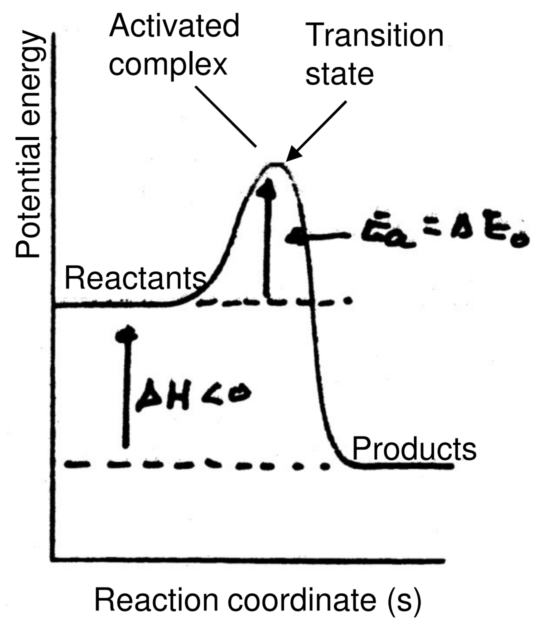
Chapitre 3 –
État de transition

Références : i) Atkins – Chap. 27, 19
ii) Science 303, 186-195 (2006)
(D. Truhlar, UMn)

1. Théorie du complexe activé



$$A + B \overset{K^*}{\longleftrightarrow} C^* \overset{k^*}{\longrightarrow} P \qquad 3.1$$

$$[C^*] = K^*[A][B] \qquad 3.2$$

$$\upsilon = \frac{d[P]}{dt} = k^*[C^*] = k^*K^*[A][B] = k_2[A][B] \qquad 3.3$$

$k_2 = k^*K^* =$ dissociation x formation

Énergie d'activation : $\Delta E_0 = E_0(C^*) - E_0(R)$; $R =$ réactifs 3.4

$E_0 = E(v=0) =$ énergie de zéro

$V(s) \simeq -\frac{1}{2}ks^2$ $\quad k = M\omega^2(s)$; $\quad \omega = i\left(\frac{k}{M}\right)^{1/2}$ $\quad i = \sqrt{-1}$

$\omega =$ fréquence de la coordonnée de réaction

$k^* = \gamma(T)\nu$

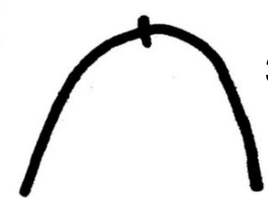
$\nu = \omega / 2\pi \left(s^{-1}\right)$ 3.5

$E = h\nu = 6.626\times10^{-34}\,Js \times 6\times10^{12}\,s^{-1} \times 6\times10^{23}\,mol^{-1} = 2.4\,kJmol^{-1}$

$\nu \simeq 6\times10^{12}\,s^{-1}$

$\tau = 1/\nu \sim 160\times10^{-15}\,s$

$\omega > 0$



$\omega \sim i$

$\gamma(T) \simeq 1 =$ facteur de transition $\gamma <$ l'effet tunnel pour $E<E_a$

Équilibre: $A + B \xleftrightarrow{K^*} C^*$

$P_x V = n_x RT$

$$K(P) = P_C / P_A P_B; \quad [A] = \frac{n_A}{V} = P_A / RT$$ 3.6

$$\left[C^*\right] = K(P) RT [A][B]$$ 3.7

$$K^* = RT \bullet K(P)$$

$$\boxed{K(P) = N_A \left(q^0_{C^*} / q^0_A q^0_B\right) e^{-\Delta E_0/RT},}$$ $N_A =$ # d'Avogadro ($6x10^{23}$) 3.8

3.9

Fonction de partition : exemple : $q_\nu = \left(1 - e^{-h\nu/k_B T}\right)^{-1}$ = # d'états quantiques accessibles

$$\omega(s) = 2\pi\nu(s)$$

s=coordonnée de réaction

$$\frac{h\nu}{k_B T} << 1 \qquad q(\nu_s) \rightarrow \frac{1}{1 - \left(1 - \frac{h\nu}{k_B T}\right)} \simeq \frac{k_B T}{h\nu(s)}$$ = # de quanta hv dans $k_B T$

<u>État de transition :</u>

$$q^0_{C^*} = q^0_{3n-7} q_{\nu_s} = \frac{k_B T}{h\nu(s)} \overline{q}^0_C$$

$$\boxed{K^* = \frac{k_B T}{h\nu} RT \bullet \frac{N_A \overline{q}^0_{C^*}}{q^A_0 q^B_0} e^{-\Delta E_0/RT}}$$ 3.10

Vitesse de réaction

$$k_2 = k^* K^* = \gamma(T)\nu \bullet \frac{k_B T}{h\nu} \bar{K}$$

$$= \gamma(T) \bullet \frac{k_B T}{h} \bar{K} \qquad 3.11$$

$$\bar{K} = RT\ N_A \left(\bar{q}^0_{C^*} / q^0_A\, q^0_B\right)\ e^{-\Delta E_0/RT} \qquad 3.12$$

Loi de Boltzmann

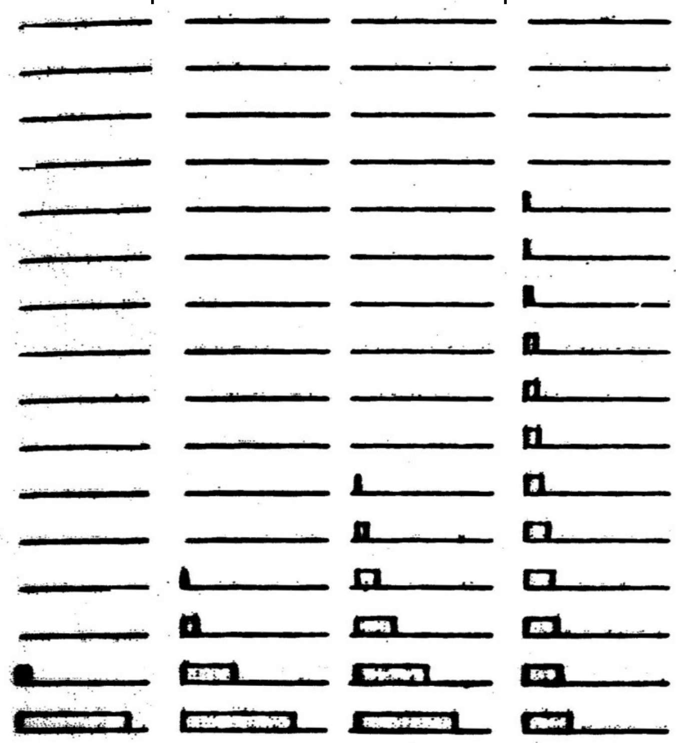
$$P_\upsilon = \frac{e^{-\beta \in_\upsilon}}{q}, \in_\upsilon = (\upsilon + 1/2) h\nu$$

$$q = \sum_{\upsilon=0}^{\infty} e^{-\beta \in_\upsilon}$$ = # d’états disponibles à T

= fonction de partition
(section 4)

$$\beta = \frac{1}{k_B T}; \qquad \in = h\nu$$

Basse température | Haute température



$\beta\in$:	3.0	1.0	0.7	0.3
q:	1.05	1.58	1.99	3.86

The populations of the energy levels

2. Énergie libre d'activation

$$\Delta G^{*} = -RT \ln \bar{K}$$ 3.13

$\bar{K} =$ Constante d'équilibre sans la coordonnée de réaction

$$k_2 = \gamma(T)\frac{k_B T}{h} \bullet e^{-\Delta G^{*}/RT}$$ 3.14

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*}$$

$$\Delta H^{*} = \Delta E + \Delta n \bullet RT(\Delta PV) \qquad \Delta n = -1$$

$$k_2 = \left[\gamma(T)\frac{k_B T}{h}\right] e^{-\Delta E_0/RT} \bullet e^{\Delta S^{*}/R} \bullet e^{1}$$

$$k_2 = A e^{-E_a/RT}$$ (Arrhenius)

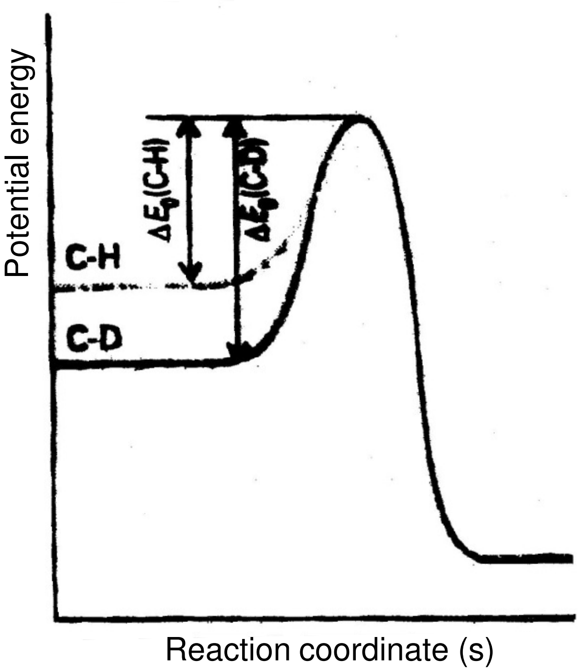
$$A = \frac{k_B}{h} T e^{1} e^{\Delta S^{*}/R}$$ (eq. 3, J. Phys. Chem A III, 5388 (2007)) 3.15

$E_a = \Delta E_0 =$ énergie d'activation

$\Delta S^{*} =$ entropie d'activation

$\Delta H^{*} = \Delta E_0 + (\Delta n) RT =$ enthalpie d'activation

3. Exemple/effet cinétique isotopique



$$\Delta E_0^{(1)} = \Delta E_0^{*} - E_0(C-H) \quad 3.16$$

$$\Delta E_0^{(2)} = E_0^{*} - E_0(C-D) \quad 3.17$$

$$\Delta E_0^{(2)} - \Delta E_0^{(1)} = E_0(C-H) - E_0(C-D) \quad 3.18$$

$$E_\upsilon = \left(\upsilon + \tfrac{1}{2}\right) h\nu \quad 3.19$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{\omega(s)}{2\pi}$$

$$\mu_{C-H} = \frac{M_C M_H}{M_C + M_H} = \frac{12}{13}$$

$$\mu_{C-D} = \frac{12\times 2}{12+2} = \frac{24}{14} \simeq 2\mu_{C-H}$$

$$\frac{k_2^{C-H}}{k_2^{C-D}} \simeq \frac{e^{-\Delta E_0^{(1)}/RT}}{e^{-\Delta E_0^{(2)}/RT}} = e^{+\left[\Delta E_0^{(2)} - \Delta E_0^{(1)}\right]} / RT \quad 3.20$$

$$= e^{+\left[E_0(CH) - \Delta E_0(C-D)\right]} / RT$$

$$E_0(C-H) = \frac{1}{2}\hbar\left[\frac{k}{\mu_{CH}}\right]^{1/2} \quad ; \quad E_0(C-D) = \frac{1}{2}\hbar\left[\frac{k}{\mu_{CD}}\right]^{1/2}$$

$$\omega = 2\pi\nu = \left(\frac{k}{\mu}\right)^{1/2} \text{ (eq. 3.5)} \qquad = \frac{1}{2}\hbar\left[\frac{k}{\mu_{CH}}\right]^{1/2}$$

$$E_0(C-H)-E_0(C-D)=\frac{1}{2}\hbar\left(\frac{k}{\mu_{CH}}\right)^{1/2}\left[1-\frac{1}{\sqrt{2}}\right]$$

$$\simeq 0.15\hbar(k/\mu_{CH})^{1/2}>0 \quad =0.15\hbar\omega \quad \omega_{C-H}\simeq 3000cm^{-1} \qquad (1\,cm^{-1}=1.19627\times 10^{-2}\ kJmol^{-1})$$

$\frac{k_2^{C-H}}{k_2^{C-D}}\simeq$ **7 à 300°K**

4. Thermodynamique statistique (Atkins, Ch. 19)

de configuration

(Boltzmann) $\longrightarrow$ $W = N!/n_0!n_1!...$ 3.21

$\ln W = \ln N! - \sum \ln n_i!$ 3.22

Approximation de Sterling: $\ln x! = x\ln x - x$

$\ln 10! = 10\ln 10 - 10 = 23 - 10 \simeq 13$
$10! = e^{13}$

$\ln W = N\ln N - N - \sum(n_i \ln n_i - n_i) \qquad \sum n_i = N$

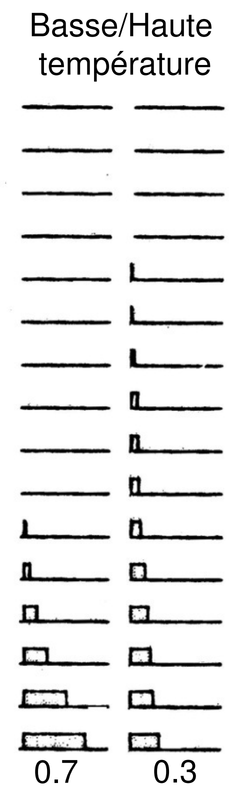
3.23

$= N\ln N - \sum n_i \ln n_i$

Constante: $\sum n_i E_i = E \qquad \sum n_i = N$

Distribution maximum : (plus probable!)

$$d\ln W = \sum \frac{\partial \ln W}{\partial n_i} dn_i = 0$$



Contraintes :

$$\beta \sum E_i dn_i = 0 \quad ; \quad \alpha \sum dn_i = 0 \qquad (\beta, \alpha = \text{paramètres de Lagrange})$$

$$\boxed{\frac{\partial \ln W}{\partial n_i} + \alpha - \beta E_i = 0} \qquad 3.24$$

$$\frac{\partial \ln W}{\partial n_i} = -\ln\left(n_i/N\right) = \beta E_i - \alpha$$

$$\frac{n_i}{N} = e^{\alpha} e^{-\beta E_i}$$

$$\sum \frac{n_i}{N} = \frac{N}{N} = 1 = e^{\alpha} \sum e^{-\beta E_i}$$

Boltzmann :

$$\boxed{\frac{n_i}{\mathrm{N}} = \frac{e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \frac{e^{-\beta E_i}}{q}} = p_i \qquad 3.25$$

Fonction de partition :

$$\boxed{q = \sum e^{-E_i/k_B T}} \quad ; \quad \beta = 1/k_B T \qquad 3.26$$

Exemple :

$$q_\upsilon = \sum_0^\infty e^{-E_\upsilon/k_B T} \quad ; \quad n_\upsilon/N = e^{-\beta E_\upsilon}/q_\upsilon$$

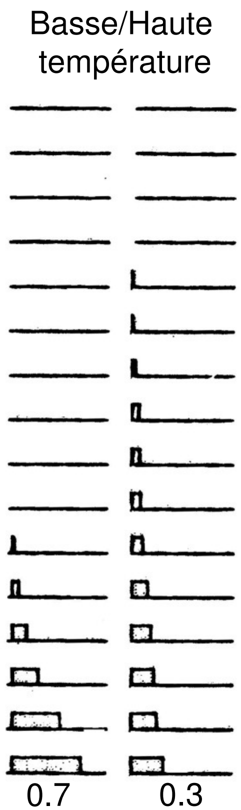
$$E_\upsilon = \left(\upsilon + \tfrac{1}{2}\right) h\nu \qquad \upsilon = 0, 1, 2 \qquad \in = h\nu$$

$$q_\upsilon = \left(1 - e^{-\beta\epsilon}\right)^{-1} = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \ldots e^{-n\beta\epsilon} + \ldots$$
$$\beta = 1/k_B T \qquad \epsilon = h\nu$$
3.27

Énergie : $E = \sum n_i E_i = N \sum p_i E_i \qquad p_i = n_i / N$ 3.28

Entropie: $\boxed{S = k_B \ln W}$

$$S = k_B N \ln N - \sum n_i \ln n_i$$
$$= k_B \sum n_i \ln N - \sum n_i \ln n_i$$
$$= k_B \sum n_i \ln \frac{N}{n_i} = -k \sum n_i \ln \frac{n_i}{N}$$
$$= -k_B N \sum_i \left(\frac{n_i}{N}\right) \ln\left(\frac{n_i}{N}\right)$$



$$\boxed{S = -k_B N \sum_i p_i \ln p_i}; \quad p_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{q}$$ 3.29

$$\sum_i p_i = 1 \;, \quad q = \sum_i e^{-\beta E_i}$$

$S = 0$ quand $p_0 = 1, \quad p_i = 0.$ 3.30

$S > 0$ quand $p_i < 1$

3.31

q molécule $= q_t \times q_{rot} \times q_v =$ translation x rotation x vibration=# d'états quantiques

de degrés de liberté: $3n = n_\upsilon + n_{rot} + n_t$; $n = \#$ d'atomes

$$n_\upsilon = 3n - 6 \qquad n_{rot} = 3 \qquad n_t = 3$$

$$A + B \leftrightarrow C^* \qquad n_A + n_B = n$$

$$n_\upsilon^a = 3n_A - 6 \qquad n_\upsilon^B = 3n_B - 6 \qquad n_\upsilon^{C^*} = 3n - 7$$

$$q_\upsilon^a = (q_\upsilon)^{3n_a - 6} \qquad q_\upsilon^B = (q_\upsilon)^{3n_B - 6} \qquad q_\upsilon^{C^*} = (q_\upsilon)^{3n-7}$$

note : $q_\upsilon^{C^*} = q_\upsilon^{(S)} (q_\upsilon)^{3N-7}$ (Coordonnée de réaction)

3.32

$$q_\upsilon(s) = \frac{k_B T}{h\nu(s)}$$

$$\boxed{q_{rot} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta(E_J)}}$$

$$E_J = BJ(J+1); \quad J = 0, 1, ---$$

$$B = \hbar^2 / 2\mu R_0^2, \quad R_0 = longueur\ de\ liaison$$

$$\boxed{q_t = V / \lambda^3 \qquad \lambda(T) = h(2\pi M k_B T)^{-1/2}}$$

$$\left\{ \begin{array}{ll} p^2/2m = k_B T/2 & \text{(thermodynamique)} \\ \lambda = h/p & \text{(de Broglie)} \end{array} \right\}$$ 3.33

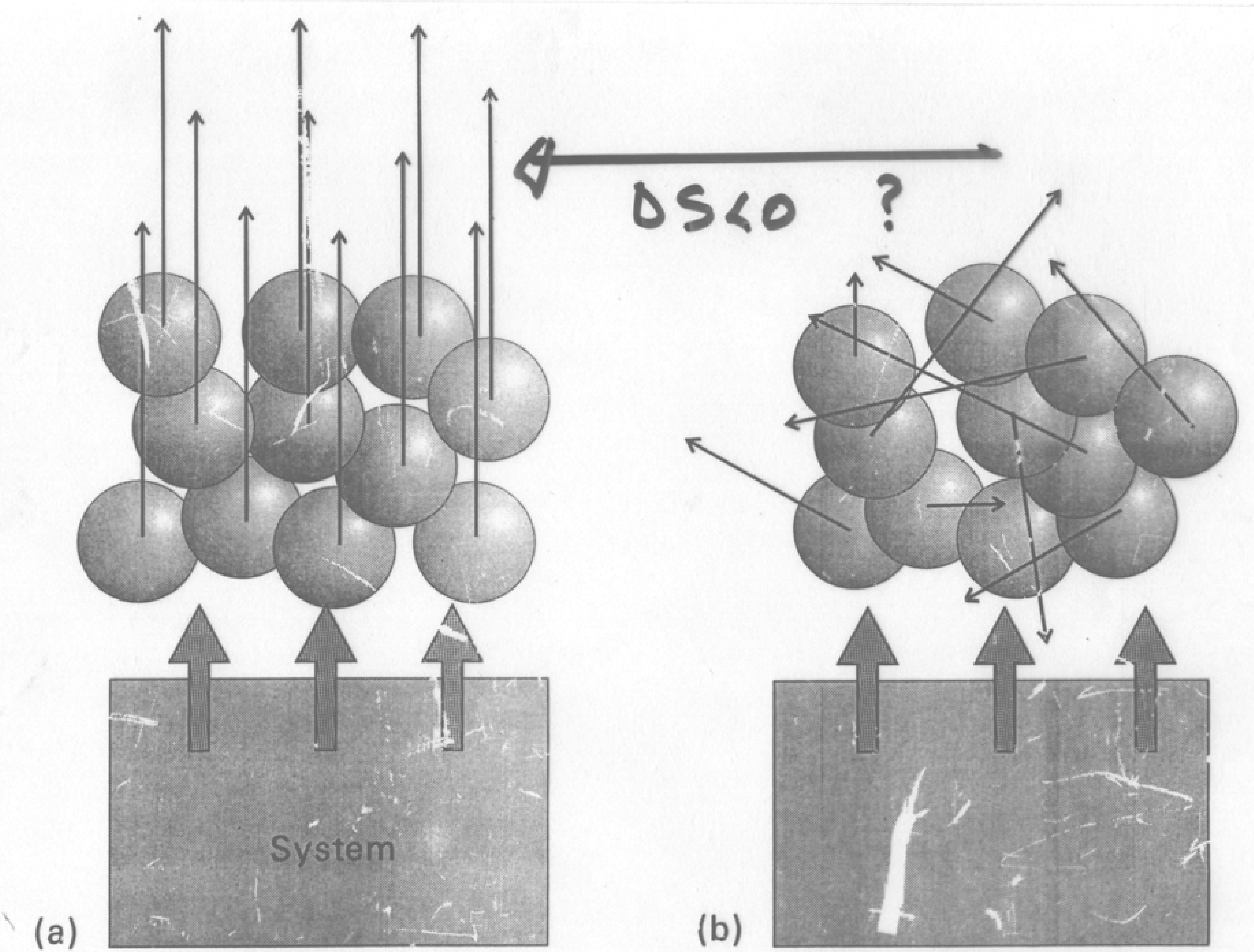


Figure 2.4
Atkins: *PHYSICAL CHEMISTRY*, fifth edition

See F. Legare, A.D. Bandrauk/Physical Review A 64, 031406 (2001)

i) $E = N\sum p_i E_i$ (Translation, rot, vib)

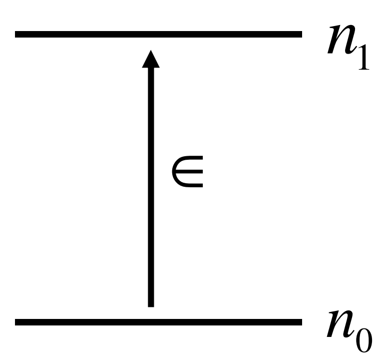
ii) $S = -k_B N \sum p_i \ln p_i$

iii) $p_i = e^{-E_i/k_BT} \big/ q; \qquad q = \sum e^{-\beta E_i}$

iv) $\Delta E_0 = E_{C^*}^0 - E_A^0 - E_B^0 \rightarrow \Delta H^* = \Delta E_0 - RT$

$\Delta S^* = S^* - S_A^0 - S_B^0$

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



Exercices Systèmes à 2 niveaux

$E_0 = 0$ $E_1 = \in$

a) Donnez les expressions pour p_0 et p_1 et prouvez ainsi que $p_0 + p_1 = 1$

b) Démontrez que dans la limite $T \to \infty$ $p_0(\infty) = p_1(\infty) = 1/2$

c) Donnez l'expression pour l'entropie S de ce système en fonction de T

d) Calculez $S(T = \infty)$

e) $\omega_{C-H} = 3000 cm^{-1}$ Prouvez que $k_2^{C-H} / k_2^{C-D} \simeq 7$ (équation 3.20)

Boltzmann

$$N_2 + O_2 \neq 2NO$$