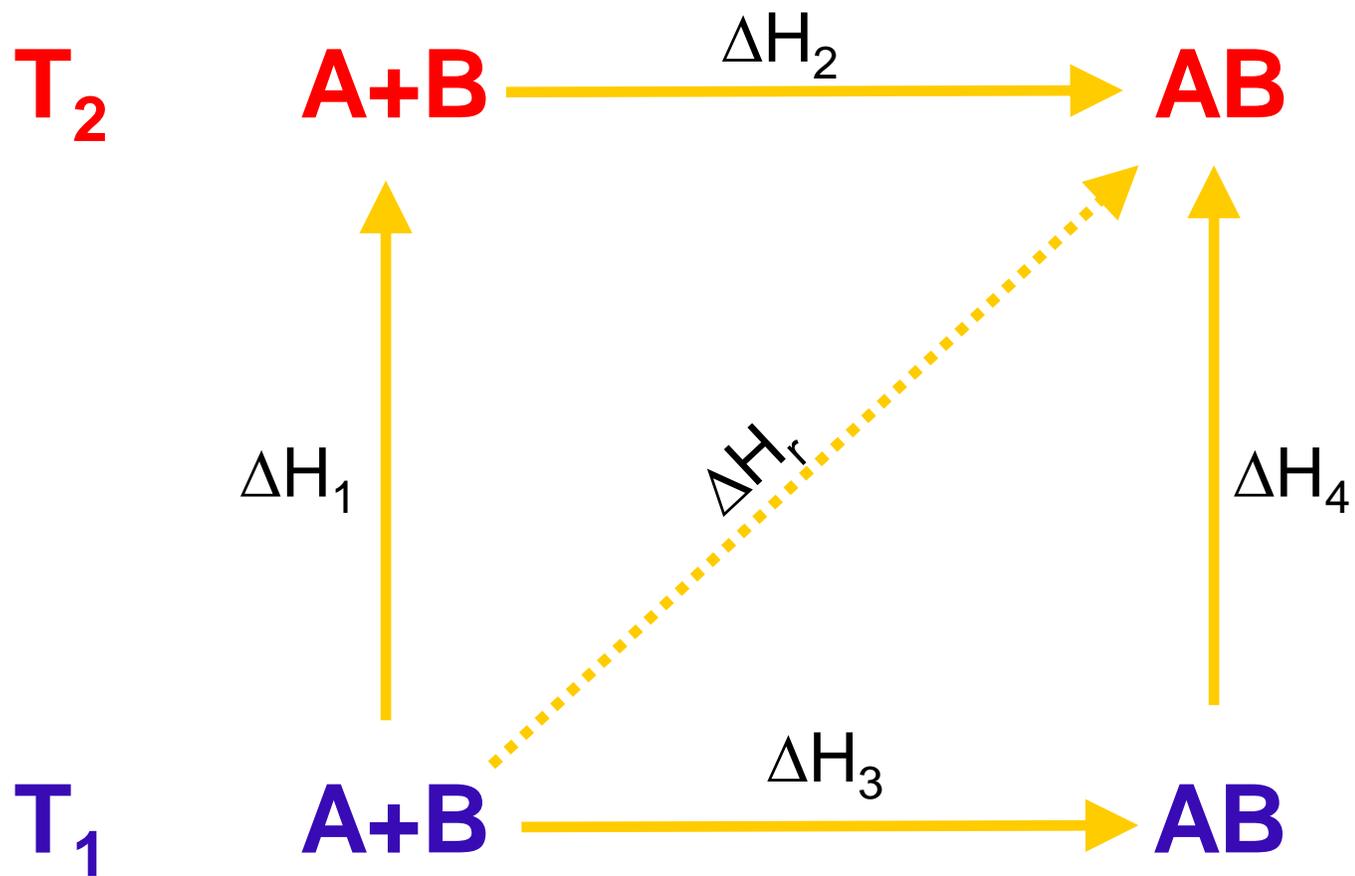
# Hess's law



The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions that can be used to describe the overall reaction

**Hess's law**

# Hess's law



$$\Delta H_r = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4$$

# Total energy of a system

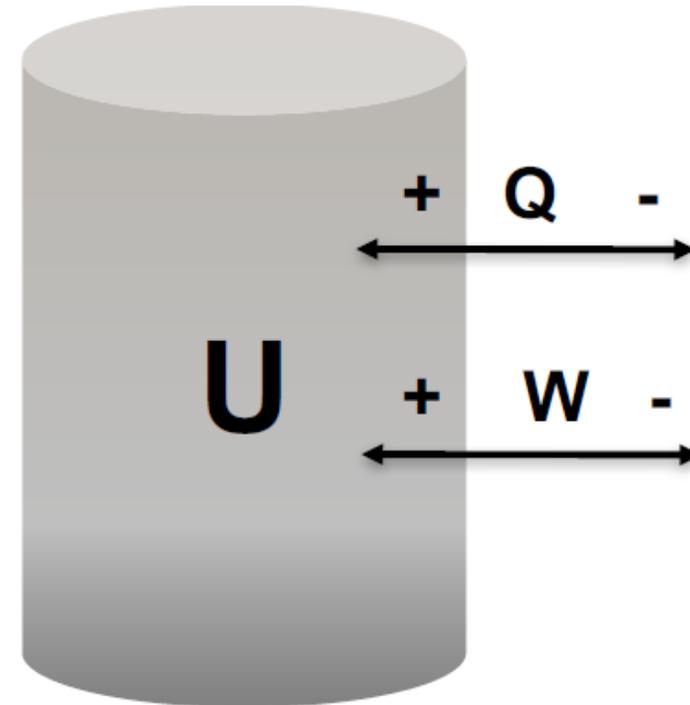
- **In general all systems can have energy transfer with its surroundings in two forms only:**
  - Heat across two different temperatures or a ‘temperature gradient’
  - Mechanical work
- **Total energy of a system in thermodynamics is called ‘internal energy’; its symbol is U**

# Total energy of a system

- **ISO 80000-5 definition:**
- **For a closed thermodynamic system,  $\Delta U = Q + W$  where  $Q$  is amount of heat transferred to the system and  $W$  is work done on the system provided that no chemical reactions occur.**
  - Energy ( $E$ ) is a quantity characterizing the ability of a system to do work
  - Heat, amount of heat ( $Q$ ) is the difference between the increase in the total energy of a physical system and the work done on the system, provided that the amounts of substances within the system are not changed ( $Q = \Delta U - W$ ).
  - Work  $W = \int P dt$ ,  $P = F \cdot v$  (Power = Force · velocity)

# Total energy of a system

- $\Delta U = Q + W$
- IUPAC sign convention is that energy transferred to a system is always positive, while energy removed from a system is negative



# Total energy, work and heat

- The work is positive, if the *surroundings* does work to the system (or raises its energy level)
- The value of work is negative, if the *system* does work to its surroundings (or releases energy as work).
- The (amount of) heat is positive, if the system *receives* heat (endothermic process) from its surroundings.
- Heat is negative, if system *loses* heat (exothermic process) or thermal energy to its surroundings

# Total energy of a system

- **The Internal energy (U) is a state function of a system, its value depends only on the current state of the system and not on processes to reach it**
- **U is an extensive quantity (depends on system size).**
- **$U=U(P, T, n_i)$**
- **“Heat” and “work” are defined only for processes, they are modes of energy transfer.**
- **Q and W used to calculate U are path functions.**
  - Often, but not always state functions use capital letters and path functions small letters.

# Total energy of a system

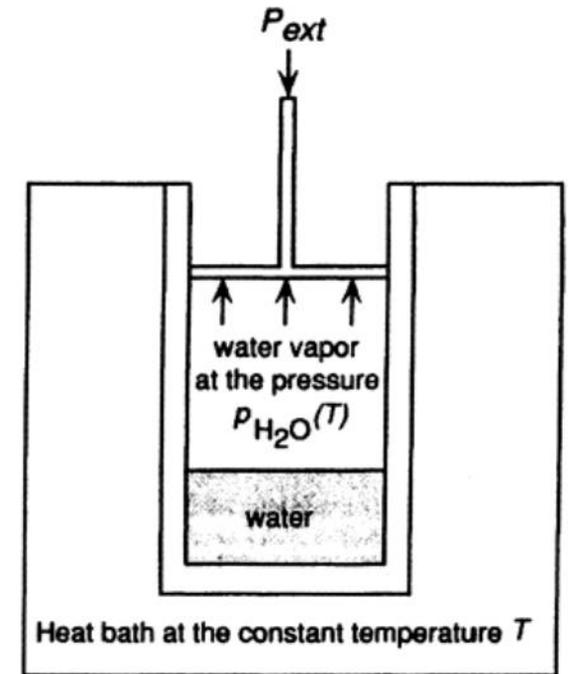
- **The absolute value of internal energy  $U$  in any system is not a measurable quantity**
- **The internal energy of given state of a system cannot be directly measured**
- **Internal energy is defined by changes starting from a reference state**
- **The reference state to determine the internal energy change has no general definition**
  
- **BUT usually in thermodynamics, standard state is 298.15 K and 1 bar (100 kPa)**

# Total energy of a system

- The internal energy of a system can change only in energy transfer between the system and its surroundings

By definition for closed system  $\Delta U = q + w$

- $q > 0$  and  $w > 0$ , heat and work to system
- $q > 0$  and  $w < 0$ , heat to system, work out
- $q < 0$  and  $w > 0$ , heat out from system, work to system
- $q < 0$  and  $w < 0$ , heat and work out from system
- $q = 0$ , adiabatic process



Source: Gaskell, *Introduction to the thermodynamics of materials*.

# 1<sup>st</sup> law of thermodynamics

- **The First law of Thermodynamics is a statement of the Principle of Conservation of Energy**
  - Energy can neither be created, nor destroyed
  - Energy can be transported or converted from one form to another
  - Chemical and/or physical changes are accompanied by changes in energy
- **IUPAC sign convention is that energy transferred to a system is always positive, while energy removed from a system is negative.**

# 1<sup>st</sup> law of thermodynamics

- The 1<sup>st</sup> law of thermodynamics is often written  $\Delta U=Q-W$
- The change of internal energy  $\Delta U$  of a closed system is equal to the amount of heat  $Q$  supplied to the system, minus the amount of work  $W$  done by the system on its surroundings.

# 1<sup>st</sup> law of thermodynamics

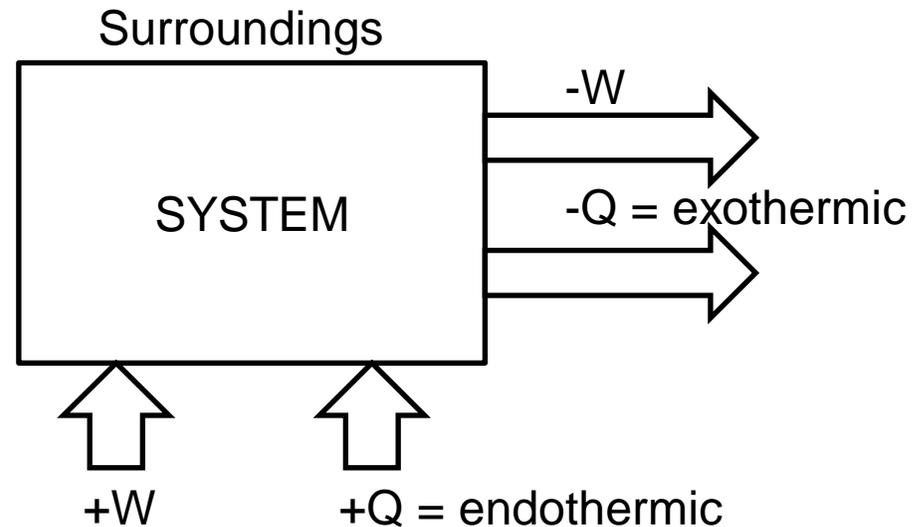
- Principle of conservation of energy
- Energy can be neither created nor destroyed. It can only change forms / In any process in an isolated system, the total energy remains the same.

$$\Delta U = Q + W$$

$$dU = dQ + dW$$

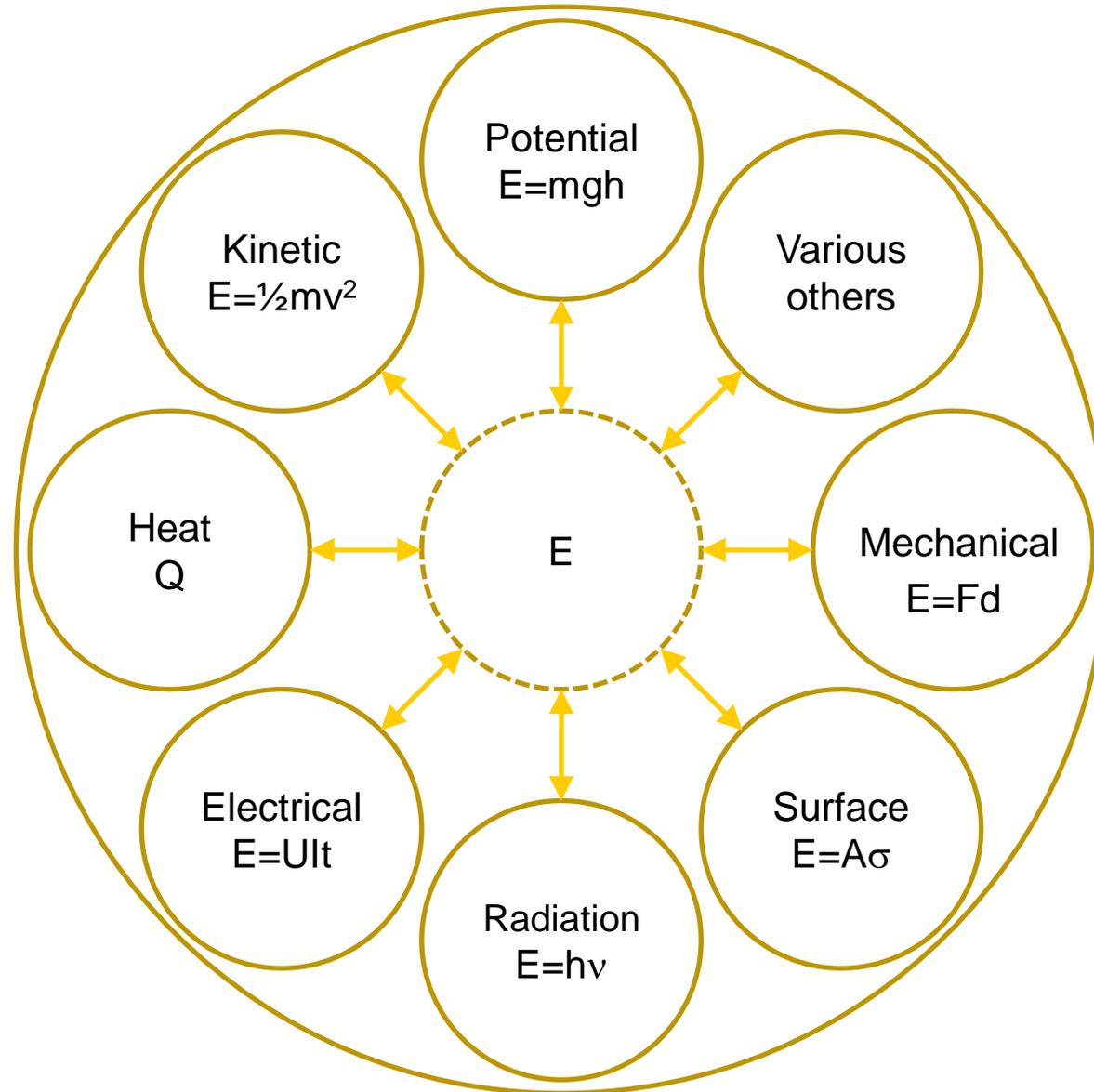
$$\Sigma dU = \Sigma dQ + \Sigma dW = 0$$

- U = internal energy
- Q = heat
- W = work



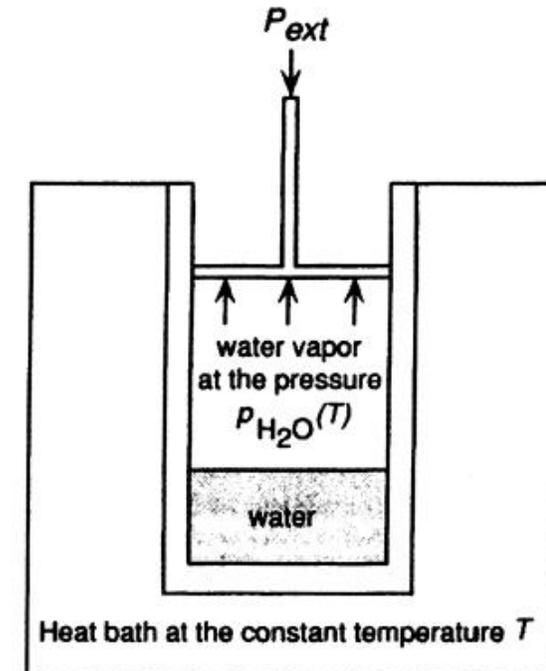
- $U$  = internal energy, sum of all forms of energy of the system
  - Kinetic energy: Sum of motions of particles – translational, rotational, vibrational
  - Potential energy: Chemical energy in chemical bonds, nuclear energy in configuration of elementary particles, etc.
- $Q$  = heat
  - When energy of the system changes as a result of temperature differences between the system and its surroundings, the energy has been transferred as *heat*
- $W$  = work
  - Work is done when an object is moved against an opposing force
  - Mechanical work: Pressure-Volume ( $-pdV$ ), elastic, surface
  - Electromagnetic: Charge transfer, electric polarization, magnetic polarization

# Conservation of energy



# Work of expansion

- In chemical systems the most important form of work is its work of expansion (in volume)
- The other forms of mechanical work have no importance in chemistry or chemical equilibria
- It is carried out (on the Earth) by the ambient atmosphere and its pressure



*Source: Gaskell, Introduction to the thermodynamics of materials.*

# Work of expansion

- The work done in expansion is:  $dw = -p_u dV$ ,  
where  $p_u$  is the external pressure and  $dV$  the change in system volume
- In constant volume processes we can always write  $dw = 0$  and thus  $dU = q$

# Enthalpy

- In a closed isobaric system, the work done by the system in state change 1→2 is

$$w = \int_1^2 P dV = P \int_1^2 dV = P(V_2 - V_1)$$

- 1st law of thermodynamics gives an equation for the change of the internal energy as

$$U_2 - U_1 = q_p - P(V_2 - V_1)$$

- The change in the heat of the system  $\Delta q$  is

$$\Delta q = q_2 - q_1 = q_p = (U_2 + PV_2) - (U_1 + PV_1)$$

- By definition  $U + PV$  is the enthalpy  $H$
- $H = U + PV$

# Enthalpy

- By definition enthalpy is a sum of total energy and term  $PV$  or  $H \equiv U + PV$
- Enthalpy is composed of state functions  $U$ ,  $P$  and  $V$ , and thus is a state function itself
- As the absolute value of  $U$  is not known also that of  $H$  is not known or measurable by experiment
- Enthalpy is the amount of heat released or absorbed by the system in an isobaric process
- Enthalpy is a function of only two state variables and the size of the system, for example  $H = H(P, T, n_i)$

# Enthalpy change in a reaction

- The enthalpy change of a chemical reaction is a difference of the enthalpies of its product(s) and reactant(s)
- For a reaction in a closed system
- $aA + bB + \dots = mM + nN + \dots$
- We always get the change of enthalpy or its heat of reaction from equation
- $\Delta H = \sum \nu_{product} H_{product} - \sum \nu_{reactant} H_{reactant}$   
where  $H_i$  are enthalpies of the substances  $i$  and  $\nu_i$  are their stoichiometric numbers in the chemical reaction above.

# Enthalpy change in a reaction

- In general, enthalpy of a heterogeneous system, composed of volumes  $\alpha$  is sum of enthalpies of the volumes or

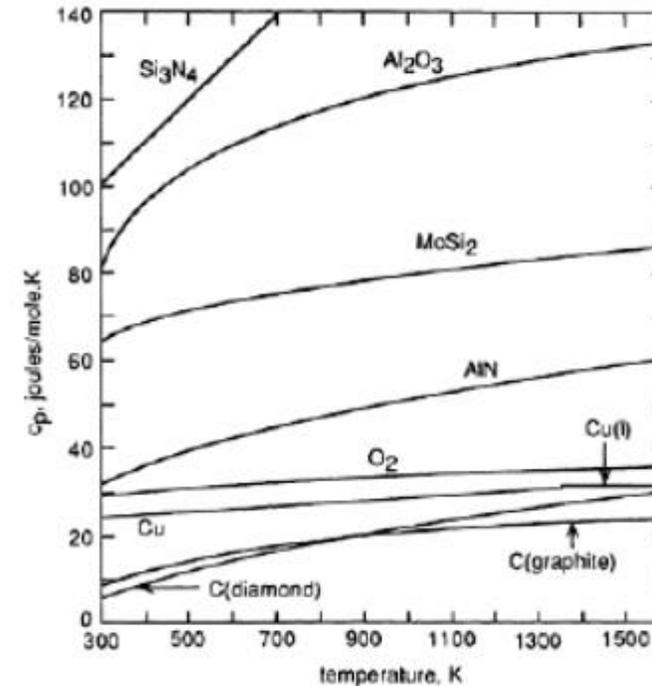
$$H_{\text{tot}} = \sum_{\alpha} H^{\alpha}$$

- This means that total enthalpy of a heterogeneous system is an additive property

# Heat capacity

- The key variable and tool in thermochemistry is a property of a substance called *heat capacity*
- It is also called *specific heat*(of a system or substance).
- In general it is the derivative of heat content  $q$  in reference with temperature

$$C = dq/dT$$



Source: Gaskell, *Introduction to the thermodynamics of materials*.

# Heat capacity

- In practical cases, heat capacity is defined and measured either in constant pressure or constant volume

$$C_p = (dq/dT)_p = dq_p/dT \quad \text{in constant pressure}$$

$$C_v = (dq/dT)_v = dq_v/dT \quad \text{in constant volume}$$

The subscript refers to the constant variable of state

# Heat capacity

Heat capacity, **C**, is the amount of heat required to change a substance's temperature by a given amount.

$$dU = dQ + dW_{PV} + dW_{\text{non-e}}$$

- If volume = constant  $\rightarrow$  No expansion work possible ( $dW_{PV}=0$ )
- Assuming no additional non-expansion work ( $dW_{\text{non-e}}=0$ )



$$dU = dQ_V$$

$$\Delta U = Q_V$$

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V$$

$C_V$  is the heat capacity at constant volume of a substance

$$dU = C_V dT$$

# Heat capacity and enthalpy

Enthalpy,  $H$  is defined as

$$H = U + PV$$

- If pressure is constant

$$dH = dQ_p$$

$$\Delta H = Q_p$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_p$$

$C_p$  is the heat capacity at constant pressure of a substance

$$dH = C_p dT$$

Due to the practical importance,  $Q_p$  measured by calorimetry can be easily related to  $\Delta H$ . Enthalpy is often called heat content

# Heat capacity

- **Heat capacity of a substance is a discontinuous property (specific to each substance)**
- **Its derivative is not continuous (i.e. contains points of discontinuity).**
- **It is non-negative for all stable substances**
  - For ions of aqueous solutions it may be negative, but that feature is result of its definition ('model') and it is not a property of a ('real') substance

# $C_p$ and $C_v$ functions

- $c_p$  is larger in value than  $c_v$  due to the fact that in constant volume processes the entire heat is consumed in changes of the system temperature
- One can show that
$$c_p - c_v = P(dV/dT)_p$$
(derivation: pp 23-24 in Gaskell 5<sup>th</sup> ed.)
- Heat capacity of a system is a function of pressure, temperature and amounts, but its molar value depends only on pressure and temperature; thus we can write  $c = c(P,T)$

# $C_p$ and $C_v$ functions

- $c = c(P,T)$  and in constant pressure  $c_p = c_p(T)$
- The value of  $c_p$  at different temperatures is given by Kelley or Maier-Kelley equation.
- Tabulated Kelley equation regression coefficients describe the polynomial series for the specific heat capacity at constant pressure

$$c_p = a + b \cdot T - c \cdot T^{-2}$$

- $dH = c_p dT$                        $(dU = c_v dT)$
- $\Delta H = \int c_p dT$                        $(\Delta U = \int c_v dT)$

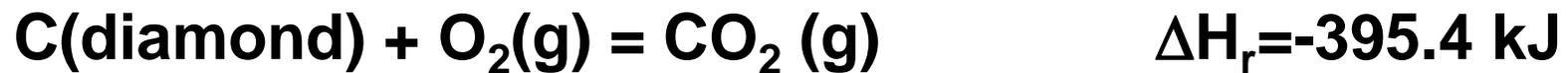
# Examples

- Calculate the heat of combustion of CO



# Examples

- Calculate the heat of transition of C(diamond)→C(graphite)



# Examples

- Calculate the heat required to heat metallic Lithium from 25 °C to 100 °C
- $C_p = 9.6 + 0.041T + 248117 T^{-2} \text{ J}/(\text{mol K})$

## Rules for Integrals

### Power Rule

$$\int x^n dx = \frac{x^{n+1}}{n+1} + C \quad n \neq -1$$

$$\int x^{-1} dx = \ln |x| + C$$

### Exponential

$$\int e^x dx = e^x + C$$

$$\int a^x dx = \frac{a^x}{\ln a} + C$$

### Constant Multiples

$$\int kf(x) dx = k \int f(x) dx$$

### Absolute Value

$$\int |x| dx = \frac{x|x|}{2} + C$$

### Sums and Differences

$$\int [f(x) + g(x)] dx = \int f(x) dx + \int g(x) dx$$

$$\int [f(x) - g(x)] dx = \int f(x) dx - \int g(x) dx$$

# Example



$q$   
 $w$  ?  
 $\Delta U$

# 2<sup>nd</sup> law of thermodynamics

- First law of thermodynamics identifies allowed changes in a system
- Second law identifies spontaneous changes among the allowed changes by introducing the state function **Entropy, S**
- **The entropy of a system and its surroundings increases in the course of a spontaneous change,  $\Delta S_{\text{total}} > 0$**
- For an open system
$$dS + dS_{\text{sur}} \geq 0$$
(= for reversible equilibrium process, > for non-reversible process)

For isolated systems  $dS \geq 0$

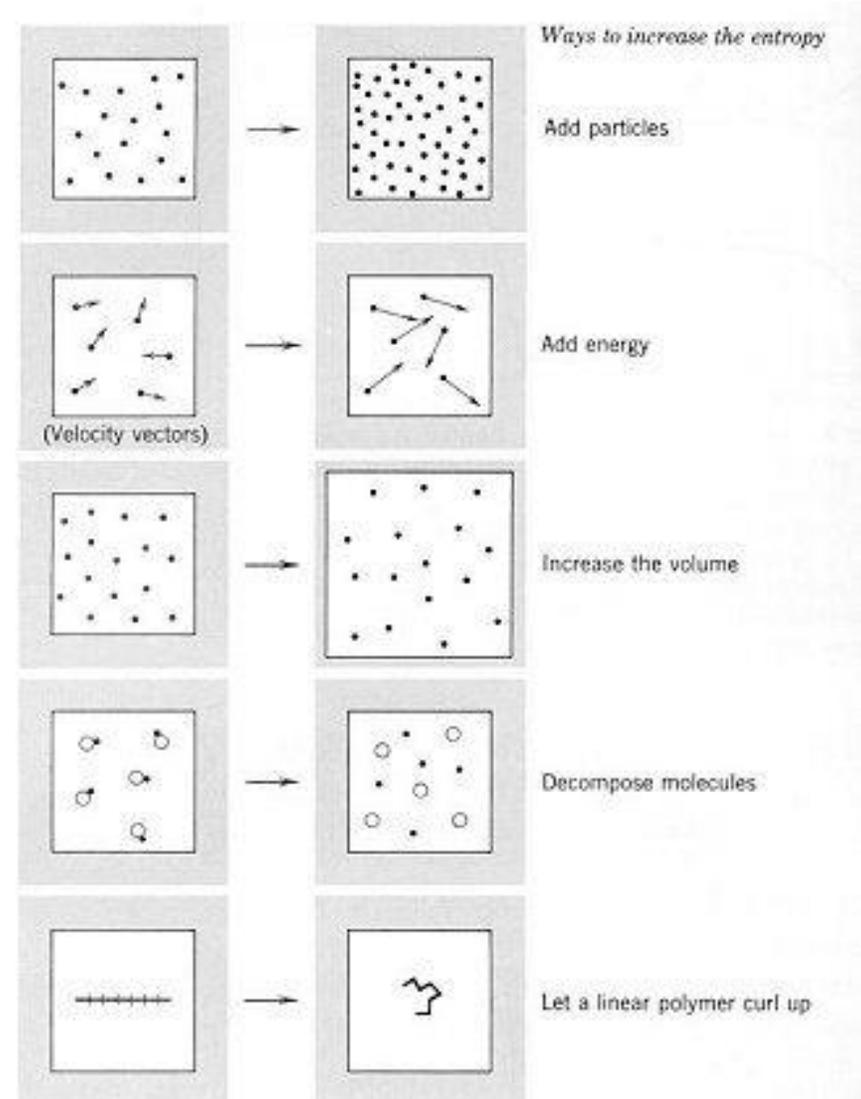
# 2<sup>nd</sup> law of thermodynamics

## *Semantics*

- Heat cannot be extracted from a body and turned entirely into work
- Every system left to itself will, on the average, change toward a condition of maximum probability
- You can't shovel manure into the rear end of a horse and expect to get hay out of its mouth

# Entropy, S

- The entropy of a system, S, is an extensive state property which is given by Boltzmann's equation as:
- $S = k_B \ln W$ 
  - $k_B$  = Boltzmann's constant
  - W (or  $\Omega$ ) is the multiplicity of the system ~ the number of possible equivalent microstates in a macrostate
- S can loosely be said to be a measure of the disorder of a system.



Factors that tend to increase the entropy of a system.

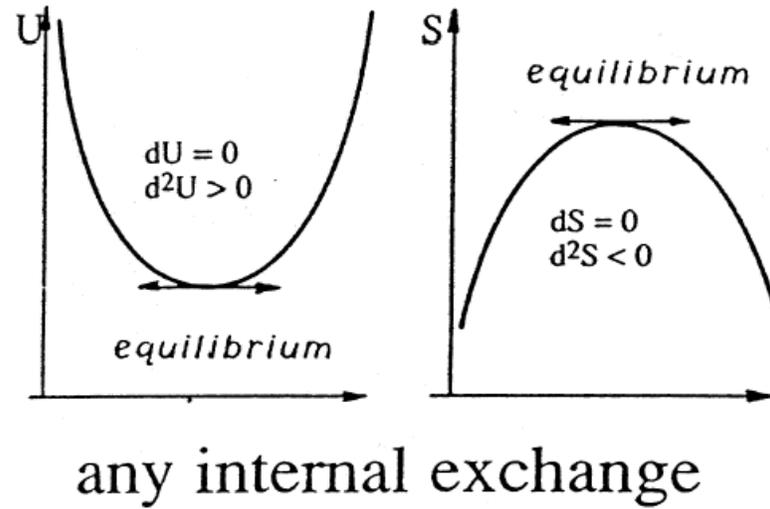
# 2<sup>nd</sup> law of thermodynamics

- The 2<sup>nd</sup> law of thermodynamics defines a new state function called entropy  $S$
- It is a property of a substance *we cannot measure directly*
- The need for this definition is the question: how much work a system can generate in a change of state when its properties change in a process  $1 \rightarrow 2$ ?
- Together with the 1<sup>st</sup> law it give the 'rule' how the thermodynamic description of a substance is given in the phase transformations as well as in chemical reactions.

# Features of entropy

- Entropy is often characterized in textbooks using the Carnot cycle, which analyses the features of heat engines; it is not illustrative for chemical processes and reactions
- Entropy  $S$  has the following properties in any change or process of an isolated system
- $\delta S = 0$  equilibrium of a system
- $\delta S > 0$  a spontaneous adiabatic change of the system
- $\delta S < 0$  a forced adiabatic change of the system

# Features of entropy



**The general principle of conservation of energy and the behavior of entropy in the minimum point of total energy (the state of equilibrium)**

# Features of entropy

- The change of entropy is connected with the thermal energy ( $\delta q$ ) of a system in very slow ('quasistatic') transformations or processes described as

$$dS = \delta q/T \text{ or } \delta q = TdS$$

- When the work of expansion made by the system is  $PdV$ , we get from the 1<sup>st</sup> law of thermodynamics

$$dU = TdS - PdV$$

# Features of entropy

- We can thus write the internal energy as  $U=U(S,V)$  and its total differential with entropy and volume as state variables is of the general form

$$dU = (\partial U/\partial S)_V dS + (\partial U/\partial V)_S dV$$

- A comparison of the above equations we get the relations:
- System temperature  $T = (\partial U/\partial S)_V$
- System pressure  $P = -(\partial U/\partial V)_S$

# Entropy change in reactions

- The change of entropy in chemical reactions is obtained analogically with enthalpy and it follows the common principles of calculating changes of state functions.
- It is difference between entropies of products and reactants as given in the following equation:

$$\Delta S = \sum \nu_{product} S_{product} - \sum \nu_{reactant} S_{reactant}$$

- In heterogeneous systems entropy is thus an additive property

$$S_{tot} = \sum_{\alpha} S_{\alpha}$$

# Statistical interpretation of entropy

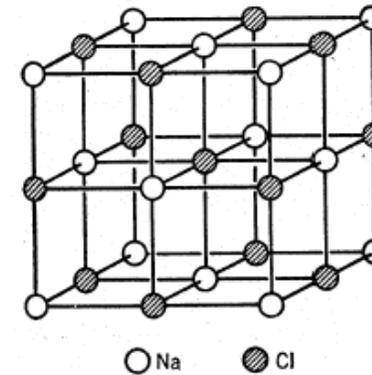
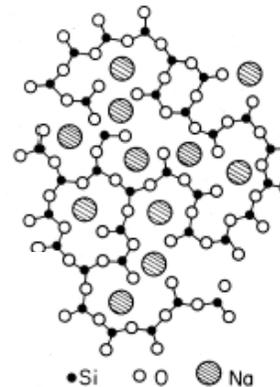
- **The 2<sup>nd</sup> law of classical thermodynamics and its physical meaning is difficult to understand, even if we can see that entropy is a well defined state function of a system in a similar way as its internal (or total) energy**
- **The validity of entropy and justification of 2<sup>nd</sup> law is the fact that perpetual motion machine has not been invented**
- **Invention of quantum mechanics brought some light in it.**

# Statistical interpretation of entropy

## Chapter 4 in Gaskell

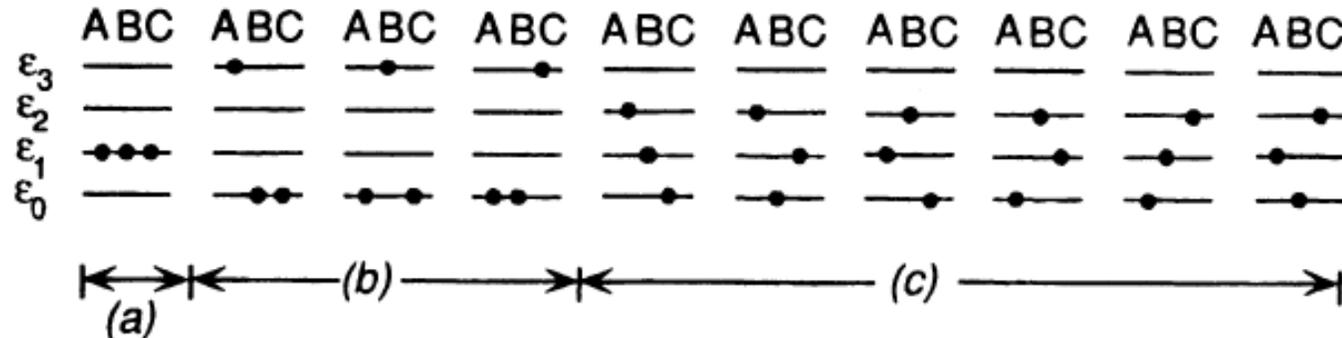
- Entropy is in qualitative sense the measure of disorder of the system
- The more equally its particles are mixed, the higher its entropy
- In a liquid, the disorder is higher than in a solid (i.e. crystalline) phase.

Na-silicate melt and  
NaCl crystal (lattice)

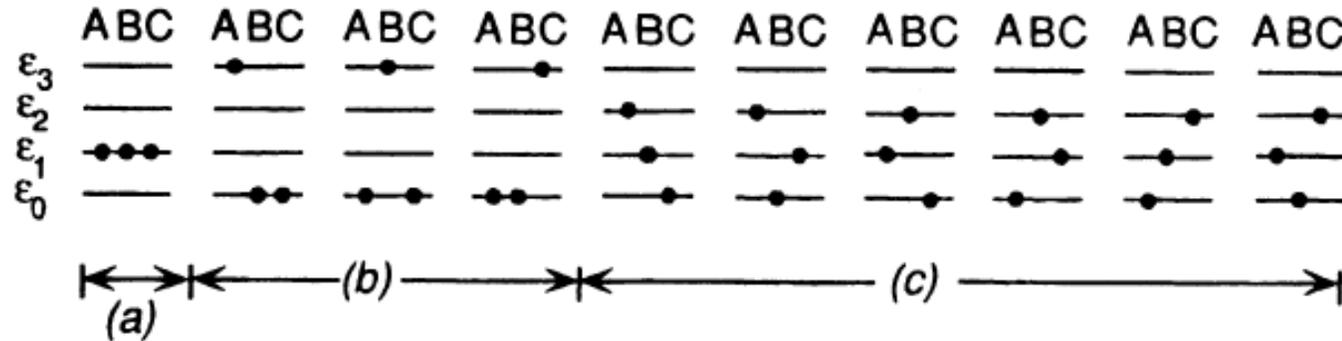


# Microstates of a system

- Assuming a particle system of four energy levels  $\varepsilon_0$ ,  $\varepsilon_1$ ,  $\varepsilon_2$ , and  $\varepsilon_3$  having an energy difference of  $u$ .
- Particle energy on level 0 is 0, and on level 3 it is  $3 \times u$ .
- The key question is how the particles (A, B and C) can be divided between the levels and maintain the system total energy  $E$ , for example  $E = 3 \times u$ ?



# Microstates of a system



- (a) put all on level 1 and thus  $E=3 \times 1u = 3 \times u$
- (b) one particle on level 3 and the other two on 0, with  $E = 2 \times 0u + 1 \times 3u$
- (c) one on levels 2, 1 and 0, respectively, with  $E = 1 \times 0u + 1 \times 1u + 1 \times 2u$
- **The number of all different configurations of A,B, and C, they are *microstates* of the macrostate**

# The number of microstates

- The macroscopic state of a system is defined by its independent state variables and its 'appearance' is the internal energy  $U$
- When a number of system's particles increases, the number of its microstates increases (e.g. 1 mol =  $6.023 \times 10^{23}$  atoms or molecules) is a lot
- The number of microstate in a situation with  $n$  particles and  $n_0$  locating on level  $\varepsilon_0$  and the highest level is  $\varepsilon_r$  with  $n_r$  particles is in general

$$\Omega = n! / (n_0!n_1!\dots n_r!) = n! / \prod_{i=0..r} n_i!$$

# The number of microstates

- In case of the previous example, possibilities for distributions a-c are thus
- $\Omega(\text{a}) = 3!/(3!0!0!) = 1$
- $\Omega(\text{b}) = 3!/(2!1!0!) = 3$
- $\Omega(\text{c}) = 3!/(1!1!1!) = 6$
  
- Total energy of the system is now:
- $U = \text{constant} = n_0\varepsilon_0 + n_1\varepsilon_1 + \dots + n_r\varepsilon_r = \sum_{i=1..r} n_i\varepsilon_i$

# The number of microstates

- **Total number of particles in the system is constant  $n$  and thus we can write**
- $$n = n_0 + n_1 + n_2 + \dots + n_r = \sum_{i=1 \dots r} n_i$$
- **Internal equilibrium of the system according to 1<sup>st</sup> law of thermodynamics is valid for the changes of microstates**
- $$\delta U = \sum_i \varepsilon_i \delta n_i = 0 \quad \text{and} \quad \delta n = \sum_i \delta n_i = 0.$$
- **If distribution function  $\Omega$  has maximum in this point,  $\delta(\ln \Omega) = 0$  and further**
- $$\delta \ln \Omega = -\sum_i (\delta n_i \ln n_i) = 0.$$

# The number of microstates

- **The point of maximum can be solved and it is**
- $n_i = n \times \exp(-\beta \times \varepsilon_i) / P,$
- **where  $P$  is called partition function and  $\beta$  is defined by equation**
- $\Sigma \exp(-\beta \times \varepsilon_i) = e^{-\beta \varepsilon_0} + e^{-\beta \varepsilon_1} + \dots ,$
- where  $\beta = 1/(kT)$  and  $k = R/N_0$ ; the factor  $k$  is Boltzmann constant and  $N_0$  Avogadro's constant.
- **This means that the most probable state of equilibrium is such where the particles have the lowest energy.**

# Boltzmann equation

- **Total energy of a system is**
- $$U = \sum_{i=1..r} n_i \varepsilon_i$$
- **and the  $n_i$  of the equilibrium point results in**
  - $U = \sum_{i=1..r} n_i \varepsilon_i = \sum_i (n/P) \times \varepsilon_i \times \exp(-\varepsilon_i/kT)$  or
  - $UP/n = \sum_i \varepsilon_i \times \exp(-\varepsilon_i/kT)$ .
- **Because particle reorganisation to their equilibrium configurations requires energy transfer, it causes changes in internal energy in isochoric and isothermic systems.**

# Boltzmann equation

- Thus it is valid as  $P$  is only  $P=P(T,\varepsilon)$ :
- $$\delta \ln \Omega = \delta U/kT = \delta S/k$$
- Integral of above equation is known as Boltzmann equation
- $$S = k \ln \Omega$$
- where  $\Omega$  is the maximum number of possible configurations in the system.
- Boltzmann's constant ( $k$ ) times Avogadro's number ( $N_0$ ) equals the gas constant ( $R$ ).

# Boltzmann equation

- Boltzmann equation  $S = k \ln \Omega$  is the quantitative relationship between the entropy of a system and its “degree of mixed-up-ness”.
- The latter, given by  $\Omega$ , is the number of ways in which the energy of the system can be distributed among the particles.
  - *The most probable state of the system is that in which  $\Omega$  has a maximum value, consistent with the fixed values of  $U$ ,  $V$ , and  $n$ .*
  - *Hence the equilibrium state of the system is that in which  $S$  is a maximum, consistent with the fixed values of  $U$ ,  $V$ , and  $n$ .*

# Some 'auxiliary' functions

- In the practical equilibrium calculations, only a limited set of thermodynamic state functions are used
- The key tools are combinations of the functions given above.
- The properties of substances which can be measured experimentally are (only) enthalpies, in particular their changes, as well as the changes of two 'auxiliary functions', Gibbs and Helmholtz energies

# Helmholtz energy

- Helmholtz (free) energy is defined as sum of system internal energy  $U$  and the term  $-T \times S$   
$$A \equiv U - T \times S$$
- Helmholtz energy is equal to the maximum amount of work that the system can perform in an isochoric thermodynamic process (constant volume)
- The Helmholtz free energy minimum provides a criterion for equilibrium in a system at constant temperature and constant volume
- $A$  is a state function  $A = A(P, T, n_i)$  and total Helmholtz energy of the system is the sum of its volumes'  $A$  functions

# Gibbs energy

- An analogous variable with Helmholtz energy is the system's Gibbs (free) energy
- It is defined as sum of system enthalpy  $H$  and the term  $-T \times S$  as

$$G \equiv H - T \times S$$

- Gibbs energy is the sum of state functions, it is also a state function  $G = G(P, T, n_k)$  and total Gibbs energy of a system is the sum of its volumes'  $G$  functions
- Gibbs energy has a specific role almost in all technical applications of chemical thermodynamics because it controls isobaric processes which is characteristic to most industrial reactors and reactions

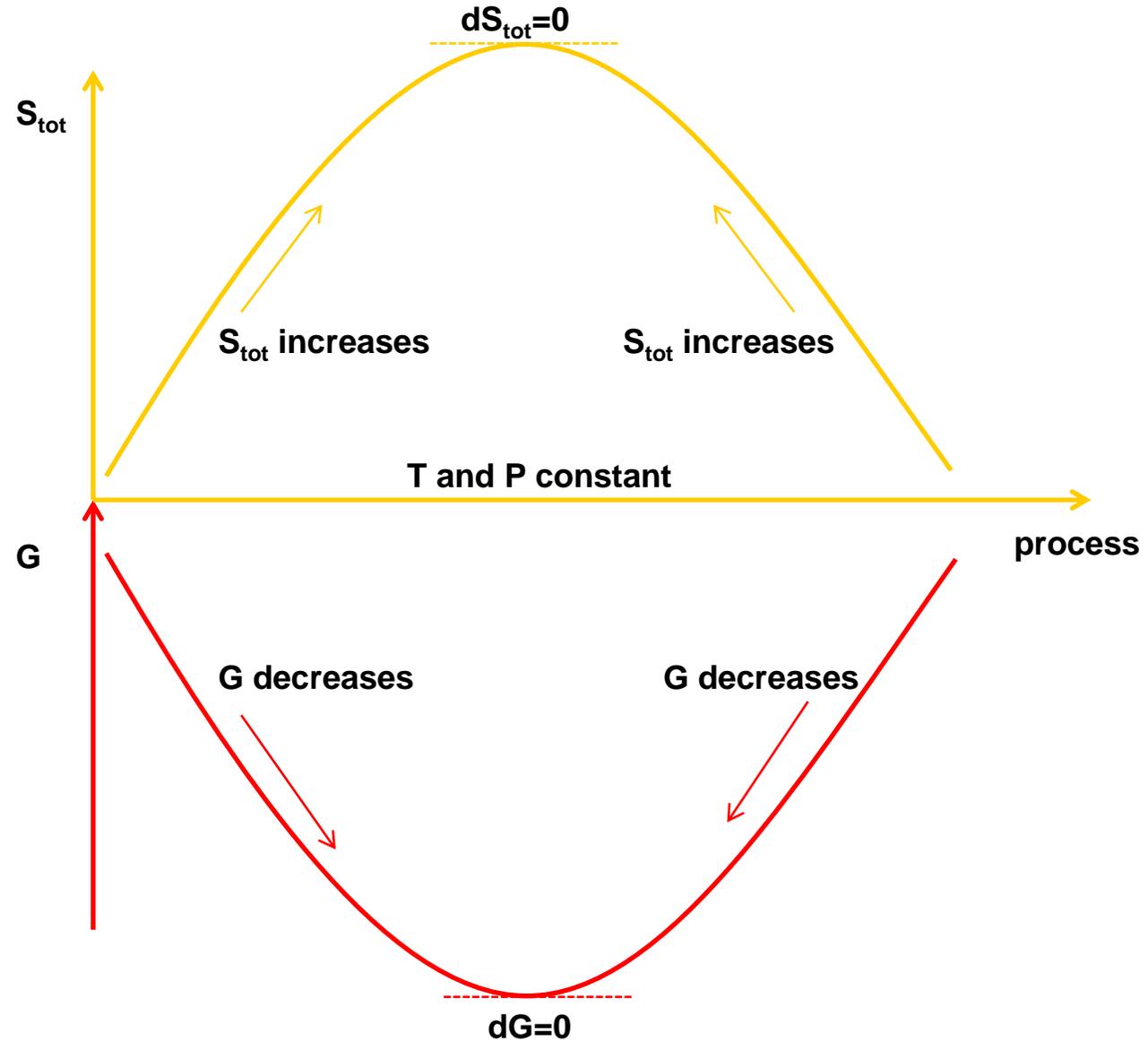
# Gibbs and Helmholtz energy

- **Gibbs (G) and Helmholtz energy (A) are sometimes connected to the term "free energies"**
- **The change in Helmholtz energy,  $\Delta A$ , gives the maximum amount of work a system can do at isothermal conditions**
- **The change in Gibbs energy,  $\Delta G$ , gives the maximum amount of non-expansion work a system can do at constant P and T**

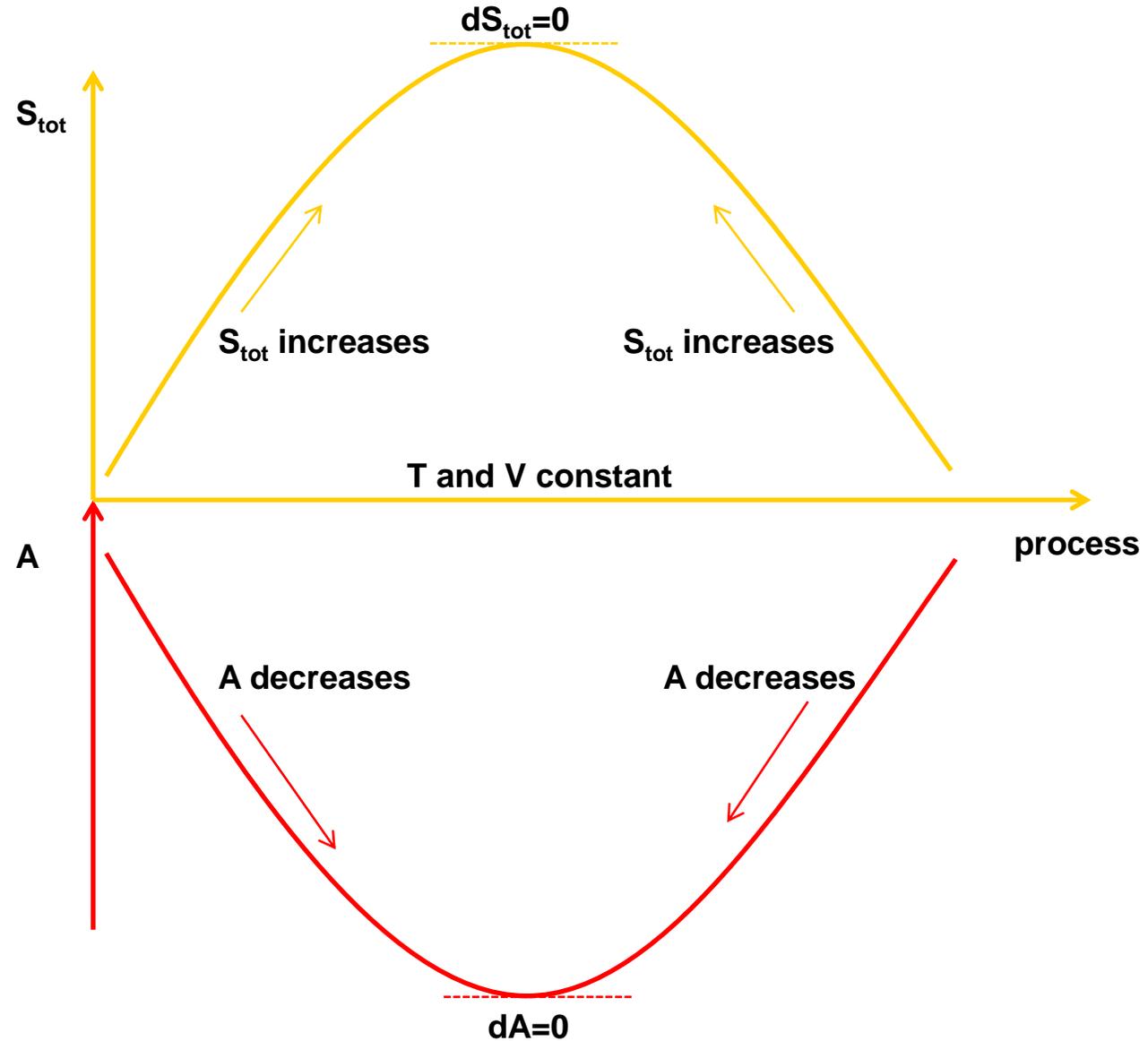
# Energy functions and spontaneous processes

- From 2nd law of thermodynamics, where  $dS \geq dQ/T$  for reversible processes (equilibrium) and spontaneous process, one can derive that
- $dG_{T,P}=0$  at equilibrium and  $dG_{T,P}<0$  for spontaneous processes (constant T and P)
- $dA_{T,V}=0$  at equilibrium and  $dA_{T,V}<0$  for spontaneous processes (constant T and V)
- $dU_{S,V}=0$  (constant S and V) and  $dH_{S,P}=0$  (constant S and P) for equilibrium but not practical conditions for studying processes

# Spontaneous process and equilibrium, Gibbs energy

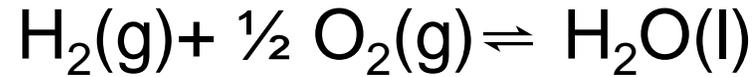


# Spontaneous process and equilibrium, Helmholtz energy



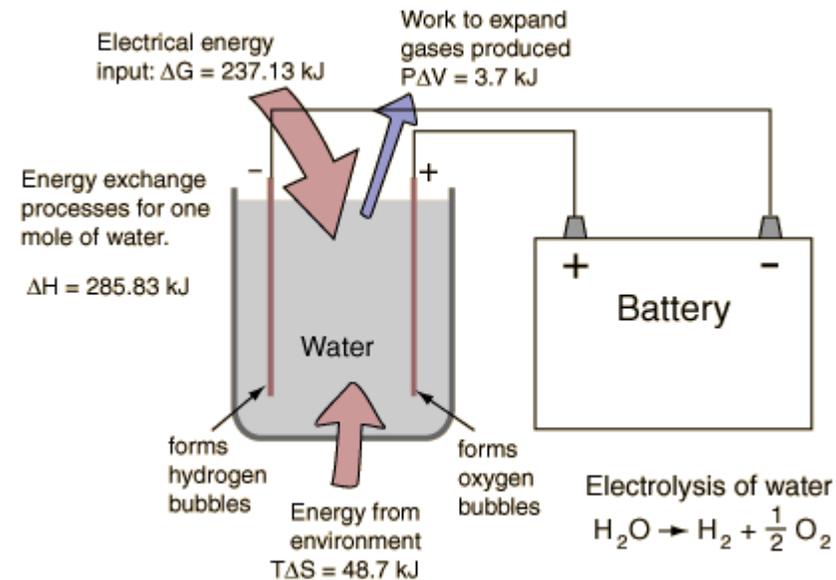
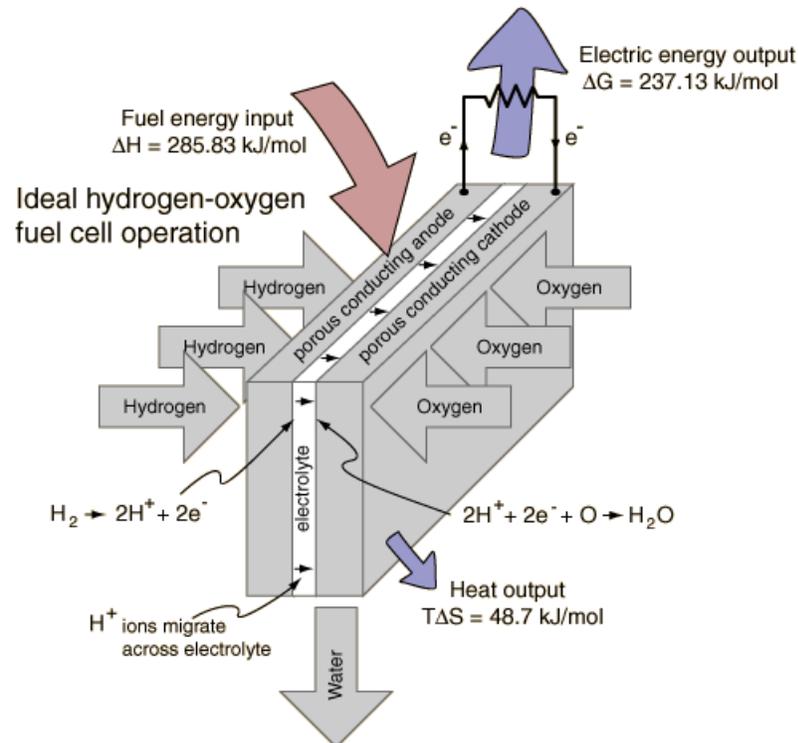
# Gibbs and Helmholtz energy

- For a reaction

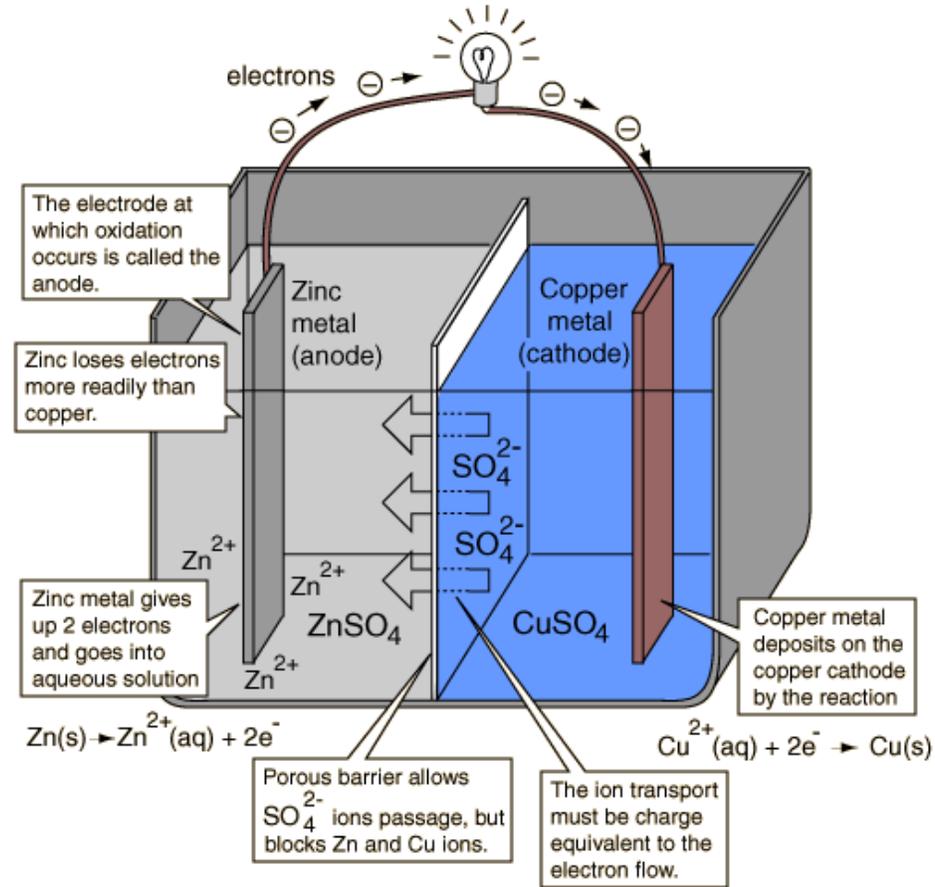


$\Delta G_r = -237 \text{ kJ}$  per mol  $\text{H}_2\text{O}$  at  $25^\circ \text{C}$  and 1 bar

Up to  $237 \text{ kJ mol}^{-1}$  of 'chemical energy' can be converted into electrical energy



# Gibbs energy and electrochemical cells



Zinc electrode (anode):  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Copper electrode (cathode):  $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Total reaction:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

# Gibbs energy and electrochemical cells

$$W_{\max} = W_{\text{electrical}} = -nFE_{\text{cell}}$$

$$\Delta G = -nFE_{\text{cell}}$$

n: number of moles of electrons transferred in the reaction

F: Faraday's constant, 96485 C/mol e<sup>-</sup>

E<sub>cell</sub>: Cell potential, given in volt

Zinc electrode (anode):  $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-}$       E = + 0.762 V

Copper electrode (cathode):  $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightarrow \text{Cu(s)}$       E = +0.340 V

**Total reaction:**

$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$       E<sub>cell</sub> = +1.102 V

$$\Delta G_1^{\circ} = -nFE_{\text{cell}}^{\circ} - (2) \cdot (96485 \text{ C/mol}) \cdot 1.102 \text{ V} = -212.6 \text{ kJ mol}^{-1}$$

Direct Gibbs energy measurements are often performed with electrochemical cells

# Summary

- **1<sup>st</sup> law of thermodynamics  $\Delta U = Q - W$**
- **2<sup>nd</sup> law of thermodynamics, the sum of entropies of the interacting thermodynamic systems increases**
- **Enthalpy,  $H \equiv U + PV$**
- **Entropy,  $dS = \delta q/T$  and  $dU = TdS - PdV$**
- **Statistical approach of Boltzmann equation links entropy and randomness  $S = k \ln \Omega$**
- **Gibbs energy,  $G \equiv H - T \times S$**