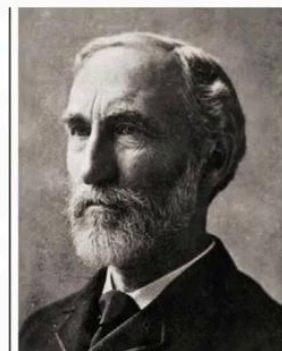


Thermodynamique

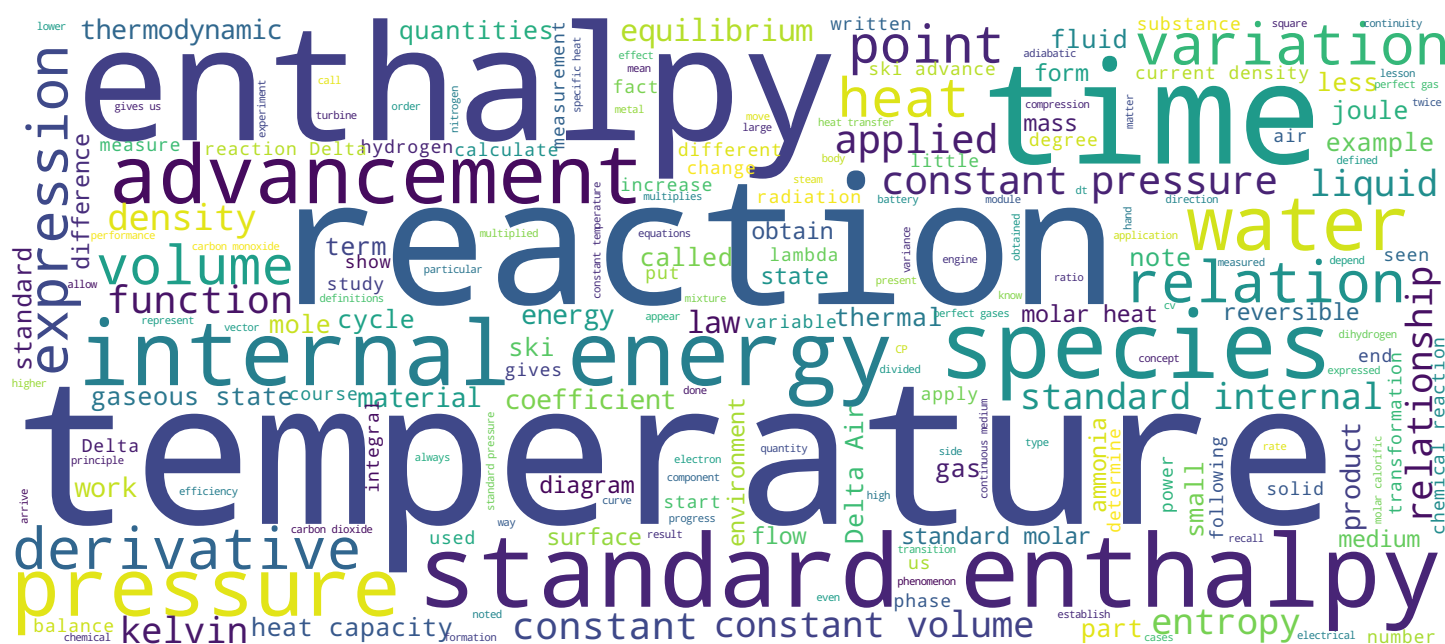
PREMIER PRINCIPE ET REACTIONS CHIMIQUES



Dr. Théophile MBANG , ENSP – Yaoundé - Cameroun



Josiah Willard Gibbs



Video





- **Définitions**
 - **Energie interne de réaction ($\Delta_r U$) et enthalpie de réaction ($\Delta_r H$)**
 - **Expression de $\Delta_r H$**
- **Grandeurs standard de réaction**
- **Influence de la température sur les grandeurs standard**
- **Lois de Kirchhoff**
- **Relation entre $\Delta_r H^\circ(T)$ et $\Delta_r U^\circ(T)$**

Thermodynamique

Hello. Welcome to the thermodynamic college of the Ecole Polytechnique Fédérale de Lausanne and PFL in Switzerland. I am a grandson, chemistry teacher at the Ecole Nationale Supérieure, Polytechnique and NSP. From Yaoundé, Cameroon. We will continue our course, thermo chemistry. Today, we will discuss the first principle thermodynamics applied to chemical reaction. To do this, we will recall some definitions. the internal energy of reaction $\Delta_r U$ and the enthalpy of reaction $\Delta_r H$. Give the expression of the enthalpy of reaction $\Delta_r H$. Define the standard reaction quantities. To study the influence of temperature on standard quantities. State the laws of Kirchhoff. Finally, we study the relationship between the enthalpy of the reactions and the standard internal energy of reaction. Then conclude.

Notes

Summary



0m 04s

Définitions



- Un système en réaction chimique possède une énergie interne U qui dépend de V, T et $\xi \Rightarrow U(V, T, \xi)$ et une enthalpie $H(T, P, \xi)$.
 U et H , grandeurs extensives, s'expriment en J.
- A toute fonction d'état extensive X du système, dépendant de T, P et ξ on associe la dérivée partielle de X par rapport à ξ ; T et P restant constantes notée $\Delta_r X$ telle que:

$$\Delta_r X = \left(\frac{\delta X}{\delta \xi} \right)_{P,T}; \Delta_r X \text{ en J.mol}^{-1} \text{ est une grandeur extensive.}$$

- Energie interne de réaction $\Delta_r U$: $\Delta_r U = \left(\frac{\delta U}{\delta \xi} \right)_{V,T}$ (en J.mol⁻¹).
- Enthalpie de la réaction $\Delta_r H$: $\Delta_r H = \left(\frac{\delta H}{\delta \xi} \right)_{P,T}$ (en J.mol⁻¹).

Thermodynamique

We will recall some definitions. A system with chemical reaction has an internal energy. In a chain, it is noted U. Which depend on the volume, the temperature and the progress of the U of. Volver. Temperature t it the advancement, which is an enthalpy that is a function. Of the temperature, the pressure P and the advancement of the delegations, which. the internal energy U and the enthalpy H. These are extensive quantities. It is expressed in joules. To any extensive state function of the system depending on temperature, pressure and advancement. On skis, we associate the partial derivative of the gain of TX with the ski advance. The temperature is, the pressure remaining constant, noted delta air X such that delta R of the X planes is the variation of the grains in relation to the ski advance at constant pressure and temperature becomes X. These measures. One joule per mole is an extensive quantity. Now we will replace perhaps the internal energy. Uh, or the enthalpy h? If grow U, we have the internal energy and reactions. Therefore delta r of U. So here, in the variation of the energy internal Delta Air, the U is equal to the variation of the in relation to the advancement skis at constant volume and temperature.

Notes

Summary



1m 22s

Définitions



- Un système en réaction chimique possède une énergie interne U qui dépend de V, T et $\xi \Rightarrow U(V, T, \xi)$ et une enthalpie $H(T, P, \xi)$.
 U et H , grandeurs extensives, s'expriment en J.
- A toute fonction d'état extensive X du système, dépendant de T, P et ξ on associe la dérivée partielle de X par rapport à ξ ; T et P restant constantes notée $\Delta_r X$ telle que:

$$\Delta_r X = \left(\frac{\delta X}{\delta \xi} \right)_{P,T}; \Delta_r X \text{ en J.mol}^{-1} \text{ est une grandeur extensive.}$$

- Energie interne de réaction $\Delta_r U$: $\Delta_r U = \left(\frac{\delta U}{\delta \xi} \right)_{V,T}$ (en J.mol⁻¹).
- Enthalpie de la réaction $\Delta_r H$: $\Delta_r H = \left(\frac{\delta H}{\delta \xi} \right)_{P,T}$ (en J.mol⁻¹).

Thermodynamique

The enthalpy of the Delta Air H reactions. Is equal to the variation of the enthalpy in relation to the ski advance at constant pressure and temperature. These two energies are measured in joules per mole.

Notes

Summary



3m 12s

Définitions



- La fonction d'état $H = U + PV$ est très souvent employée pour caractériser l'effet thermique d'une réaction.
- L'enthalpie H d'un système en réaction chimique dépend des quantités de matière n_B des espèces B en réaction par la relation $H = \sum_B n_B H_B$ où H_B = enthalpie molaire de l'espèce B .

Thermodynamique

Still in the definitions, the enthalpy state function h equal to the internal energy U . Plus the product of pressure. Once the volume is very often used to characterize the thermal effect of a reaction. The enthalpy H of a system with reaction chemical depends on the quantities of matter n_b of the large species b . In response to the relationship, the enthalpy H is equal to the sum of the quantities of matter of b times the enthalpy of b applied to all the species b in reaction, therefore not the expression of the enthalpy of reaction $\Delta_r H$.

Notes

Summary



3m 28s

Expression de l'enthalpie de réaction: $\Delta_r H$



- **Exemple:**

Système fermé à P et T constantes où on réalise la réaction de synthèse :

Eq. bilan	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$		
Etat initial /mol	a	b	0
Bilan à ξ /mol	$a - \xi$	$b - 3\xi$	2ξ
Bilan à $\xi + d\xi$ /mol	$a - \xi - d\xi$	$b - 3\xi - 3d\xi$	$2\xi + 2d\xi$

Enthalpie du système réactionnel à ξ

$$(1) \quad H(\xi) = (a - \xi)H_{N_2} + (b - 3\xi)H_{H_2} + 2\xi H_{NH_3}$$

Enthalpie du système réactionnel à $\xi + d\xi$

$$(2) \quad H(\xi + d\xi) = (a - \xi - d\xi)H_{N_2} + (b - 3\xi - 3d\xi)H_{H_2} + (2\xi + 2d\xi)H_{NH_3}$$

Thermodynamique

We will establish it and if we take the example of a closed system with pressure and constant temperature, the synthesis of ammonia is carried out. The language used, the method of advancement of reactions, the first line. The balance equation must be written. The nitrogen in the gaseous state reacts with the water dihydrogen in the state to give ammonia in its gaseous state. The second line. We will put the quantities, the materials in the initial state in mol. Nitrogen was introduced little by little. Small hydrogen downside we did not have ammonia, so no zero products in the front on my little ski. We have small to mol of nitrogen, which. And for the hydrogen, we have small three times. The advance at least mol is hydrogen and it formed twice the advancement of the ski. of Ammonia. We take stock when the progress has varied a little of the small dice therefore with skis smaller of the. What do we have in the reaction medium? We are slowly making progress, which is less the variation of the skis, the molar advancement of the diazote small B minus for minus fake, advancing in skiing less than three times the variation due to the soft skis and hydrogen and it was formed two times the advancement with skis, plus two small soft ammonia skis.

Notes

Summary



4m 11s

Expression de l'enthalpie de réaction: $\Delta_r H$



- **Exemple:**

Système fermé à P et T constantes où on réalise la réaction de synthèse :



Etat initial /mol $a \quad b \quad 0$

Bilan à ξ /mol $a - \xi \quad b - 3\xi \quad 2\xi$

Bilan à $\xi + d\xi$ /mol $a - \xi - d\xi \quad b - 3\xi - 3d\xi \quad 2\xi + 2d\xi$

Enthalpie du système réactionnel à ξ

(1) $H(\xi) = (a - \xi)H_{N_2} + (b - 3\xi)H_{H_2} + 2\xi H_{NH_3}$

Enthalpie du système réactionnel à $\xi + d\xi$

(2) $H(\xi + d\xi) = (a - \xi - d\xi)H_{N_2} + (b - 3\xi - 3d\xi)H_{H_2} + (2\xi + 2d\xi)H_{NH_3}$

Thermodynamique

But here, the enthalpy is calculated at each step. In the case of the reaction system with ski advancement, this was noted one. The enthalpy at the advancement Aski is equal, as we have seen previously, to the sum of the quantities of materials of B applied to all species.

Notes

Summary



5m 49s

Expression de l'enthalpie de réaction: $\Delta_r H$



- **Exemple:**

Système fermé à P et T constantes où on réalise la réaction de synthèse :



Etat initial /mol $a \quad b \quad 0$

Bilan à ξ /mol $a - \xi \quad b - 3\xi \quad 2\xi$

Bilan à $\xi + d\xi$ /mol $a - \xi - d\xi \quad b - 3\xi - 3d\xi \quad 2\xi + 2d\xi$

Enthalpie du système réactionnel à ξ

(1) $H(\xi) = (a - \xi)H_{N_2} + (b - 3\xi)H_{H_2} + 2\xi H_{NH_3}$

Enthalpie du système réactionnel à $\xi + d\xi$

(2) $H(\xi + d\xi) = (a - \xi - d\xi)H_{N_2} + (b - 3\xi - 3d\xi)H_{H_2} + (2\xi + 2d\xi)H_{NH_3}$

Thermodynamique

So the enthalpy at the advancement, which is equal to small to Minsky times the enthalpy of the smaller nitrogen b, less than three times the ASCII advancement, or even the enthalpy of dihydrogen, plus twice the ASCII advancement, or even the enthalpy. Ammonia, but not at the advancement, which is smaller. D. Let us also note two the enthalpy of the advancement, which is smaller ten variation which is equal to minus the advancement on skis minus small of the blades of the ski advance, factor multiplied by. The enthalpy of nitrogen plus ten p, less than three times the advancement, which is less than three times goes to the times the enthalpy of dihydrogen, plus twice the advancement, which plus two times small d advancement, 50 times the enthalpy of ammonia.

Notes

Summary



6m 09s

Grandeurs standard de réaction



- $\Delta_r H^\circ = \left(\frac{dH^\circ}{d\xi} \right)_{P,T} = \sum_B \nu_B H_B^\circ$

H_B° = enthalpie molaire standard de l'espèce B en J.mol⁻¹ ;

$\Delta_r H^\circ$ = enthalpie standard de réaction ;

- $\Delta_r U^\circ = \left(\frac{dU^\circ}{d\xi} \right)_{V,T} = \sum_B \nu_B U_B^\circ$

U_B° = énergie interne molaire standard de l'espèce B en J.mol⁻¹ ;

$\Delta_r U^\circ$ = énergie interne standard de réaction .

Thermodynamique

We make the difference between two men whose enthalpy at advancement, which is smaller d, which is minus the enthalpy at the advancement, which is equal to the variation of the enthalpy. This is twice the enthalpy of ammonia, at least three times the enthalpy of dihydrogen, the enthalpy of nitrogen times the variation of the ski advance. This implies, if we divide, that the variation of the enthalpy here is equal to th HG with respect to the derivative of the enthalpy in relation to the advancement at constant pressure and temperature is equal to twice the enthalpy of ammonia. Less than three times the enthalpy of dihydrogen. The enthalpy of nitrogen is the sum of of the molar enthalpy in the reactant of the products, each being multiplied by the corresponding stoichiometric coefficient. So the enthalpy of reaction is the derivative of the enthalpy with respect to at constant pressure is equal to the sum of number times the enthalpy of species B applied to all species, but in this case we can pass for the standard sizes, it will be the same thing applied. So the standard enthalpy of reaction Delta RH is equal to the derivative of the standard enthalpy with respect to at constant pressure and temperature is equal to the sum of the NURBS.

Notes

Summary



7m 09s

Grandeurs standard de réaction



- $\Delta_r H^\circ = \left(\frac{dH^\circ}{d\xi} \right)_{P,T} = \sum_B \nu_B H_B^\circ$

H_B° = enthalpie molaire standard de l'espèce B en J.mol⁻¹ ;

$\Delta_r H^\circ$ = enthalpie standard de réaction ;

- $\Delta_r U^\circ = \left(\frac{dU^\circ}{d\xi} \right)_{V,T} = \sum_B \nu_B U_B^\circ$

U_B° = énergie interne molaire standard de l'espèce B en J.mol⁻¹ ;

$\Delta_r U^\circ$ = énergie interne standard de réaction .

Thermodynamique

Times the standard enthalpy of B applied to all species B. Similarly, the internal energy is standard. The reaction is equal to the variation of the standard internal energy with respect to the advancement, what has volume is constant and is the sum of the U_B times the energy standard internal of B applied to all species.

Notes

Summary



8m 40s

Influence de la température sur les grandeurs standard



- Pour un corps pur, nous avons:

$$\left(\frac{dH_B^\circ}{dT}\right)_P = C_P^\circ(B) = \text{Capacité calorifique molaire standard de l'espèce } B \text{ à pression constante (en J.K}^{-1}\text{.mol}^{-1}\text{).}$$

$$\left(\frac{dU_B^\circ}{dT}\right)_V = C_V^\circ(B) = \text{Capacité calorifique molaire standard de l'espèce } B \text{ à volume constant (en J.K}^{-1}\text{.mol}^{-1}\text{).}$$

- Les dérivées de $\Delta_r U^\circ$ et $\Delta_r H^\circ$ par rapport à la température donnent les relations (lois) de Kirchhoff.

Thermodynamique

The influence of the temperature of the standard index. Standard enthalpy. Internal energy is standard. For a pure body, we have. The variation of the standard enthalpy of B with respect to the temperature at pressure constant is equal to the standard molar heat capacity of the species B at constant pressure and the variation of the internal energy of B with respect to the temperature at constant volume is equal to the capacity standard molar calorific value of the species b. At constant volume, these two capacities are measured in joules per kelvin per mole. The derivatives of the standard internal energy of reaction and of the standard enthalpy of reaction in relation to the temperature give the heating laws, whose derivative with respect to the temperature.

Notes

Summary



9m 06s



- $$\frac{d}{dT} \Delta_r U^\circ(T) = \frac{d}{dT} \sum_B \nu_B U_B^\circ = \sum_B \nu_B \frac{dU_B^\circ}{dT} = \sum_B \nu_B C_V^\circ(B) = \Delta_r C_V^\circ$$

et

- $$\frac{d}{dT} \Delta_r H^\circ(T) = \frac{d}{dT} \sum_B \nu_B H_B^\circ = \sum_B \nu_B \frac{dH_B^\circ}{dT} = \sum_B \nu_B C_P^\circ(B) = \Delta_r C_P^\circ$$

Thermodynamique

the internal energy of the reactions. Is equal to the derivative with respect to temperature of the sums of a BU. Times the standard internal energy of B applied to the species B. We get out of an Uber together constants the sum of an Uber that multiplies the derivative of the standard internal energy of B with respect to temperature. However, the derivative of the internal energy is standard. The B in relation to the temperature is nothing other than the heat capacity molar of the species B at constant volume, which is equal to the sum of the UB times the molar heat capacity of B at constant volume which is equal to the molar heat capacity of a reaction at constant volume. Delta Air C. Zero V. And the derivative of the standard enthalpy of reaction is equal to the derivative with respect to the sum temperature of one time. The standard enthalpy of B. Applied to all reaction species is equal to the sum of a UB multiplied by the derivative of the enthalpy standard of B with respect to temperature. The sum of a Huber times the capacity standard molar calorific value of B at constant pressure C C is equal to to the molar heat capacity of reaction at constant pressure delta RC0P.

Notes

Summary

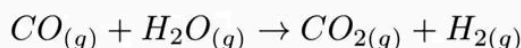


9m 59s



• Exemple d'application :

Déterminer à 1000K, l'enthalpie standard de la réaction de conversion du monoxyde de carbone par la vapeur d'eau selon l'équation bilan :



connaissant que $\Delta_r H^\circ(298K) = -41,17 \text{ kJ.mol}^{-1}$ et les capacités calorifiques molaires standard des divers corps purs (en $\text{J.K}^{-1}.\text{mol}^{-1}$):

$$CO : 27,6 + 4,18.10^{-3} T$$

$$H_2 : 28,83 + 4,2.10^{-3} T$$

$$CO_2 \text{ ou } H_2O : 30,54 + 1,05 - 10^{-2} T$$

Thermodynamique

Let's do an example of law enforcement that heats up. Now we're going to take the seats or we will try to apply this law which will allow us to calculate the enthalpy of the reactions determined at 1000 kelvins, the standard enthalpy of the convection reaction of carbon monoxide C or by the water vapor H2O according to the balance equation. Carbon monoxide in its gaseous state reacts with water in its gaseous state to give carbon dioxide in the gaseous state. More hydrogen in the gaseous state knowing that the standard enthalpy of reaction at 298 kelvin is equal to -41.17 kilos. Plays the role and the calorific capacities of the various pure bodies are given in joule per mole. So, for carbon monoxide, it's O. The standard molar heat capacity is 27.6 plus 4.18 dix. Average power three times the temperature Joule per Kelvin per mole. Likewise for the other bodies of hydrogen, carbon dioxide and water, as we see in the SS, but they are of an isolated length.

Notes

Summary



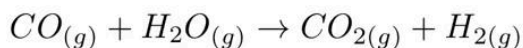
11m 30s



- Solution**

Enthalpie standard de réaction à $T = 1000K$: $\Delta_r H^\circ(T)$

Réaction:



- Loi de Kirchhoff :**

Or
$$\frac{d}{dT} \Delta_r H^\circ(T) = \Delta_r C_P^\circ \Rightarrow \int_{298}^T d\Delta_r H^\circ(T) = \int_{298}^T \Delta_r C_P^\circ dT$$

$$\Delta_r C_P^\circ = \sum_B \nu_B C_P^\circ(B) \Rightarrow$$

$$\Delta_r H^\circ(1000) - \Delta_r H^\circ(298) = \int_{298}^{1000} (1,23 + 2 \cdot 10^{-5} T) dT$$

$$\Rightarrow \text{A.N: } \Delta_r H^\circ(1000) \simeq -40,3 \text{ kJ.mol}^{-1}$$

Thermodynamique

If there's a sitting, there's David. We are asked to calculate the standard enthalpy of reaction at 1000 Kelvin that we note the Delta Air zero summer, reaction and carbon monoxide. If the gas reacts with water gas to give carbon dioxide in a gaseous state and hydrogen. The law of heating that the derivative with respect to temperature is. The standard enthalpy of reaction is equal to the molar heat capacity. The standard version is, if we give the integral of 298 to the capacity of the derivative of the standard enthalpy of reaction which is equal to the integral of the two five. On the side of the standard molar heat capacity of reaction that multiplies DT. The standard molar heat capacity of reaction at constant pressure is equal to. Sum of a UV-B times the capacity molar calorific value of the species B at constant pressure. Thus the standard enthalpy of reaction at 1000 kelvin. Standard enthalpy. The reactions at 298 Kelvin is equal to the integral of the two 5000 Kelvin of 1.23 plus two times ten to the lesser power of five. Finally the summer temperature. By doing the numerical application, we can only the standard enthalpy of reaction at 1000 kelvins and approximately equal to -48.3 kilo joule per mole of water.

Notes

Summary



12m 45s

Enthalpie standard et énergie interne standard de réaction



- Pour chaque espèce B, prise sous la pression standard P° , H_B° et U_B° sont liées par la relation:

$$H_B^\circ = U_B^\circ + P^\circ V_m^\circ \quad \text{où } V_m^\circ \text{ est le volume molaire standard de l'espèce } B$$

- Pour une phase condensée (solide ou liquide) : $P^\circ V_m^\circ \ll U_B^\circ \Rightarrow H_B^\circ \cong U_B^\circ$
- Pour une phase gazeuse ne comportant que des gaz parfaits :

$$\Delta_r H^\circ(T) = \Delta_r U^\circ(T) + \left(\sum_B \nu_{B, gaz} \right) RT$$

Remarques:

- $\Delta_r H^\circ(T) > 0$, réaction endothermique
- $\Delta_r H^\circ(T) = 0$, réaction athermique
- $\Delta_r H^\circ(T) < 0$, réaction exothermique

Thermodynamique

Here, for each species where we speak the standard internal enthalpy for each species. Granby taken under standard pressure is zero. The standard enthalpy of B and the energy standard internal of B are related by the relation The standard enthalpy of B is equal to the standard internal usage of the species B. Plus the product of the standard pressure times the standard molar volume $v_0 m$ of B for a phase is condensed from a phase that is solid or liquid. The product water. Standard pressure. Times the standard molar volume. This product is negligible compared to the standard internal energy of B. One gives that the standard enthalpy of the species b is approximately equal to to the internal and standard energy of the species b. For solid or liquid condensed phases, for a gas phase containing only perfect gases. The standard enthalpy of reaction is equal to the standard internal energy of reaction plus 109 B. Cold gas R D, r being the coefficient of perfect gases and the temperature. From there, we can make some remarks. As my colleague said, see how we can apply the law of the customs officer here. If the standard enthalpy of reaction is positive, then the reaction is endothermic.

Notes

Summary



14m 23s

Enthalpie standard et énergie Interne standard de réaction



- Pour chaque espèce B, prise sous la pression standard P° , H_B° et U_B° sont liées par la relation:

$$H_B^\circ = U_B^\circ + P^\circ V_m^\circ \quad \text{où } V_m^\circ \text{ est le volume molaire standard de l'espèce } B$$

- Pour une phase condensée (solide ou liquide) : $P^\circ V_m^\circ \ll U_B^\circ \Rightarrow H_B^\circ \cong U_B^\circ$
- Pour une phase gazeuse ne comportant que des gaz parfaits :

$$\Delta_r H^\circ(T) = \Delta_r U^\circ(T) + \left(\sum_B \nu_{B, gaz} \right) RT$$

Remarques:

- $\Delta_r H^\circ(T) > 0$, réaction endothermique
- $\Delta_r H^\circ(T) = 0$, réaction athermique
- $\Delta_r H^\circ(T) < 0$, réaction exothermique

Thermodynamique

The system absorbs heat. If the standard enthalpy of the reaction is equal to zero, the system is thermal and if the standard enthalpy of the reaction is lower than zero, the reaction is exothermal from which heat is released.

Notes

Summary



15m 56s

CONCLUSION



- L'enthalpie H d'un système en réaction chimique: $H = \sum_B n_B H_B$

- Enthalpie standard de réaction ($\Delta_r H^\circ$) :

$$\Delta_r H^\circ = \left(\frac{dH^\circ}{d\xi} \right)_{P,T} = \sum_B \nu_B H_B^\circ \text{ en J.mol}^{-1}$$

- Energie interne standard de réaction ($\Delta_r U^\circ$) :

$$\Delta_r U^\circ = \left(\frac{dU^\circ}{d\xi} \right)_{V,T} = \sum_B \nu_B U_B^\circ \text{ en J.mol}^{-1}$$

Thermodynamique

We have completed this lesson where we have seen that the enthalpy H of a system with chemical reaction is equal to the sum of the quantities of the small materials NB the species b times the enthalpy and the species b applied to all species. And that the standard enthalpy of reaction $\Delta_r H^\circ$ is the derivative of the standard enthalpy in relation to the advancement of the reaction at constant pressure and temperature is equal to the sum of ν_B times the standard enthalpy of B . Applied to all species B in reaction and these measurements in joules per mole. And that the internal energy is standard. Feedback. $\Delta_r U^\circ$ is equal to the variation of the energy internal U with respect to the advancement of the reaction at constant volume is equal to the sum of ν_B times the internal and standard energy of species B applied to all species. And these measurements in joules per mole. Thank you and goodbye.

Notes

Summary



16m 13s