تفريغ فيزيكال

اسم الموضوع:

Thermodynamics

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لجان الدفعات

بسم الله الرحمن الرحيم

Thermodynamics

Learning objectives

- Understand the theory of thermodynamics and its use for describing energy-related changes in reactions.
- Understand the first law of thermodynamics and its use.
- Understand the second law of thermodynamics and its use.
- Understand the third law of thermodynamics and its use.
- Define and calculate free energy functions and apply them to pharmaceutically relevant issues.
- Understand the basic principles of the impact of thermodynamics on pharmaceutically relevant applications

Introduction

Heat Power

- Thermodynamics is derived from two words: '*Thermo*' which means '*Heat*' and '*Dynamics*' which means '*Power*'.
- Thermodynamics is a branch of physics that deals with the quantitative relationships of interconversion of the various forms of energy, including mechanical, chemical, electric, and radiant energy.
- The main forms of energy of interest in thermodynamics are heat (Q) and work (W).

فرع من أفرع الفيزياء يتعامل مع العلاقات الكمية quanty not quality

و يتعامل مع الطاقة باشكالها المختلفة

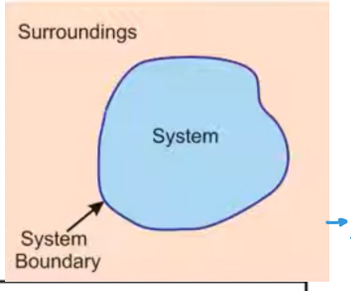
الشغل و الحرارة

Introduction

- Thermodynamics is based on three laws or facts of experience that have never been proven in a direct way, in part due to the ideal conditions for which they were derived.

تعتمد على 3 قوانين دائم إثباتها بشكل مباشر بل صفة الظروف المثالية التي أشتقت من أجلها

عند تسليط النظر لبقعة ما بالكون أو نظرية أو أي شيء نسميه System وما يحيط به هي Surrounding والحد الفاصل بينهما هو boundary

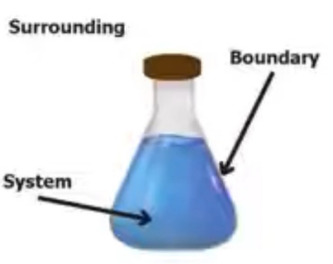


صعدة خارجية

Thermodynamic system

- System is the sample for which the energy is studied (e.g. chemical reaction in a test tube).
- Surrounding is every thing outside the system (e.g. the surrounding of a chemical reaction is the water bath in which it is immersed).
- Boundary is the barrier that separate the system from its surrounding (e.g. the wall of the flask).
- Universe is the system and its surroundings.

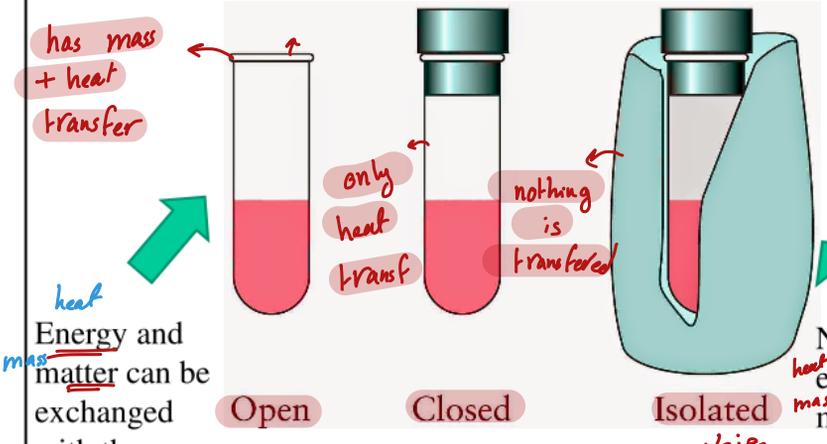
حد فاصل أو حاجز



صعدة خارجية

Thermodynamic system

- Three types of systems are frequently used to describe thermodynamic properties:

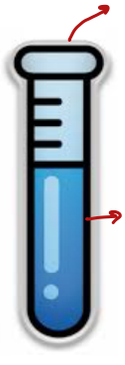


Open: Energy and matter can be exchanged with the surrounding

Closed

Isolated: Neither energy nor matter can be exchanged with the surrounding

معزول



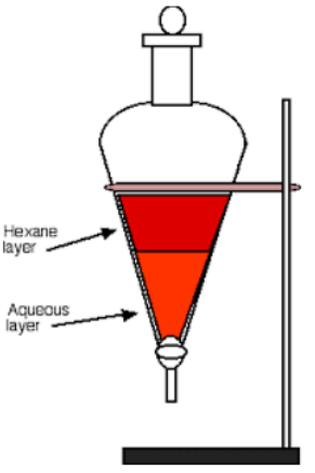
مضمون بمعنى انتقال mass (matter)

مضمون انتقال heat (energy)

Thermodynamic system

Example

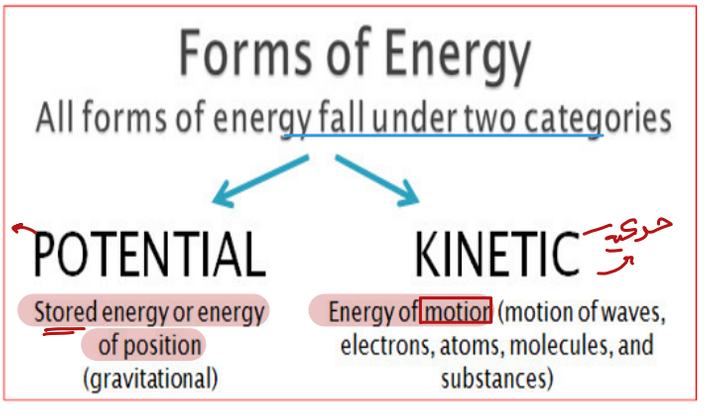
- If two immiscible solvents, water and hexane, are confined in a closed container and iodine is distributed between the two phases, each phase is an open system, yet the total system made up of the two phases is closed because it does not exchange matter with its surroundings.



Energy

- Energy is a fundamental property of a system.
- In chemical reactions, energy determines what reactions may occur, how fast the reaction may proceed and in which direction the reaction will occur.

the role of energy in chemical reactions!



نص قانون حفظ الطاقة :
الطاقة لا تنعدم ولا تستحدث لكن تتحول من شكل لآخر

Energy

- All forms of energy are related, but in converting between the various types it is not possible to create or destroy energy. This forms the basis of the *law of conservation of energy*. قانون حفظ الطاقة
- The *internal energy U of a system is the sum* (مجموع) of all the kinetic and potential energy contributions to the energy of all the atoms, ions and molecules in that system.

وإلي بهمنا هو التغير في الطاقة ليس فقط طاقة بدائية أو نهائية.

Energy

- In thermodynamics we are concerned with change in internal energy (ΔU) rather than the internal energy itself (U).
- We may change the internal energy of a closed system (one that cannot exchange matter with its surroundings) in only two ways: by transferring energy as work (W) or as heat (Q).

How can internal energy of closed system be changed?
by transferring energy as work (W) / heat (Q)

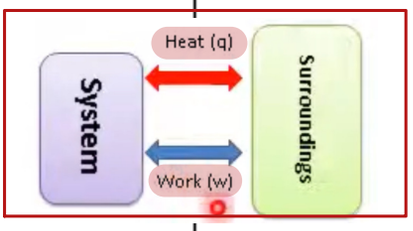
ماتنسى إنه closed system هو إلي ما بصير انتقال مع matter / mass مع المحيط

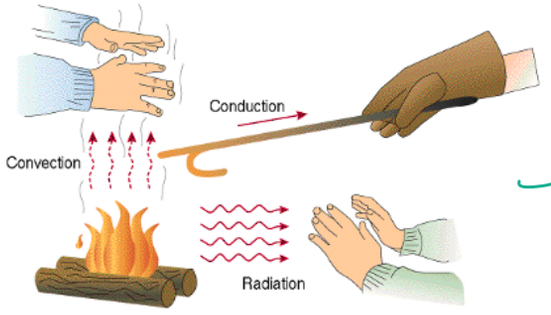
في حال صار عنا اختلاف في حرارة النظام والمحيط

بعرفتها نقيس تبادل الحرارة ووحدتها J / cal

Energy

- **Heat (Q)** is a form of energy that is transferred as the result of a temperature difference between a system and it surroundings.
- Heat is expressed in joules (J) or calories (cal).





شرح هذه الصورة في السلايد التحت

$W = F \cdot S$

$F = \frac{W}{S}$

$S = \frac{W}{F}$

أما الشغل فهو عبارة عن قوة وصافة

Energy

الشغل هو إحداث تغيير في النظام أبعاد، شكل، ...

Work is the product of a force and a distance:

W = force × distance $= F * \Delta d$

$W = (\text{area} \times \text{pressure}) \times \text{distance}$ (area = مساحة، force = قوة)

$W = A \times P \times \Delta d \quad \because \quad \Delta V = A \times \Delta d$ (volume)

$\therefore W = P\Delta V \qquad (\Delta V = V2 - V1)$

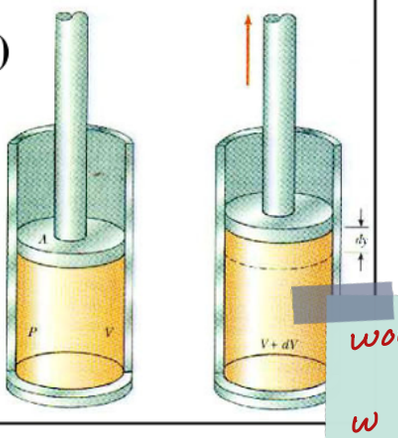
$W = -P\,\Delta\,V$

إذا كان الشغل ضد حركة الجسم أي تبطئه

area : A pressure : P

distance: Δd

Volume = area × distance



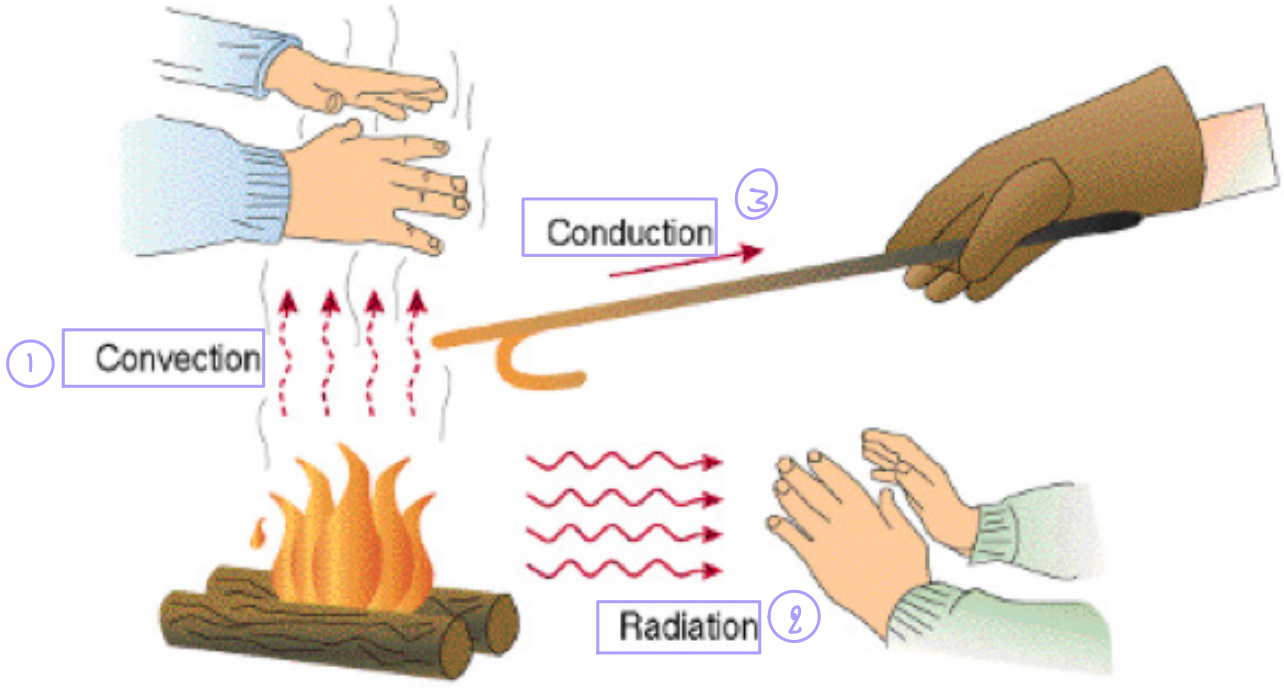
انتقالها يعني أن الطاقة تنتقل من النظام system إلى المحيط surr... عن طريق heat أو work

work = Force * distance

$w = [\text{area} \times \text{pressure}] * \Delta d$

$w = \text{Volume} * \text{pressure}$

$w = P\Delta V$



انتقال الحرارة يصير عن طريق 3 عمليات

① Convection : يعني تنتقل من مصدر النار إلى الجسم الآخر
عن طريق الرياح ، ليس الفراغ أكيد

② Radiation : عن طريق الفراغ

③ Conduction : لو حبيت مادة معينة مثل حديد مو صل للحرارة في تنتقل الحرارة

كلمة iso معناها أي ثابت؛ يعني لو أجيت مع حرارة بتصير حرارة ثابتة

iso = constant ثابت

تكون تفهم أكثر !!

process حكينا معناها التغير من حالة لأخرى صح لو حكينا isothermal process يعني التغير من حالة لأخرى بس بثبوت الحرارة . تم !

Thermodynamic processes

مثال حلو : سلعة البيض

يبدأ الماء بالغليان وبعدها كانه بارد و تتحول البيضة من شيء سائل للحالة الصلبة يعني أن الماء بقيت ثابتة . تمام

- Process is the change of a system from one equilibrium state to another.
- Isothermal process is a process in which the temperature of the system is kept constant.
- e.g. Placing the system in a constant-temperature bath so that heat is exchanged without affecting the temperature.

$P_{initial} = P_{final}$

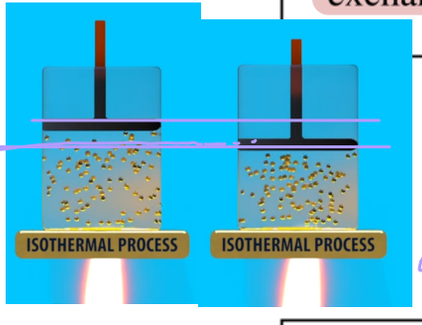
- Isobaric (pressure) process is a process in which pressure of the system remains constant.

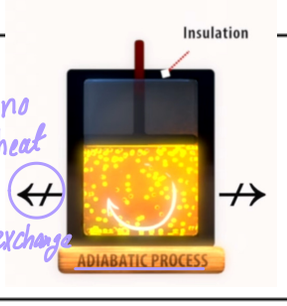
$V_{initial} = V_{final}$

- Isochoric (space/volume) process is a process in which volume of the system remains constant

يعزل عن ← يستحيل تبادل الحرارة

- Adiabatic process is a process in which no heat is exchanged with the surroundings





Thermodynamic state

هي حالة النظام التي يتم تحديدها من خلال مجموعة يتم مع المعلومات المعروفة

- Thermodynamic state means the condition of the system that is identified by values of a set of parameters known as state functions or state variables (e.g. temperature, pressure and volume...etc).

تعتمد على الحالة الحالية للنظام وهي مستقلة عن الطريقة التي تم بها الوصول إلى الحالة

- State function is a property with a unique value that depends only on the current state of the system and is independent of the manner in which the state was reached (i.e. the path).
- Equation of state is any equation relating the state functions. e.g. the ideal gas law and the van der Waals equation.

$PV = nRT$

$\left[P + \frac{an^2}{V^2}\right] * [V - nb] = nRT$

Thermodynamic state

- The change of internal energy, ΔU, depends only on the initial and final thermodynamic states (does not depend on the path) $\Rightarrow$ ΔU is a state function..
- E.g. a 85 g sample of water at 37°C and 1 atm has the same internal energy whether it is synthesized from H_2 and O_2 or distilled from a solution or melted from ice.
- Both Q and W depend on the manner in which the state of the system is reached (depend on the path). Hence, Q and W are **not** state functions.

Thermodynamic state

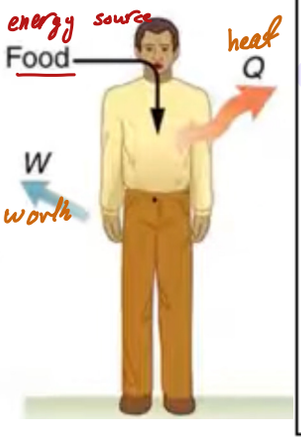
- **Extensive variables** are variables that depend on the size of the system; e.g. mass and volume
- **Intensive variables** are variables that do not depend on size; e.g. pressure and temperature.

size or volume

The first law of thermodynamics

- The first law of thermodynamics states that energy can be transformed from one form to another, but cannot be created or destroyed.
- The total energy of an isolated system cannot change.
- This statement means that various forms of energy are equivalent, and when one kind is formed (e.g. work), an equal amount of another kind must disappear (e.g. heat).
- If an amount of heat (Q) is supplied to a system, a part of it may increase the internal energy (ΔU), while the remaining may be used as a work done by the system

$$\Delta U = W + Q$$



The first law of thermodynamics

- If the system releases its energy *to the* surroundings *ΔU is negative*, *i.e. the total* internal energy has been reduced.
  - Heat is absorbed → endothermic process → ↑ of internal energy → *q is positive.*
  - Heat is released → exothermic process → ↓ of internal energy → *q is negative*
- Similarly, when energy is supplied *to the* system as work, *w is positive; and when the* system loses energy by doing work, *w is* negative.

q charge can be

positive (+)

- If the heat is absorbed

Endothermic process

⇓

increase of internal Energy

negative (−)

- If heat is released

Exothermic process

⇓

Decrease of internal Energy

When energy is supplied to a system as work so W is (+)

but if the system lose energy by doing work, then the W is (−)

حتى ΔU تساوي صفر ؟ كما تم تزويد النظام بالحرارة تسبب صافي مجال تتوسع وبالتالي هذا يصير انجاز شغل
بالتالي الاتي إلي تغير إنه الطاقة الداخلية ازدادت فقط من الحرارة الممتصة

The first law of thermodynamics

Enthalpy [Heat content]

محتوى حراري

هو أي صورة من صور الطاقة, لثانية والي منها يعطي تتحول لحرارة

- Let us consider that a system absorbs heat but is not allowed to expand. Under this condition no work is done on the system or by the system because ΔV is equal to zero. Thus, the heat absorbed is now the increase in internal energy of the system.
- However, most chemical studies are conducted at constant pressure. (The reaction is open to the atmosphere, and P=1atm).
- In this case some energy will have been lost by the work done (against the atmosphere) during the expansion of the system.
- From the first law:

$$\Delta U = W_p + Q_p \quad \Rightarrow \quad Q_p = \Delta U - W_p$$

$$\text{Since } W_p = -P\,\Delta V \quad \text{then } Q_p = \Delta U + P\,\Delta V$$

$$\text{Since } \Delta H = Q \text{ at constant pressure then}$$

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

The first law of thermodynamics

Enthalpy

في حال ثبوت الضغط الحرارة المكتسبة أو المفقودة اسمها enthalpy change وبما انها طاقة فإن الوحدة joule ويمكن قياسه

- The enthalpy change is the amount of heat gained or lost in a process at constant pressure. ($\Delta H = Q_P$)
- ΔH does not depend on the path between the states of the system (ΔH is a state function)
- Since enthalpy is an energy, it is measured in the usual energy units e.g. joule.
- ΔH is more useful than ΔU because chemical and biochemical processes commonly happen in system open to atmosphere and free to expand or contract.
- Only changes in enthalpy (ΔH) can be measured in practice (as with all energy quantities), (It is difficult to measure the absolute value of H).

The first law of thermodynamics

Enthalpy ΔV is small when

- For chemical processes involving only solids and liquids, *ΔV is usually quite small, so:*

$$\Delta H \approx \Delta U,$$

- For gases *ΔV* may be substantial, so: ضروري أو ممكن

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

- From the ideal gas law:

$$PV = nRT \quad \Rightarrow \quad P\Delta V = (\Delta n)RT$$

Then: $\Delta H = \Delta U + (\Delta n)RT$

The first law of thermodynamics

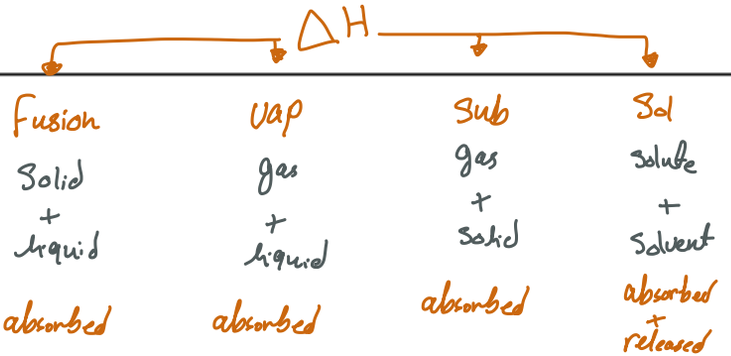
Enthalpy

- Specific symbols and names are used to identify H with particular physical changes:
- The enthalpy of fusion (ΔH_{fusion}) is the heat absorbed by 1 mole of solid on melting

  ➢ $\Delta H_{fusion} = H_{liquid} - H_{solid}$

- The enthalpy of vaporization (ΔH_{vap}) is the heat absorbed by 1 mole of liquid on vaporization.

  ➢ $\Delta H_{vap} = H_{gas} - H_{liquid}$



The first law of thermodynamics

Enthalpy

- The enthalpy of sublimation (ΔH_{sub}) is the heat absorbed by 1 mole of solid on sublimation.
  - $\Delta H_{sub} = H_{gas} - H_{solid}$
- The enthalpy of solution (ΔH_{Sol}) is the heat absorbed or released when a 1mole of solute dissolves in a solvent.
- These are molar properties .E.g. ΔH_{vap} (water, 25°C) = 44KJ/mol.

The first law of thermodynamics

Enthalpy

- ΔH (forward change) = $-\Delta H$ (reverse change)
- ΔH is positive for physical change from a more condensed to a less condensed phase (melting, vaporization and sublimation).(energy is required to break the intermolecular forces in a more condensed phase).
- ΔH is negative for physical change from a less condensed to a more condensed phase (freezing, condensation, and deposition). (energy is released when intermolecular forces is formed in a less condensed phase).

positive
from more condensed to less condensed
e.g. melting, Sublimation and Vaporization

negative
Gain
e.g. freezing, Condensation and deposition

ΔH for chemical rxn called enthalpy of rxn or heat of rxn and its (+) if the heat is absorbed and (-) if the heat is evolved

The first law of thermodynamics

يتعامل مع تغيرات الحرارة

- Thermochemistry is a part of thermodynamics deals with the heat changes (ΔH) accompanying isothermal chemical reactions at constant pressure or volume.
- The enthalpy of the reaction depends on the states of reactants and products and the temperature, therefore these factors are specified:

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

$\Delta H(25°C) = -890$ kJ/mole

The first law of thermodynamics

- For a chemical reaction ΔH is called enthalpy of reaction or heat of reaction.
- The enthalpy of reaction may be positive (heat is absorbed) or negative (heat is evolved).

$$\Delta H = H_{products} - H_{reactants}$$

في كتابة المعادلة بالعكس فإنه اشارة التفاعل بتتغير من سالب لموجب والعكس

- By writing a reaction in reverse direction, its ΔH changes sign:

$6C(s)+3H_2(g) \rightarrow C_6H_6(l)$ $\Delta H = (+)11.7$ kcal/mol

$C_6H_6(l) \rightarrow 6C(s)+3H_2(g)$ $\Delta H = (-)11.7$ kcal/mol

ملخص سريع: عنا مفهومين واحد اسمه internal energy وهو مجموع كل الطاقات الداخلة في التفاعل عندي أما enthalpy فهي المحتوى/الطاقة الحراري فقط
حرارة وضغط

The first law of thermodynamics

- Enthalpy is a state function (independent of the path).
- The heat evolved or absorbed in a chemical process is the same whether the change occurs in one stage or through intermediate stages.
- A reaction enthalpy is the sum of the enthalpies of any sequence of reactions that forms the overall reaction.

heat can't flow it self from cold to hot

The second law of thermodynamics

Thermodynamic spontaneity تلقائي

- Some processes happen spontaneously, other processes don't. (E.g. Objects fall down spontaneously, but throwing them up requires an external work)
- A spontaneous process is one that occurs "naturally" (without intervention) .
- A non-spontaneous process is one that does not occur "naturally" (needs intervention to occur). E.g. throwing objects up.

رمي الاشياء يحتاج مجهود دفع منا

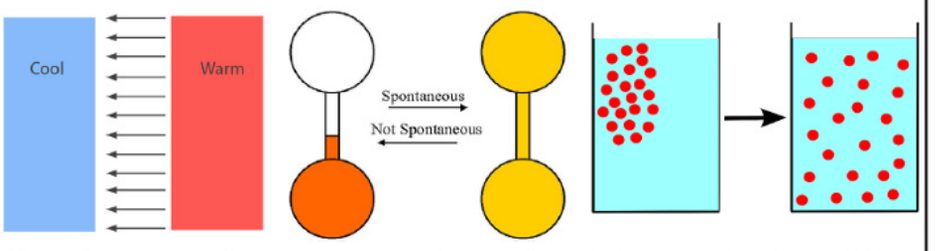
أما وقوع الاشياء فهي تلقائية من نفسها

تلقائي نفسها

والطاقة الحرارية ممكن تكون تلقائية لازم تنتقل من الحرارة الاعلى للاقل
أما العكس فهي غير تلقائية

The second law of thermodynamics

Thermodynamic spontaneity



Heat flows naturally only from hotter to colder bodies

Gases expand naturally from higher to lower pressures

Solute molecules diffuse from a region of higher to one of lower concentration.

These spontaneous processes will not proceed in reverse without the intervention of some external force to facilitate their occurrence.

The second law of thermodynamics

Thermodynamic spontaneity

- It was once thought that a negative ΔH (evolution of heat) was itself proof of a spontaneous reaction.
- Many natural reactions do occur with an evolution of heat; however, the spontaneous melting of ice at 25°C is accompanied by absorption of heat (ΔH is positive)
- Therefore; the function state (enthalpy change, ΔH) in the first law, does not determine whether the process occurs spontaneously or not.

التغير في حيّة الانظام ΔS

The second law of thermodynamics

Thermodynamic spontaneity

- The second law of thermodynamics states that the entropy (S) of a system and its surroundings increases in a spontaneous change.

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings}$$

- Then the second law says

$\Delta S_{univ} > 0$ (spontaneous processes)

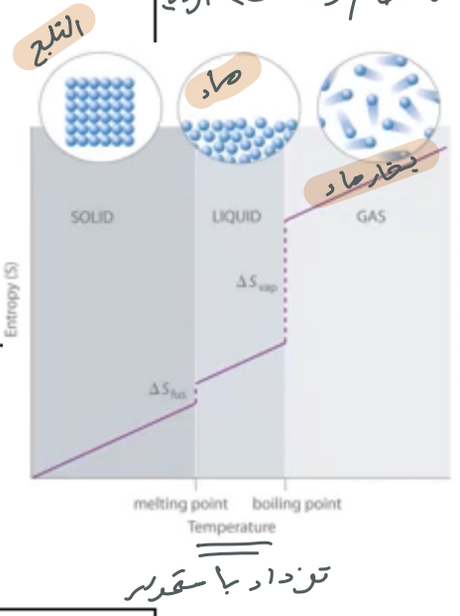
$\Delta S_{univ} = 0$ (system at equilibrium)

$\Delta S_{univ} < 0$ (non-spontaneous processes)

تشتت

يحكي أن النظام البارد تزداد entropy تبعاً بزيادة حرارته

العلاقة بين الحرارة و اللا نظام (تشتت) طردية



تزداد بـ سقوس

Entropy increases with:

- Increase in the number of molecules.
- Increase of volume.
- Increase of enthalpy (ΔH).
- Increase of the size of molecule.
- Degree of freedom inside the molecule (free rotation).

The third law of thermodynamics

3 تدل على القانون

- At absolute zero all the thermal motions of the atoms of the lattice of a crystal will have ceased and the solid will have no disorder and hence a zero entropy.
- This conclusion forms the basis of the third law of thermodynamics, which states that the entropy of a perfectly crystalline material is zero when T = 0 K.
- The third law of thermodynamics refers to an ideal state (0 K) which is practically impossible.

no more kinetic energy means no more temperature so we got absolute zero then everything ganna be solid

Free energy (ΔG)

- The free energy is derived from the entropy and is, in many ways, a more useful function to use.
- There are two factors involved in determining the direction of chemical change:
  - The system seeks to minimize its energy (ΔH)
  - The system seeks to maximize its entropy (ΔS).
- Gibbs free energy ΔG, is a state function that links the first and second law of thermodynamics and determine the direction of a chemical change

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

ΔH: طاقة حرة (enthalpy) — (+) غير تلقائي، (−) تلقائي
T: temperature
ΔS: entropy

طبيعيا / المفروض بدنا اياها صغيرة لانه بالتفاعل رح يطلع الجواب سالب يعني التفاعل تلقائي وبدنا ΔS كبيرة

Free energy (ΔG)

- If $\Delta G < 0$, the process occurs spontaneously. تلقائي
- If $\Delta G = 0$, the system is at equilibrium. متوازن
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

الجواب سالب

الجواب موجب

غير تلقائي في اتجاه التفاعل بس لو عكسنا التفاعل رح تصير تلقائية

Free energy (ΔG)

- A more negative ΔH and a more positive ΔS favors spontaneous reaction, by making ΔG more negative.
  - If TΔS < ΔH , and ΔH is negative, then ΔG will be negative (i.e. the process is spontaneous).
  - If TΔS < ΔH , and ΔH is positive, then ΔG will be positive (i.e. the process is not spontaneous).
  - If TΔS > ΔH , then ΔG will be negative (i.e. the process is spontaneous regardless whether ΔH is negative or positive).

Free energy (ΔG)

Example 1

ΔH and ΔS for the transition from ice to liquid water at 25 °C and 1 atm are +1650 cal/mole and +6 cal/mole deg), respectively Compute ΔG for the phase change and indicate whether the process is spontaneous.

The process leads to:

An increased freedom of molecular movement (ΔS is positive)

A increased molecular energy (ΔH is positive)

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

$\Delta G = 1650 - (298 \times 6) = -138$ cal/mole

The process is spontaneous because T ΔS is sufficiently larger than the positive value of ΔH to make ΔG negative

Free energy (ΔG)

Example 2

ΔH and ΔS for the transition from liquid water to ice at −10°C and at 1 atm pressure are −1343 cal/mole and −4.91 cal/mole deg, respectively. Compute ΔG for the phase change and indicate whether the process is spontaneous.

The process leads to:

A decreased freedom of molecular movement (ΔS is negative)

A decreased molecular energy (ΔH is negative)

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

$\Delta G = (-1343) - [263 \times (-4.91)] = -51.67$ cal/mole

The process is spontaneous, as reflected by the negative value of ΔG.

سُبْحَانَ اللهِ، وَالْحَمْدُ للهِ، وَلاَ إِلَهَ إِلاّ اللهُ، وَاللهُ أَكْبَرُ

لا إِلهَ إِلاّ اللهُ وحدَهُ لاَ شرِيكَ لَهُ، لَهُ الملْكُ، ولَهُ الحمْدُ، وهُوَ عَلَى كُلِّ شيءٍ قديرٌ

سبحان اللهِ وبحمدِه، ولا إله إلا اللهُ، واللهُ أكبرُ، عددَ خلقِه، ورضا نفسِه، وزِنَةَ عرشِه، ومِدادَ

استغفر الله العظيم وأتوب اليه

اللهم اغفر لي ولوالدي وللمسلمين والمسلمات الاحياء والاموات

اللهم انصر اخواننا المسلمين في كل مكان وزلزل قلوب اعداء الاسلام واعوانهم