لجان الدفعات

PHYSICAL PHARMACY

MORPHINE ACADEMY

MORPHINE ACADEMY

Thermodynamics

heat power/Energy

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Learning objectives

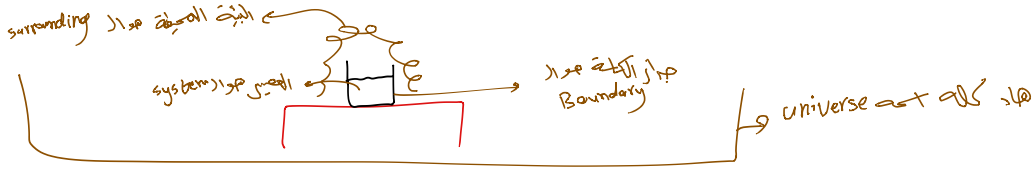
- Understand the theory of thermodynamics and its use for describing energy-related changes in reactions.
- Understand the first law of thermodynamics and its use.
- Understand the second law of thermodynamics and its use.
- Understand the third law of thermodynamics and its use.
- Define and calculate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

Introduction

- 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).

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.

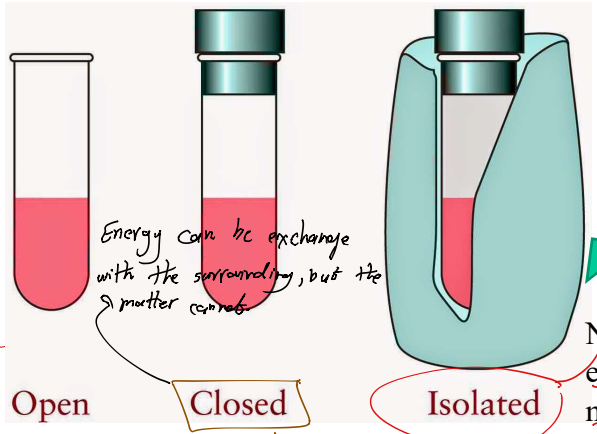


Thermodynamic system

- 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.

Thermodynamic system

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



Energy and matter can be exchanged with the surrounding

Neither energy nor matter can be exchanged with the surrounding

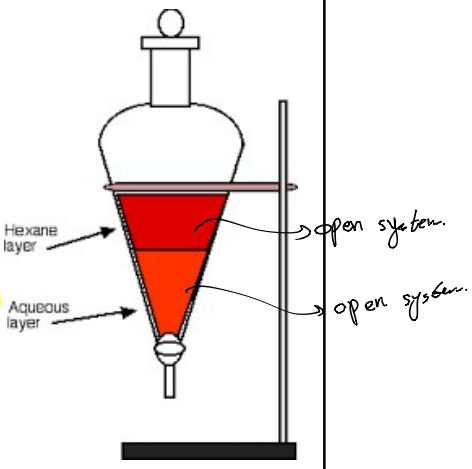
كيف بنوصف هذا ال iodin system؟ المي والهكسان منفصلين عن بعض ،فكل واحد منهم بشكل system لحال،طيب ال iodin بقدر ينتقل بين هدول ال two systems ولا لا؟ بقدر ، فهو يسمح بتبادل المادة ،لذا بنقدر نحكي انه هدول ال two systems هم open to each other .

طيب هل هذا ال system بسمح لل iodin انه يطلع لبرا؟لا ما بسمح،لانه ال container مسكر ،معناها هدول ال two systems هم close على ال surrounding

Thermodynamic system

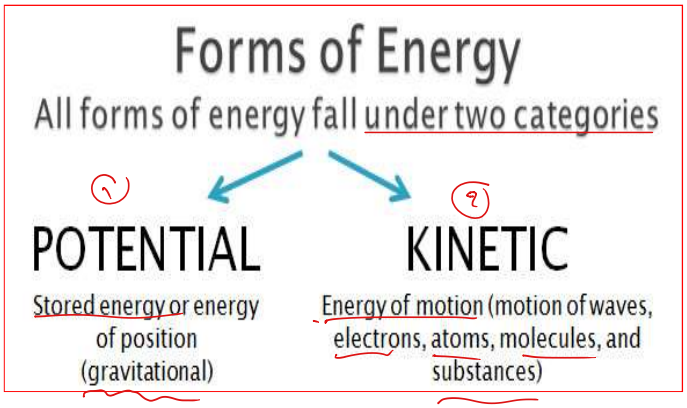
Example

- 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.



Energy

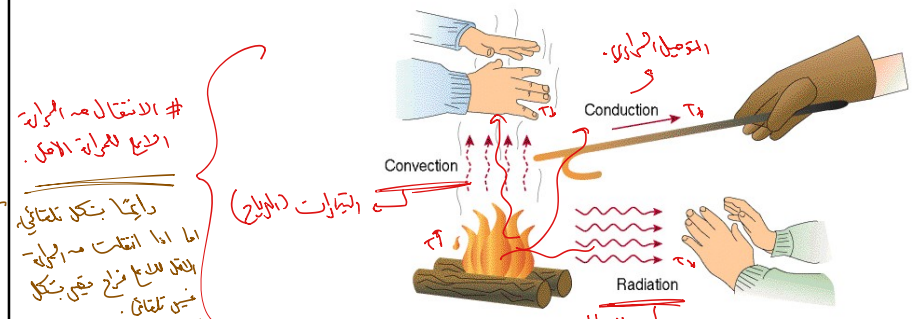
- All forms of energy are related, but in converting between the various types it is not possible to create or destroy energy. This forms the basis of the *law of conservation of energy*.
- The *internal energy U of a system is the sum* of all the kinetic and potential energy contributions to the energy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

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).

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).



Energy

Work is the product of a force and a distance:

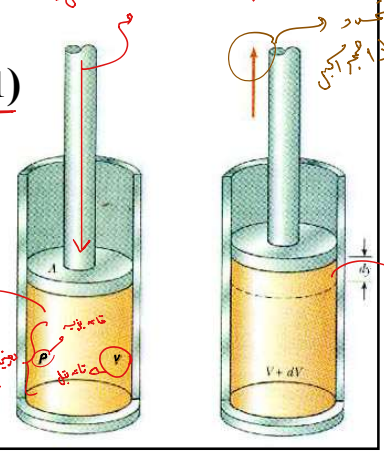
W = force × distance

W = (area×pressure)×distance

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

$\therefore W = P\Delta V \qquad (\Delta V = V_2 - V_1)$

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



Work done by the system :

النظام هو اللي بذل الشغل،زي الغاز يتمدد او انه المكبس اندفع للأعلى،فالحجم يزيد،فالتغير بالحجم موجب ،فالشغل سالب

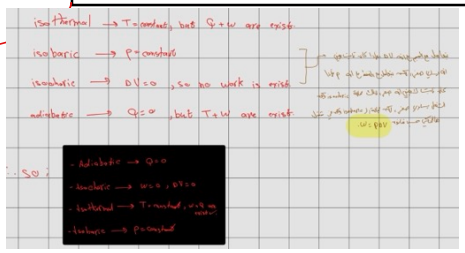
Work done on the system:

المحيط هو اللي بذل الشغل عالنظام ،زي انك تضغط المكبس لتحت،فالحجم قل،بالتغير بالحجم سالب،فالشغل موجب

إشارة W	ماذا يحدث للحجم؟	من بذل الشغل؟	العبارة
–	يتمدد (Expansion)	النظام	Done by the system
+	ينضغط (Compression)	المحيط (Surroundings)	Done on the system

Thermodynamic processes

- 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.
- Isobaric process is a process in which pressure of the system remains constant.
- Isochoric process is a process in which volume of the system remains constant
- Adiabatic process is a process in which no heat is exchanged with the surroundings



Thermodynamic state

- 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).
- 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.

$$P.V = nR.T$$

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

Thermodynamic state

- The change of internal energy, ΔU, depends only on the initial and final thermodynamic states (does not depend on the path) ⇒ 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.

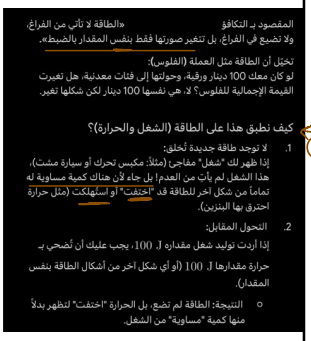
Thermodynamic state

- **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.

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.

$$\Delta U = W + Q$$



الحالة	الإشارة	شو بصير بالطاقة الداخلية؟
النظام يمتص حرارة من surroundings	$Q > 0$	تميل تزيد
النظام يفقد حرارة لـ surroundings	$Q < 0$	تميل تقل
Work done on the system	$W > 0$	تميل تزيد
Work done by the system	$W < 0$	تميل تقل

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.

work done on the system → W = +

work done by the system → W = −

The first law of thermodynamics

Enthalpy

- 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.
- The enthalpy change is the amount of heat gained or lost in a process at constant pressure. ($\Delta H = Q_p$)

The first law of thermodynamics

Enthalpy

- 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).

طيب نحنا ليش ممكن نقيس التغير بال enthalpy مو ال enthalpy نفسها؟

هسا ال enthalpy نفسها صعب علي انه أقيسها لانه عشان تقيس المحتوى الحراري للسستيم على ضغط ثابت راح تحتاج تحسب ال internal energy لكل ذرة بالسستيم ،فالأفضل والأسهل نحسب التغير

تفاعل داخل وعاء صلب ومغلق (Rigid container)،

(A) ايش اللي راح يكون ثابت؟

A) Pressure — لـ ΔH — work

B) Volume — ΔU — Q

لأن متغير = صلب Rigid، معناها الحجم ثابت، وبالتالي $\Delta V = 0$ فالشغل $W = -P\Delta V = 0$

$\therefore Q_v = \Delta U$

مش ΔH

يكون Constant pressure

$\Delta H = Q_p$

(B) هل التفاعل تساوي ΔU و ΔH؟

تخيل عندك علبة صودا صلبة جيا، وطلعت منها غاز وسخنتها وبعدين سخنتها، ستو بصير؟ الغاز راح يتمدد والطاقة الداخلية تزيد، لكن الغاز يقدر يكبل ويمنع التمدد؟ لأن الله التمدد صلب فالحجم ثابت، وكمان الحجم ثابت نتذكر قانون الشغل: $W = -P\Delta V$، وبما أن $\Delta V = 0$ فإذا $W = 0$، يعني مفيش شغل، طيب الحرارة اللي دخلت وين راحت؟

تخيل انه دخلت حرارة مقدارها 100J، هل جزء منها راح للشغل؟ أكيد لأ، ليش؟ لأنه مفيش تمدد، فكل الـ 100J راحت لزيادة الطاقة الداخلية، يعني $Q = \Delta U$، لحد متى ستزيد ΔU؟ طالما الحجم والضغط ثابت، ممكن كاسة مفتوحة ايضا سخنتها فالغاز يقدر يتمدد ويطلع لفوق ويعني جزء من الحرارة يروح يعمل شغل ويسخن الهواء، لهيك ما بصير $Q = \Delta U$، لأنه جزء منه Q راح للشغل.

ΔV is exchanged.

باختصار:

* وعاء صلب:
  - الحجم ثابت
  - مافي شغل
  - $Q = \Delta U$

* كأس مفتوح:
  - الضغط ثابت
  - في شغل عند
  - $Q = \Delta H$

#

The first law of thermodynamics

Enthalpy

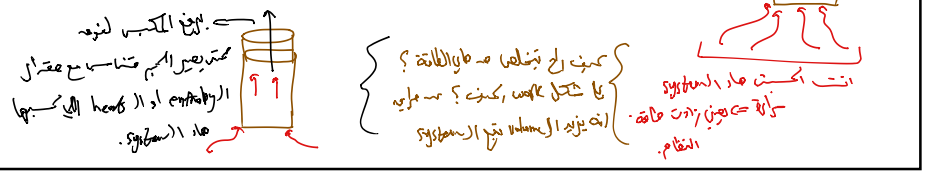
- From the first law:

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

Since $W_p = -P\,\Delta V$ then $Q_p = \Delta U + P\,\Delta V$

Since $\Delta H = Q$ at constant pressure then

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



The first law of thermodynamics

Enthalpy

- 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:

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

- From the ideal gas law:

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

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

(sublimation) solid → gas
(melting/fusion) solid → liquid
(vaporization) liquid → gas
solid → liquid → gas
} ΔH > 0

The first law of thermodynamics

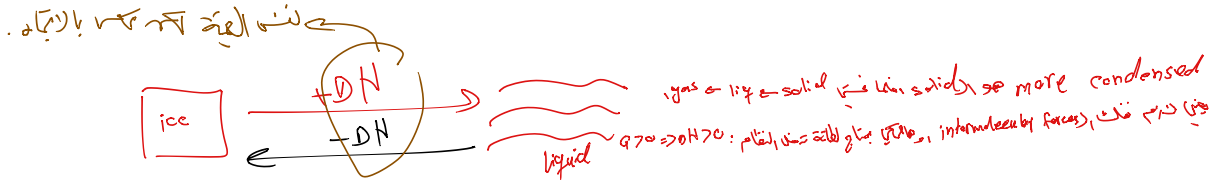
Enthalpy

- 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) = -ΔH (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).

The first law of thermodynamics

- 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:

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

$$\Delta H(25°C) = -890 \text{ kJ/mole}$$

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).

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

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

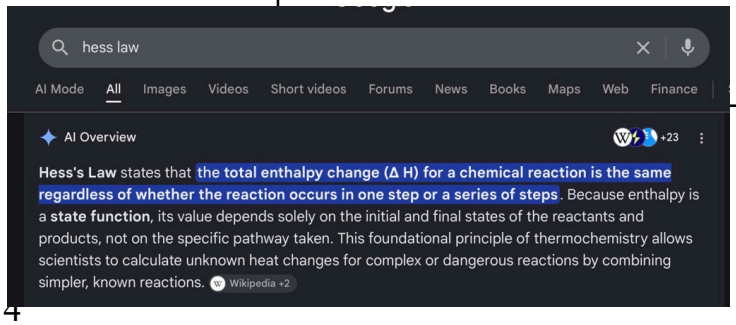
$$6C(s)+3H_2(g) \rightarrow C_6H_6(l) \quad \Delta H = +11.7 \text{ kcal/mol}$$

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

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.

Hess's law



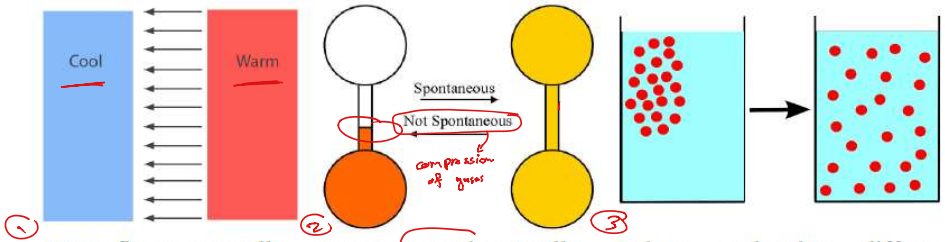
The second law of thermodynamics

Thermodynamic spontaneity

- 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.

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.

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)

مش عشوائية النظام هي اللي بتحدد إذا التفاعل تلقائي او لا ،وإنما عشوائي ال universe ،يعني النظام وال surrounding سوا،يعني تمام إذا زادت عشوائية ال system هالاشي بساعد العملية تكون تلقائية،لكن لازم نحسب تأثير ال surroundings كمان

S = zero
0 كلفن = -273 °C
zero K متى الـ S تساوي صفر؟ عند حالة معينة بس وهي لما تكون درجة حرارة
perfect crystal الحركة الجزيئية تكون اقل ما يمكن ، وال
((Disorder مافي)) درجة لاضطراب
S = 0 وبـ

القانون ما بحكي انه اي system عند صفر كلفن عنده ال S بتكون تساوي صفر، وإنما ال perfect crystal at 0K بتكون S=0

The third law of thermodynamics

- 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.

الحساب الحقيقي عالب اعين انا بالتفاعل تلقائي أو لا

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:
  1. The system seeks to minimize its energy (ΔH) (-)
  2. 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

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

(K)

1 ← system عامل يقلل الـ ΔH بقدر
2 ← system عامل يزيد الـ ΔS بقدر
بكون كبير.
فأي system اخ عامل يقلل طاقته ويزيد من عشوائيته

ΔH > T.ΔS
* ΔG = +
* Not spontaneous rxn.
بكون بعيد تلقائي بالتفاعل الكيميائي

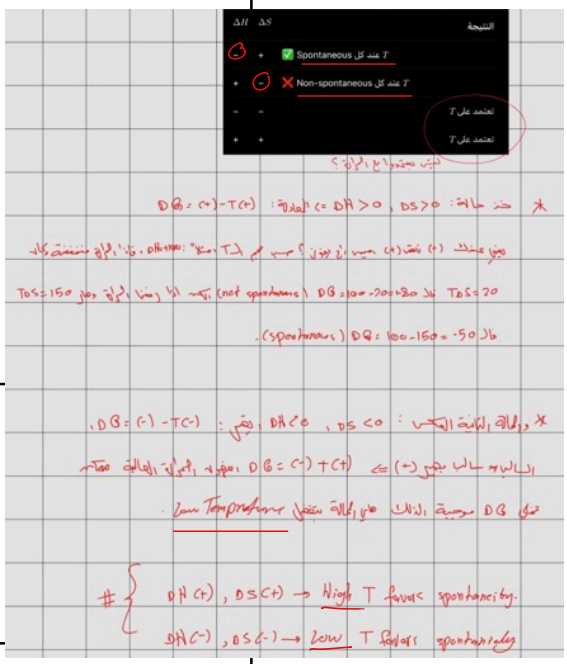
ΔH = T.ΔS
* ΔG = 0
* Equilibrium rxn.

ΔH < T.ΔS
* ΔG = -
* spontaneous rxn.

على أساس هدول الشغلتين بنقدر نحدد الـ chemical change
من وين لوين حيصير، يعني عندك الشكل A والشكل B
A → B
مين من هدول الشكلين راح يكون في عنده طاقة اقل وعشوائية اعلى ؟ الاتجاه تبع التغير الكيميائي راح يكون اله
يعني لو الشكل A في عنده طاقة اقل وعشوائية اعلى راح يكون الاتجاه راح يكون هيك ← ، وإذا انه الشكل B عنده طاقة اقل وعشوا اعلى فالاتجاه بكون هيك →

Free energy (ΔG)

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



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.

القانون	الفكرة الأساسية	على ماذا يدل؟	أهم قانون/قاعدة
First Law القانون الأول	Conservation of Energy حفظ الطاقة	الطاقة لا تُخلق ولا تُفنى، وإنما تنتقل كـ Heat أو Work	
Second Law القانون الثاني	Spontaneity & Entropy	يحدد اتجاه العملية وهل هي تلقائية أم لا، باستخدام تغير Entropy للـuniverse	
Third Law القانون الثالث	Entropy at absolute zero	يعطي مرجعًا للـEntropy	للـperfect crystal

→ اتجاهية بـ Entropy لل perfect crystal عند الصفر

S = 0 كاملة؟

First law

work done on (+)

work done by (-)

Second law

ΔS > 0 universe → spontaneous → ΔG < 0

ΔS = 0 universe → Equilibrium → ΔG = 0

ΔS < 0 universe → non-spontaneous → ΔG > 0