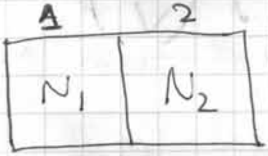
1.1.1.

$$S = k_B \ln P \qquad P = C_N^{N_1} p_1^{o\,N_1} p_2^{o\,N_2} = \frac{N!}{N_1!\,N_2!}\frac{1}{2^{N_1}}\frac{1}{2^{N_2}}$$

$$S_B = -k_B N \int d^3\vec{r}\, d^3\vec{p}\, f(\vec{r},\vec{p},t)\ln f(\vec{r},\vec{p},t) + S_0 \to$$

$$\to -k_B N \sum_i P_i \ln P_i + S_0$$

$$P_1 = \frac{N_1}{N} \qquad P_2 = \frac{N_2}{N}$$



$N = N_1 + N_2$

$$S_B = -k_B N\left(\frac{N_1}{N}\ln\frac{N_1}{N} + \frac{N_2}{N}\ln\frac{N_2}{N}\right) + S_0 = \cancel{+k_B \ln \frac{N^N}{N_1^{N_1} N_2^{N_2}} + S_0}$$

$$\cancel{S = k_B \ln P = k_B \ln\left(\frac{N!}{N_1!\,N_2!}\right) - k_B N \ln 2}$$

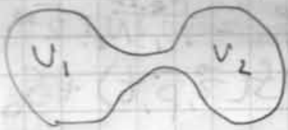
$$= -k_B\left(N_1 \ln\frac{N_1}{N} + N_2 \ln\frac{N_2}{N}\right) + S_0 = -k_B\left(N_1 \ln N_1 - N_1 \ln N +\right.$$

$$\left. + N_2 \ln N_2 - N_2 \ln N\right) + S_0 = -k_B \ln\frac{N_1^{N_1} N_2^{N_2}}{N^N} = k_B \ln\frac{N^N}{N_1^{N_1} N_2^{N_2}} + S_0$$

$$S = k_B \ln P = k_B \ln\left(\frac{N!}{N_1!\,N_2!}\right) \approx k_B \ln\left(\frac{N^N}{N_1^{N_1} N_2^{N_2}}\right) +$$

$$N! \approx N^N \sqrt{2\pi N}\, e^{-N} \qquad + k_B \ln\left(\frac{\sqrt{2\pi N}}{\sqrt{2\pi N_1}\sqrt{2\pi N_2}}\right) =$$

$$= S_B - S_0 + \frac{1}{2} k_B \ln\left(\frac{N}{2\pi N_1 N_2}\right)$$



$N_1 \qquad N_2$

$$P = C_N^{N_1}\left(\frac{V_1}{V}\right)^{N_1}\left(\frac{V_2}{V}\right)^{N_2} = \frac{N!}{N_1!\,N_2!}\left(\frac{V_1}{V}\right)^{N_1}\left(\frac{V_2}{V}\right)^{N_2}$$

Стан термодин. рівноваги:

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{(V_1+V_2)} = \frac{N}{V}$$

$$S = k_B \ln P = k_B \ln\left(\frac{N!}{N_1 N_2!}\right) + N_1 k_B \ln\frac{V_1}{V} +$$

$$+ N_2 k_B \ln\frac{V_2}{V}$$

$$\frac{N!}{N_1!\,N_2!} = \frac{N^N\sqrt{2\pi N}\,\cancel{e^{-N}}}{N_1^{N_1}\,N_2^{N_2}\sqrt{2\pi N_1\,2\pi N_2}\,\cancel{e^{-N_1}}\,\cancel{e^{-N_2}}} \approx$$

$$\approx \frac{N^N}{} = \dots$$

1.1.3. а) $$P(N_1, N_2, N_3) = \frac{N!}{N_1!\,N_2!\,N_3!}\left(\frac{V_1}{V}\right)^{N_1}\left(\frac{V_2}{V}\right)^{N_2}\left(\frac{V_3}{V}\right)^{N_3}$$

$$S = k_B \ln P$$

б) $$P = \frac{N!}{\prod_i N_i!}\, p_i^{N_i} \dots$$

1.2.1

$$A + B \to X + Y \qquad \text{спорідненість} \quad A = -\sum_{\gamma} \nu_{\gamma}\mu_{\gamma}$$

$$dn_A = dn_B = -dn_x = -dn_y = -d\xi$$

$$\nu_x = \nu_y = 1; \quad \nu_A = \nu_B = -1$$

$$A = \mu_A + \mu_B - \mu_x - \mu_y = \zeta(P,T) + RT\left(\ln n_A + \ln n_B - \ln \mu_x - \ln \mu_y\right) = \zeta(P,T) + RT \ln \frac{n_A n_B}{n_x n_y}$$

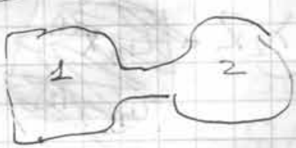
1.2.2.

$$2H_2 + O_2 \to 2H_2O$$

$$\nu_{H_2O} = 2 \qquad \nu_{O_2} = -1 \qquad \nu_{H_2} = -2$$

$$A = 2\mu_{H_2} + \mu_{O_2} - 2\mu_{H_2O} = \zeta(P,T) + RT \ln \frac{n_{H_2}^2 n_{O_2}}{n_{H_2O}^2}$$

1.2.3.



$$X_T = X_1$$

$$X_m = X_2$$

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \qquad L_{12} = L_{21}$$

$$\frac{d_i S}{dt} = \sum_{i,j} L_{ij} X_i X_j = L'_{11}(X'_1)^2 + L'_{22}(X'_2)^2$$

$$L'_{11}, L'_{22} > 0$$

$$L_{11}x_1^2 + L_{22}x_2^2 + 2L_{12}x_1x_2 = L'_{11}(x'_1)^2 + L'_{22}(x'_2)^2$$

Власні значення матриці

$$L\vec{x} = \lambda\vec{x}$$

$$\begin{vmatrix} L_{11}-\lambda & L_{12} \\ L_{12} & L_{22}-\lambda \end{vmatrix} = 0 = (L_{11}-\lambda)(L_{22}-\lambda) - L_{12}^2 =$$

$$= \lambda^2 - \lambda(L_{11}+L_{22}) + L_{11}L_{22} - L_{12}^2$$

$$\lambda_{1,2} = \frac{(L_{11}+L_{22})}{2} \pm \sqrt{\frac{(L_{11}+L_{22})^2}{4} - (L_{11}L_{22}-L_{12}^2)}$$

$$L\vec{x}_{1,2} = \lambda_{1,2}\vec{x}_{1,2}$$

$$\vec{x} = a\vec{x}_1 + b\vec{x}_2 = x^{(1)}\vec{e}_1 + x^{(2)}\vec{e}_2$$

$$L\vec{x} = aL\vec{x}_1 + bL\vec{x}_2 = a\lambda_1\vec{x}_1 + b\lambda_2\vec{x}_2 = \cancel{\begin{pmatrix} L'_{11}x^{(1)} \\ L'_{22}x^{(2)} \end{pmatrix}}$$

$$\begin{pmatrix} a x_1^{(1)} + b x_2^{(1)} \\ a x_1^{(2)} + b x_2^{(2)} \end{pmatrix} = \begin{pmatrix} x^{(1)} \\ x^{(2)} \end{pmatrix}$$

$$\vec{x}' = \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} x_1^{(1)} & x_2^{(1)} \\ x_1^{(2)} & x_2^{(2)} \end{pmatrix}^{-1} \begin{pmatrix} x^{(1)} \\ x^{(2)} \end{pmatrix} =$$

$$= \frac{1}{(x_1^{(1)}x_2^{(2)} - x_1^{(2)}x_2^{(1)})} \begin{pmatrix} x_2^{(2)} & -x_2^{(1)} \\ -x_1^{(2)} & x_1^{(1)} \end{pmatrix}\vec{x}$$

$$\overset{\prime}{L}\vec{x}^{\,\prime} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \vec{x}^{\,\prime}$$

$$\lambda_1, \lambda_2 \geq 0$$

13.1.

$$2H_2 + O_2 \to 2H_2O$$

надлишкове вир-во ентропії?

$$\nu_{H_2O} = 2 \qquad \nu_{O_2} = -1 \qquad \nu_{H_2} = -2$$

швидкість реакції $\quad v = \alpha\, n_{H_2}^2 \cdot n_{O_2}$ $\quad \alpha = \mathrm{const}$

Спорідненість $\quad A = 2\mu_{H_2} + \mu_{O_2} - 2\mu_{H_2O} =$

$$= f(p,T) + RT \ln \frac{n_{H_2}^2 \cdot n_{O_2}}{n_{H_2O}^2}$$

Варіюємо n_{O_2}

$$\delta J \equiv \delta v = \alpha\, n_{H_2}^2\, \delta n_{O_2}$$

$$\delta X = \frac{\delta A}{T} = R \cancel{\frac{n_{H_2O}^2}{n_{H_2}^2 n_{O_2}}} \cancel{\frac{n_{H_2}^2}{n_{H_2O}^2}} \delta n_{O_2} = \frac{R\, \delta n_{O_2}}{n_{O_2}}$$

$$\frac{1}{2}\frac{\partial}{\partial t}\delta^2 S = \frac{\alpha R n_{H_2}^2}{n_{O_2}} \left(\delta n_{O_2}\right)^2 \geq 0$$

Варіюємо n_{H_2}

$$\delta J \equiv \delta v = 2\alpha\, n_{H_2} n_{O_2}\, \delta n_{H_2}$$

$$\delta X = \frac{\delta A}{T} = 2R\, \frac{\delta n_{H_2}}{n_{H_2}}$$

$$\frac{1}{2}\frac{\partial}{\partial t}\delta^2 S = \delta J \delta X = 4\alpha R n_{O_2} (\delta n_{H_2})^2 \geq 0$$

$\frac{1}{2}\frac{\partial}{\partial t}\delta^2 S \geq 0$, оскільки в даному випадку термодин. рівновага не може порушуватися (р-ція не є р-цією автокаталіт. типу).

20.03.12
1.4.1.

$$f(E) = \exp\left(\frac{F + \alpha E - 0{,}5\gamma E^2}{D}\right)$$

$$F = \frac{\alpha^2}{2\gamma} - D\left[\frac{1}{2}\ln\frac{\pi\gamma}{2D} + \ln\left(1 + \frac{\alpha D}{\gamma}\,\Sigma_\gamma\,\frac{\alpha}{\sqrt{2\gamma D}}\right)\right]$$

а) Відсутн. зворот. зв'язку: $\alpha\delta = -\alpha$

$$f(E) = \frac{\delta}{D}\exp\left(-\frac{\delta}{D}E\right)$$

$$\langle E\rangle = \frac{D}{\delta}$$

$\delta_1,\ \delta_2$

$$f_1(E) = \frac{\delta_1}{D}\exp\left(-\frac{\delta_1}{D}E\right)$$

$$f_2(E) = \frac{\delta_2}{D}\exp\left(-\frac{\delta_2}{D}E\right)$$

$$\langle E_1\rangle = \frac{D}{\delta_1} \qquad \langle E_2\rangle = \frac{D}{\delta_2}$$

$$S_1 = 1 + \ln\frac{D}{\delta_1}$$

$$S_2 = 1 + \ln\frac{D}{\delta_2}$$

перенормування

$2 \to D_2$ $\quad \frac{D}{\delta_1} = \frac{D_2}{\delta_2} \quad D_2 = \frac{\delta_2}{\delta_1}D$

$$\tilde{f}_2(E) = \frac{\delta_2}{\frac{\delta_2}{\delta_1}D}\exp\left(-\frac{\delta_2}{\frac{\delta_2}{\delta_1}D}E\right) =$$

$$= \frac{\delta_1}{D} \exp\left(-\frac{\delta_1}{D} E\right)$$

$$\Rightarrow \tilde{S}_1 = \tilde{S}_2$$

Режим розвиненої генерації:

$$f(E) = \sqrt{\frac{\gamma}{2\pi D}} \exp\left[-\frac{\gamma}{2D}\left(E - \frac{\alpha}{\gamma}\right)^2\right]$$

$$\langle E \rangle = \frac{\alpha}{\gamma} \qquad S = \frac{1}{2}\left(1 + \ln\frac{2\pi D}{\gamma}\right)$$

α_1, α_2

перетвори

$\alpha_2 \to \cancel{\delta_2}$

$$\frac{\alpha_1}{\gamma} = \frac{\alpha_2}{\gamma_2}$$

$$\gamma_2 = \frac{\alpha_2}{\alpha_1}\gamma$$

$$\tilde{f}_2(E) = \sqrt{\frac{\frac{\alpha_2}{\alpha_1}\gamma}{2\pi D}} \exp\left[-\frac{\frac{\alpha_2}{\alpha_1}\gamma}{2D}\left(E - \frac{\alpha_2}{\frac{\alpha_2 \gamma}{\alpha_1}}\right)^2\right]$$

$$\tilde{S}_1 = S_1 = \frac{1}{2}\left(1 + \ln\frac{2\pi D}{\gamma}\right)$$

$$\tilde{S}_2 = \frac{1}{2}\left(1 + \ln\left(\frac{2\pi D}{\gamma}\frac{\alpha_1}{\alpha_2}\right)\right)$$

$$\alpha_1 > \alpha_2 \Rightarrow \tilde{S}_2 > \tilde{S}_1$$

$$\alpha_1 < \alpha_2 \Rightarrow \tilde{S}_2 < \tilde{S}_1$$

Стан, що відповідає відсутності зворотного звязку

$$f_1(E) = \frac{\delta}{D} \exp\left(-\frac{\delta}{D} E\right)$$

$$\langle E_1 \rangle = \frac{D}{\delta}$$

$$S_1 = 1 + \ln \frac{D}{\delta}$$

стан, що відповідає порогу самозбудження

$$f_2(E) = \sqrt{\frac{2\gamma}{\pi D}} \exp\left(-\frac{\gamma}{2D} E^2\right)$$

$$\langle E_2 \rangle = \left(\frac{2D}{\pi\gamma}\right)^{1/2}$$

$$S_2 = \frac{1}{2}\left(1 + \ln \frac{\pi D}{2\gamma}\right)$$

Фіксов. ен. першого стану. $\tilde{S}_1 = S_1$

для другого: D_2

$$\frac{D}{\delta} = \left(\frac{2D_2}{\pi\gamma}\right)^{1/2}$$

$$D_2 = \frac{\pi\gamma}{2}\left(\frac{D}{\delta}\right)^2$$

$$\tilde{S}_2 = \frac{1}{2}\left(1 + \ln\left(\frac{\pi \cancel{D_2}}{2\cancel{\gamma}} \frac{\pi \cancel{\gamma}}{2}\left(\frac{D}{\delta}\right)^2\right)\right) =$$

$$= \frac{1}{2}\left(1 + \ln\left(\frac{\pi^2}{4}\left(\frac{D}{\delta}\right)^2\right)\right) = \frac{1}{2} + \cancel{2} \ln\left(\frac{\pi}{2}\frac{D}{\delta}\right)$$

Фікс. ен. другого стану $\tilde{S}_2 = S_2$

$$\left(\frac{2D}{\pi\gamma}\right)^{1/2} = \frac{D_1}{\delta}$$

$$\tilde{S}_1 = 1 + \frac{1}{2}\ln\left(\frac{2D}{\pi\gamma}\right)$$