

# Les grandeurs de réaction

T1 – Thermochimie – Chapitre 2

## I. Définitions

$$\xi = \frac{n_i - n_0}{\nu_i} \quad d\xi = \frac{dn_i}{\nu_i} \quad \tau = \frac{\xi}{\xi_{max}}$$

$$X_i^0 = X_m(B_i, T, P^0)$$

$$\Delta_r X(T, P, \xi) = \left( \frac{\partial X}{\partial \xi} \right)_{T, P} = \sum \nu_i \bar{X}_i$$

$$\Delta_r X_a^0(T) = \sum \nu_i X_i^0$$

$\xi$  (mol) : avancement  
 $n_i$  (mol) : quantité de constituant  $B_i$  à  $t$   
 $n_0$  (mol) : quantité de constituant  $B_i$  à  $t = 0$

$X_i^0$  : grandeur standard du constituant  $B_i$   
 $\Delta_r X_a(T, P, \xi)$  : grandeur de la réaction  
 $\Delta_r X_a^0(T)$  : grandeur standard de la réaction (a)

## II. Réactions homologuées

| Notation                                            |     | Nom                 | Équation (es = état stable à T)                                 |
|-----------------------------------------------------|-----|---------------------|-----------------------------------------------------------------|
| $\Delta_f X^0(A_a B_b C_c, \text{etat}, T)$         | f   | Formation           | $aA_{(es)} + bB_{(es)} + cC_{(es)} = A_a B_b C_c (\text{etat})$ |
| $\Delta_{at} X^0(A_a B_b C_c, \text{etat}, T)$      | at  | Atomisation         | $A_a B_b C_c (\text{etat}) = aA_{(es)} + bB_{(es)} + cC_{(es)}$ |
| $\Delta_c X^0(B, \text{etat}, T)$                   | c   | Combustion          | $B_{(\text{etat})} + x_1 O_{2(g)} = x_2 CO_2 + x_3 D_{(es)}$    |
| $\Delta_{hyd} X^0(B, T)$                            | hyd | Hydratation         | $B = B_{(aq)}$                                                  |
| $\Delta_{fus} X^0(B, T)$                            | fus | Fusion              | $B_{(s)} = B_{(l)}$                                             |
| $\Delta_{vap} X^0(B, T)$                            | vap | Vaporisation        | $B_{(l)} = B_{(g)}$                                             |
| $\Delta_{sub} X^0(B, T)$                            | sub | Sublimation         | $B_{(s)} = B_{(g)}$                                             |
| $\Delta_{trs} X^0(S_\alpha \rightarrow S_\beta, T)$ | trs | Transition de phase | $S_\alpha (s) = S_\beta (g)$                                    |

## III. Calcul des grandeurs standard de réactions

|                                   |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |  |  |
|-----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|
| Réactions liées                   | $(1) = a(2) + b(3) \Rightarrow \Delta_r X_1^0(T) = a \Delta_r X_2^0(T) + b \Delta_r X_3^0(T)$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |  |  |
| Loi de Hess                       | $\Delta_r X_a^0(T) = \sum \nu_i \Delta_f X^0(B_i, \text{etat}, T)$<br>etat = état de $B_i$ dans (a)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |  |
| Kirchhoff                         | $\frac{d\Delta_r H_a^0(T)}{dT} = \sum (\nu_i C_{p,i}^0)_a \Rightarrow \Delta_r H_a^0(T_2) = \Delta_r H_a^0(T_1) + \int_{T_1}^{T_2} \sum (\nu_i C_{p,i}^0)_a dT$ $\frac{d\Delta_r S_a^0(T)}{dT} = \sum \frac{(\nu_i C_{p,i}^0)_a}{T} \Rightarrow \Delta_r S_a^0(T_2) = \Delta_r S_a^0(T_1) + \int_{T_1}^{T_2} \sum (\nu_i C_{p,i}^0)_a \frac{dT}{T}$                                                                                                                                                                                                                                                                                                                        |  |  |
| Relations entre $\Delta_r X^0(T)$ | $G_m = H_m - TS_m \Rightarrow \Delta_r G_a^0(T) = \Delta_r H_a^0(T) - T\Delta_r S_a^0(T)$ $\frac{d\left(\frac{G_m}{T}\right)}{dT} = -\frac{H_m}{T^2} \Rightarrow \frac{d\left(\frac{\Delta_r G_a^0(T)}{T}\right)}{dT} = -\frac{\Delta_r H_a^0(T)}{T^2} \Rightarrow \frac{\Delta_r G_a^0(T_2)}{T_2} = \frac{\Delta_r G_a^0(T_1)}{T_1} - \int_{T_1}^{T_2} \Delta_r H_a^0(T) \frac{dT}{T^2}$ $\frac{dG_m}{dT} = -S_m \Rightarrow \frac{d\Delta_r G_a^0(T)}{dT} = -\Delta_r S_a^0(T) \Rightarrow \Delta_r G_a^0(T_2) = \Delta_r G_a^0(T_1) - \int_{T_1}^{T_2} \Delta_r S_a^0(T) dT$ $H_m = U_m + PV_m \Rightarrow \Delta_r H_a^0(T) = \Delta_r U_a^0(T) + \sum \nu_{i,gaz} RT$ |  |  |

### Remarques :

- $\Delta H_f^0(B_i, \text{etat stable de } B_i \text{ à } T, T) = 0$
- Pour les mélanges idéaux,  $\Delta_r H = \Delta_r H^0$  et  $\Delta_r U = \Delta_r U^0$ .