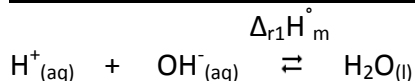


TD 2 Thermodynamique – Exercices supplémentaires

Exercice 5

Enthalpie de neutralisation d'un acide fort par une base forte dans l'eau :

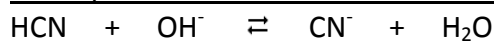


$$\Delta_{\text{r1}}\overset{\circ}{H}_m = \Delta_{\text{f}}\overset{\circ}{H}_m(\text{H}_2\text{O}, \text{l}) - \Delta_{\text{f}}\overset{\circ}{H}_m(\text{H}^+, \text{aq}) - \Delta_{\text{f}}\overset{\circ}{H}_m(\text{OH}^-, \text{aq})$$

$$\Delta_{\text{f}}\overset{\circ}{H}_m(\text{H}^+, \text{aq}) = 0 \text{ car c'est un corps pur}$$

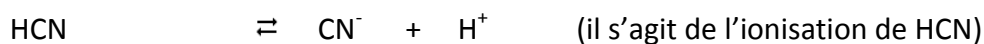
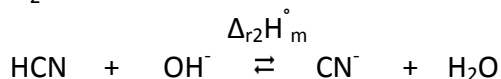
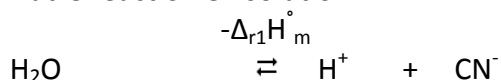
$$\Delta_{\text{r1}}\overset{\circ}{H}_m = -285,2 - (-230) = \mathbf{-55,5 \text{ kJ}\cdot\text{mol}^{-1}}$$

Enthalpie d'ionisation de HCN dans l'eau :



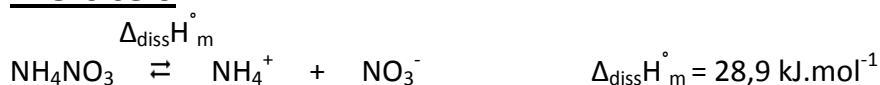
$$\Delta_{\text{r2}}\overset{\circ}{H}_m = 2,5 \text{ kcal}\cdot\text{mol}^{-1}$$

Autre réaction en solution :



$$\Delta_{\text{r3}}\overset{\circ}{H}_m = -\Delta_{\text{r1}}\overset{\circ}{H}_m + \Delta_{\text{r2}}\overset{\circ}{H}_m = -(-55,5) \times 1000 + 2,5 \times 1000 \times 4,18 = \mathbf{65,95 \text{ kJ}\cdot\text{mol}^{-1}}$$

Exercice 6



On mélange 10 g de NH_4NO_3 (nitrate d'ammonium) avec 50 g d'eau

Hypothèse : il n'y a pas d'échange de chaleur entre le récipient et le milieu extérieur

$$Q(\text{NH}_4\text{NO}_3) + Q(\text{eau}) = 0 \quad (\text{avec } Q \text{ en J})$$

A P_{atm} = constante, on a $\Delta_r\overset{\circ}{H} = Q_p$

$$\text{Donc : } \Delta_{\text{diss}}\overset{\circ}{H}_m = Q(\text{NH}_4\text{NO}_3) \text{ (attention à l'unité : kJ}\cdot\text{mol}^{-1}\text{)}$$

$$n(\text{NH}_4\text{NO}_3) \times Q(\text{NH}_4\text{NO}_3) + Q(\text{eau}) = 0$$

$$\frac{m(\text{NH}_4\text{NO}_3)}{M(\text{NH}_4\text{NO}_3)} \times \Delta_{\text{diss}}H_m^0 + Q(\text{eau}) = 0$$

$$\text{Or : } Q(\text{H}_2\text{O}) = \int_{T_i}^{T_f} \delta Q = \int_{T_i}^{T_f} m_{\text{eau}} \times C_p(\text{eau}, l) \times dt = m_{\text{eau}} \times C_p(\text{eau}, l) \times (T_f - T_i)$$

D'où :

$$\frac{m(\text{NH}_4\text{NO}_3)}{M(\text{NH}_4\text{NO}_3)} \times \Delta_{\text{diss}}H_m^0 + m_{\text{eau}} \times c_p(\text{eau}, l) \times (T_f - T_i) = 0$$

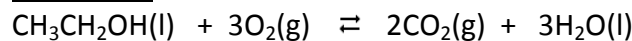
$$T_f - T_i = \Delta T = -\frac{m(\text{NH}_4\text{NO}_3)}{M(\text{NH}_4\text{NO}_3)} \times \Delta_{\text{diss}}H_m^0 \times \frac{1}{m_{\text{eau}} \times C_p(\text{eau}, l)}$$

$$T_f - T_i = \Delta T = -\frac{10}{80,1} \times 28,9 \times 10^3 \times \frac{1}{50 \times 4,18} = -17,3 \text{ K} = -17,3 \text{ }^\circ\text{C}$$

Exercice 7

P = constant = 1 atm

Question a



Question b

	$\text{CH}_3\text{CH}_2\text{OH}(l)$	+	$3\text{O}_2(g)$	\rightleftharpoons	$2\text{CO}_2(g)$	+	$3\text{H}_2\text{O}(l)$
A t_0	$n(\text{EtOH})$		$n(\text{O}_2)$		0		0
A t_{eq}	$n(\text{EtOH}) - x$		$n(\text{O}_2) - 3x$		2x		3x

A $t=0$, on a $V(\text{O}_2)_i = 22,4 \text{ L}$

A la fin de la réaction, il reste $V(\text{O}_2)_f = 5,6 \text{ L}$

D'où : $V(\text{O}_2)_{\text{consommé}} = 22,4 - 5,6 = 16,8 \text{ L}$

O_2 est un gaz parfait : d'où $P(\text{O}_2)V = n(\text{O}_2)RT$

$$n(\text{O}_2) = \frac{P(\text{O}_2) \times V}{R \times T} = \frac{1,01325 \times 10^5 \times 16,8 \times 10^{-3}}{8,314 \times 273,15} = 0,75 \text{ mol}$$

A partir du tableau d'avancement : $n(\text{O}_2) - 3x = 0 \rightarrow x = \frac{n(\text{O}_2)}{3} = 0,25 \text{ mol} = n(\text{EtOH})$

Question c

A P = constante, $\Delta_r H^\circ = Q_p = n \Delta_r H_m^\circ$

$Q_p = -342,76 \text{ kJ}$ (il s'agit d'une perte de chaleur)

$$\rightarrow \Delta_r H_m^\circ = \frac{Q_p}{n} = \frac{-342,76}{0,25} = -1371,04 \text{ kJ.mol}^{-1}$$

Question d

A $273,15 \text{ K}$ $\Delta_{\text{comb}}H_m^\circ(\text{CH}_3\text{COOH}, l) = -873,62 \text{ kJ.mol}^{-1}$

On cherche : $\Delta_r H^\circ$ de la réaction : $\text{CH}_3\text{CH}_2\text{OH}(l) + \text{O}_2(g) \rightleftharpoons \text{CH}_3\text{COOH}(l) + \text{H}_2\text{O}(g)$

Etape 1 :

$$\underline{1} \quad \Delta_r H^\circ_1 = \Delta_f H^\circ_{m,298}(\text{H}_2\text{O}, l) = -285,2 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

Etapes 2 et 4 : changement de température, sans changement d'état

$$\Delta_r H^\circ = Q_p = \int_{T_i}^{T_f} n \cdot C_p \cdot dT \text{ ou } \Delta_r H^\circ_m = \int_{T_i}^{T_f} C_p \cdot dT$$

$$\underline{2} \quad \Delta_r H^\circ_2 = \int_{298}^{373} C_p(\text{H}_2\text{O}, l) dT = C_p(\text{H}_2\text{O}, l) \times (373 - 298) = 75,3 \times (373 - 298) = 5640 \text{ J} \cdot \text{mol}^{-1}$$

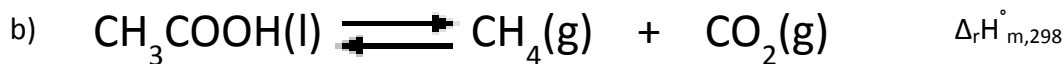
$$\underline{4} \quad \Delta_r H^\circ_4 = \int_{373}^{298} C_p(\text{H}_2\text{O}, g) dT = C_p(\text{H}_2\text{O}, g) \times (298 - 373) = 75,3 \times (298 - 373) = -2520 \text{ J} \cdot \text{mol}^{-1}$$

Etape 3 : changement d'état (à température constante)

$$\Delta_r H^\circ = n \cdot L_{\text{vap}} = n \cdot \Delta_{\text{vap}} H^\circ_m \text{ ou } \Delta_r H^\circ_m = \Delta_{\text{vap}} H^\circ_m$$

$$\Delta_r H^\circ_3 = \Delta_{\text{vap}} H^\circ_m = 44 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta_r H^\circ_{m,298} &= \Delta_f H^\circ_{m,298}(\text{H}_2\text{O}, g) = \Delta_r H^\circ_1 + \Delta_r H^\circ_2 + \Delta_r H^\circ_3 + \Delta_r H^\circ_4 \\ &= -285 \times 10^3 + 5648 + 44 \times 10^3 - 2520 \\ &= -238 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$



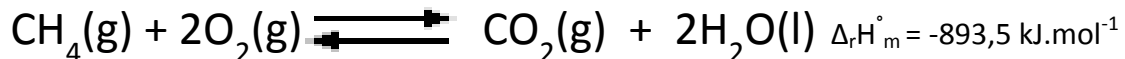
$$\Delta_r H^\circ_{m,298} = \Delta_f H^\circ_m(\text{CH}_4, g) + \Delta_f H^\circ_m(\text{CO}_2, g) - \Delta_f H^\circ_m(\text{CH}_3\text{COOH}, l)$$

Avec $\Delta_f H^\circ_m(\text{CH}_4, g)$ inconnue

Formation de $\text{CH}_4(g)$:



Donnée :

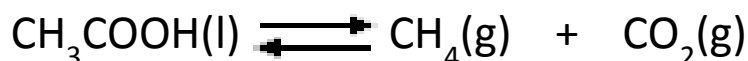


$$\Delta_r H^\circ_m = \Delta_f H^\circ_m(\text{CO}_2, g) + 2\Delta_f H^\circ_m(\text{H}_2\text{O}, l) - 2\Delta_f H^\circ_m(\text{O}_2, g) - \Delta_f H^\circ_m(\text{CH}_4, g)$$

Avec $2\Delta_f H^\circ_m(\text{O}_2, g) = 0$ car corps simple

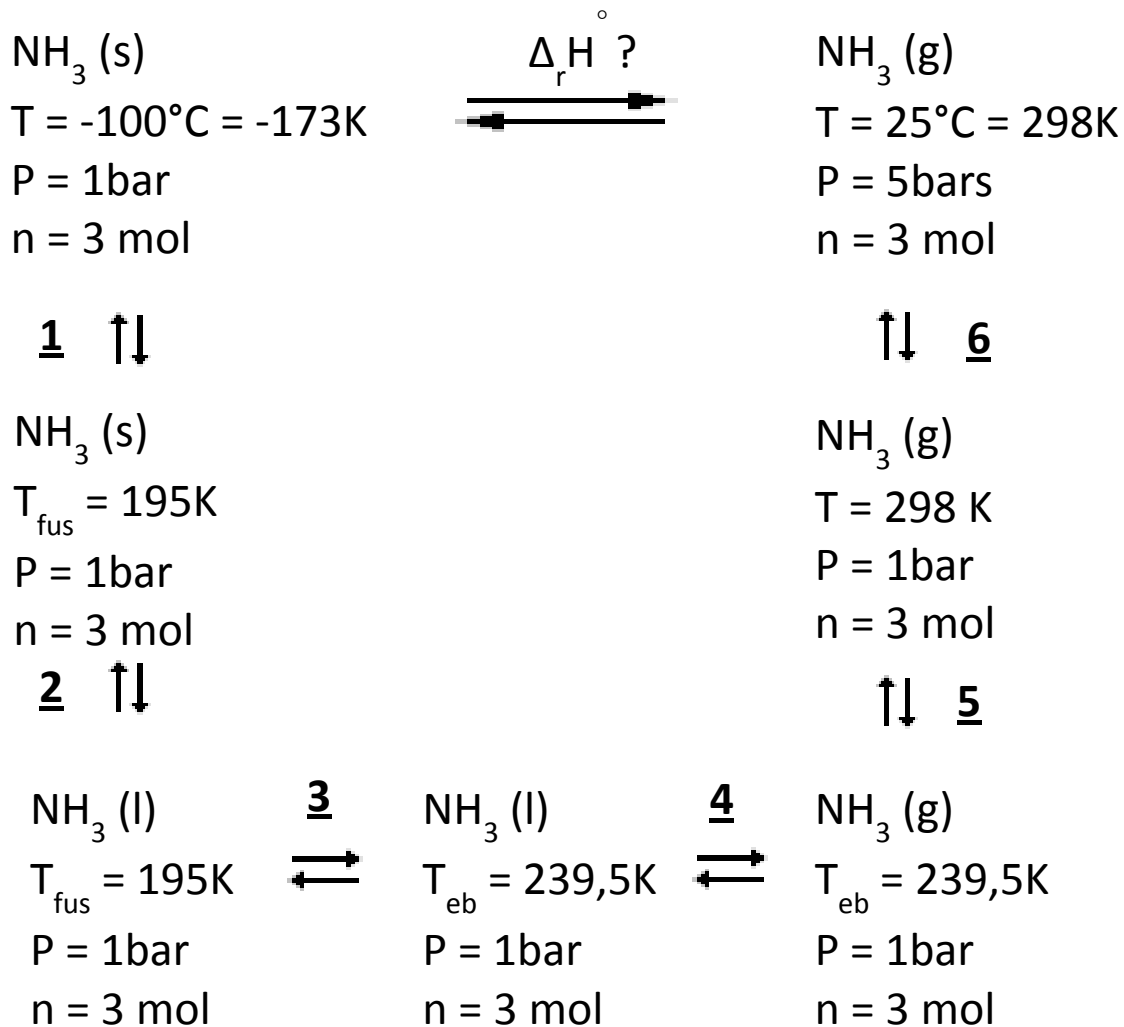
$$\begin{aligned} \text{D'où } \Delta_f H^\circ_m(\text{CH}_4, g) &= \Delta_f H^\circ_m(\text{CO}_2, g) + 2\Delta_f H^\circ_m(\text{H}_2\text{O}, l) - \Delta_r H^\circ_m \\ &= (-393,5) + 2 \times (-285,2) - (-893,5) \\ &= -70,4 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Enthalpie de la réaction :



$$\begin{aligned} \Delta_r H^\circ_m &= \Delta_f H^\circ_m(\text{CH}_4, g) + \Delta_f H^\circ_m(\text{CO}_2, g) - \Delta_f H^\circ_m(\text{CH}_3\text{COOH}, l) \\ &= -70,4 - 393,5 + 486,5 = 22,6 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Exercice 9 :



Etapes 1, 3, 5 : Changement de T à pression constante

$$\text{Donc } \Delta_r H^\circ = Q_p = \int_{T_i}^{T_f} n \cdot C_p \cdot dT$$

$$\Delta_r H^\circ_1 = \int_{173}^{195} n \times C_p(\text{NH}_3, \text{s}) dT = 3 \times 35,67 \times (195 - 173) = 2354 \text{ J}$$

$$\Delta_r H^\circ_3 = \int_{195}^{239,5} n \times C_p(\text{NH}_3, \text{l}) dT = 3 \times 74,82 \times (239,5 - 195) = 9988 \text{ J}$$

$$\Delta_r H^\circ_5 = \int_{239,5}^{298} n \times C_p(\text{NH}_3, \text{g}) dT = 3 \times 35,1 \times (298 - 239,5) = 6160 \text{ J}$$

Etapes 2 et 4 : Changement d'état à P constante

$$\text{Donc } \Delta_r H^\circ = Q_p = n \cdot L$$

$$\Delta_r H^\circ_2 = n \cdot L_{\text{fus}} = 3 \times 5,7 \times 10^3 = 1,71 \times 10^4 \text{ J}$$

$$\Delta_r H^\circ_4 = n \cdot L_{\text{vap}} = 3 \times 23,4 \times 10^3 = 7,02 \times 10^4 \text{ J}$$

Etape 6 : Augmentation de pression à T constante

$$\Delta_r H^\circ_6 = \int_{T_i}^{T_f} n \times C_p \times dT = 0 \text{ (car } T = \text{ constante)}$$

Conclusion :

$$\begin{aligned}\Delta_r H^\circ &= \Delta_r H^\circ_1 + \Delta_r H^\circ_2 + \Delta_r H^\circ_3 + \Delta_r H^\circ_4 + \Delta_r H^\circ_5 + \Delta_r H^\circ_6 \\ &= 2354 + 1,71 \times 10^4 + 9988 + 7,02 \times 10^4 + 6160 + 0 = 105,80 \text{ kJ}\end{aligned}$$