Chapter 8: Part A
Equilibrium between phases or chemical species

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Purpose of the chapter

- **Beyond a single phase**
- **Beyond a single component**
- **Generally, beyond several species in several phases**

- **Phase equilibrium**
- **Chemical equilibrium**

Isolated system

- An isolated system is a thermodynamic system which is completely enclosed by walls through which **can pass neither matter nor energy**.
- The walls of an isolated thermodynamic system are **adiabatic, rigid, and impermeable to matter.**
- An isolated system obeys the conservation law that **its total energy - mass stays constant**.

Thermally isolated system

- A thermally isolated system can exchange no mass or heat energy with its environment, but may exchange work energy with its environment.
- The internal energy of a thermally isolated system may therefore change due to the exchange of work energy.
- The entropy of a thermally isolated system will increase if it is not at equilibrium.
- Its entropy will be at a maximum and constant value and will not change if it is at equilibrium.

Closed/open systems

- An closed system, which is selectively enclosed by walls through which energy but not matter can pass;
- An open system, which both matter and energy can enter or exit, though it may have variously impermeable walls in parts of its boundaries.

General equilibrium conditions
8.1 Isolated systems

Considering a thermally isolated system A, the system tends to achieve the larger entropy

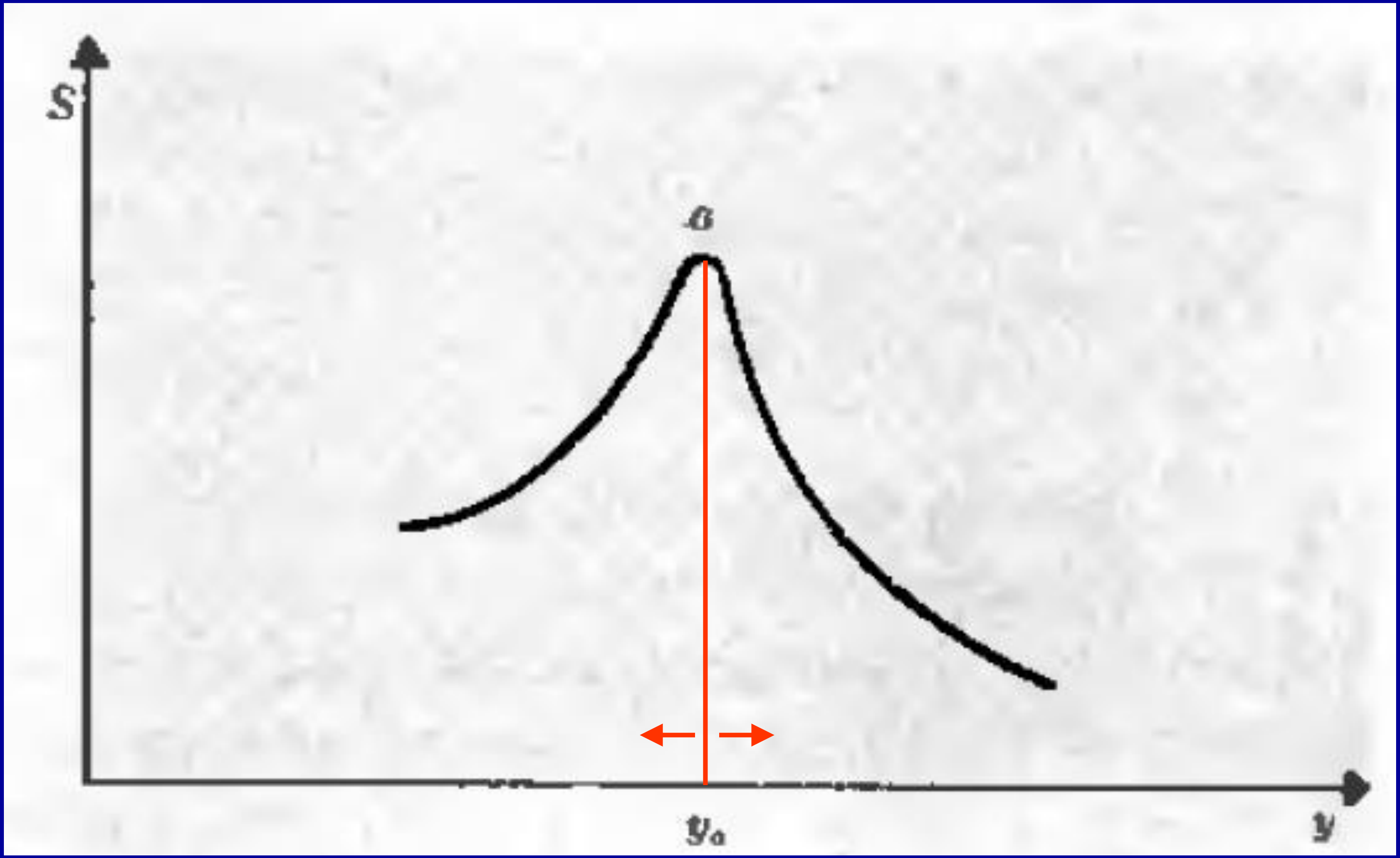
In statistical term , the system approaches to a situation of larger intrinsic probability

Direction: $\Delta S \geq 0$ ⟺ Ω increases

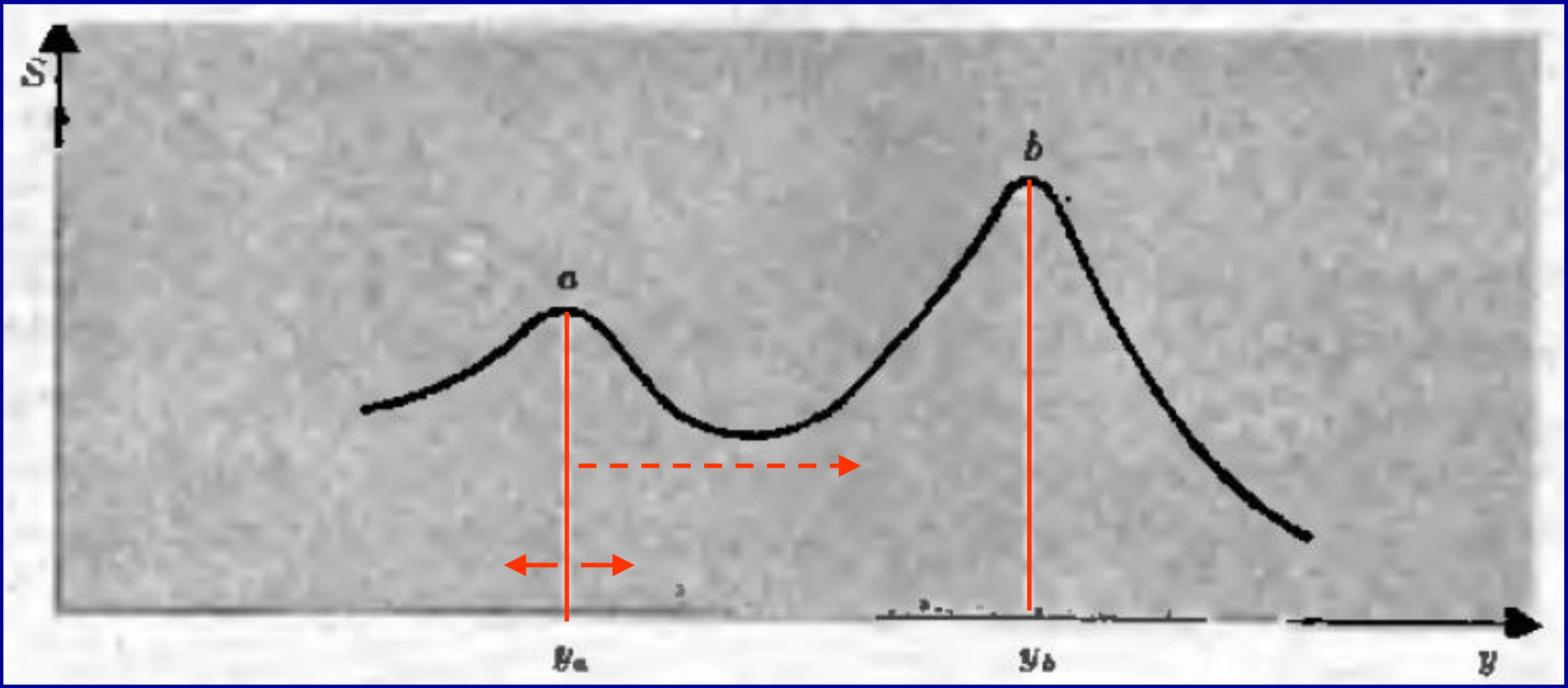
For a thermally isolated system, the stable equilibrium situation is characterized by the fact

$$S = \text{maximum}$$

General equilibrium conditions
8.1 Isolated systems



General equilibrium conditions
8.1 Isolated systems



General equilibrium conditions
8.1 Isolated systems

In a thermally isolated system

$$Q = 0 = W + \Delta\bar{E} \quad \Longrightarrow \quad W = -\Delta\bar{E}$$

If the external parameters are kept fixed, then

$$\bar{E} = \text{constant}$$

$$S = \text{maximum}$$

Can be discussed in statistical term

General equilibrium conditions
8.1 Isolated systems

Ω(y) denotes the number of accessible states in [y, y+dy], the probability for y in [y, y+dy]

$$P(y) \propto \Omega(y) = e^{S(y)/k}$$

$$\boxed{\frac{P(y)}{P_{max}} = e^{\Delta_m S/k}}$$

$$\Delta_m S = S(y) - S_{max}$$

Eqs. provide quantitative statements, and allow one to calculate the probability of occurrence of fluctuations where $S \neq S_{max}$

General equilibrium conditions
8.1 Isolated systems: remarks

If S depends on a single y, then at $y=y_m$ where $S=S_m$

$$\frac{\partial S}{\partial y} = 0$$

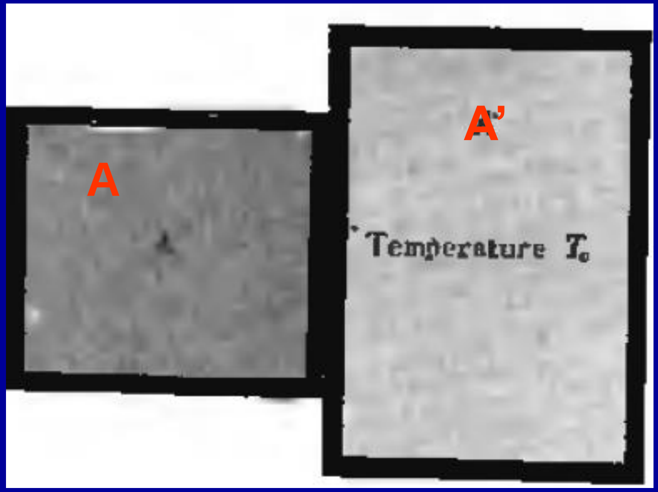
The expansion gives $\quad < 0$

$$S(y) = S_{\max} + \frac{1}{2}\left(\frac{\partial^2 S}{\partial y^2}\right)(y - \bar{y})^2 + \cdots$$

$$\boxed{P(y) \propto \exp\left[-\frac{1}{2k}\left|\frac{\partial^2 S}{\partial y^2}\right|(y - \bar{y})^2\right]}$$

General equilibrium conditions
8.2 System in contact with a reservoir at constant T

Purpose: much expt. work is done under conditions of T_0



A^0

For A^0

$$\Delta S^{(0)} \geq 0$$

$$\Delta S^{(0)} = \Delta S + \Delta S'$$

If A absorbs Q heat from A’, then A’ absorbs –Q ($T=T_0$)

$$\Delta S' = \frac{(-Q)}{T_0}$$

1st law gives

$$Q = \Delta \bar{E} + W$$

General equilibrium conditions
8.2 System in contact with a reservoir at constant T

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0}$$
$$= \frac{T_0 \Delta S - (\Delta \bar{E} + W)}{T_0}$$
$$= \frac{\Delta(T_0 S - \bar{E}) - W}{T_0}$$

$$\Delta S^{(0)} = \frac{-\Delta F_0 - W}{T_0}$$

Helmholtz free energy $F = \bar{E} - TS$

General equilibrium conditions
8.2 System in contact with a reservoir at constant T

$$\boxed{-\Delta F_0 \geq W}$$

Means that maximum work which can be done by a system in contact with a heat reservoir is given by $-\Delta F_0$

If the external para. Is kept fixed $W = 0$

$$\Delta F_0 \leq 0$$

In a system whose para is fixed, is in thermal contact with a heat reservoir, the stable equilibrium condition is

$$\boxed{F_0 = \text{minimum}}$$

General equilibrium conditions
8.2 System in contact with a reservoir at constant T

$$W = 0$$

$$\Delta S^{(0)} = \frac{-\Delta F_0 - W}{T_0}$$

$$\Delta S^{(0)} = -\frac{\Delta F_0}{T_0}$$

$$S^{(0)}(y) = S^{(0)}(y_1) - \frac{\Delta F_0}{T_0} = S^{(0)}(y_1) - \frac{F_0(y) - F_0(y_1)}{T_0}$$

$$P(y) \propto \Omega^{(0)}(y) = e^{S^{(0)}(y)/k}$$

$$P(y) \propto e^{-F_0(y)/kT_0}$$

General equilibrium conditions
8.2 System in contact with a reservoir at constant T: remarks

For canonical ensemble

$$P(y) \propto \sum_r e^{-\beta_0 E_r}, \qquad \beta_0 = (kT_0)^{-1}$$

The sum is over all states for which y is in [y, y+dy]

$$P(y) \propto \sum_E \Omega(E; y)\, e^{-\beta_0 E}$$

Only E=E (mean) contributes to the sum

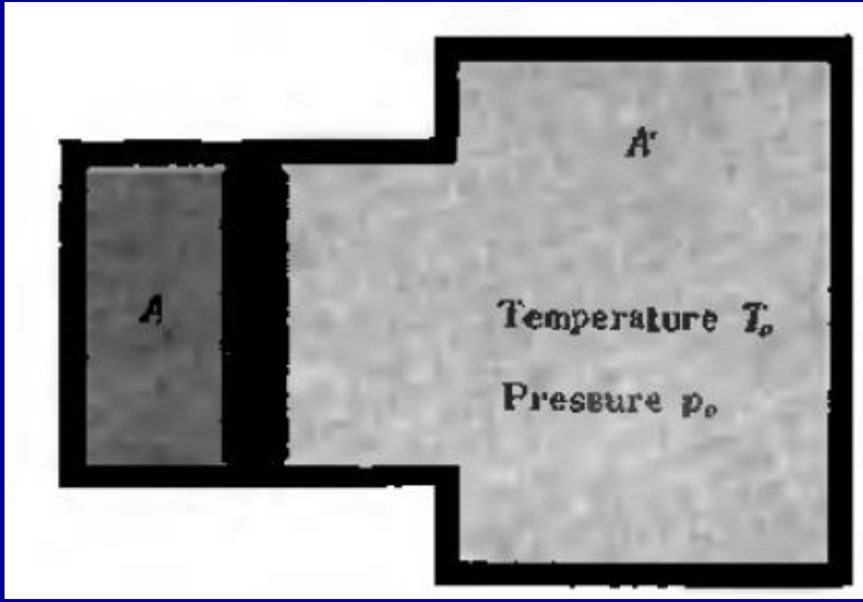
S

$$P(y) \propto \Omega(\bar{E}; y)\, e^{-\beta_0 \bar{E}(y)} = e^{S(y)/k - \beta_0 \bar{E}(y)} = e^{-\beta_0 F_0(y)}$$

General equilibrium conditions

8.3 System in contact with a reservoir at constant T and pressure

$$\Delta S^{(0)} = \Delta S + \Delta S' \geq 0$$



$$A^{(0)} = A + A'$$

If A absorbs Q heat from A',

$$\Delta S' = -Q/T_0$$

1st law gives

$$Q = \Delta \bar{E} + p_0 \Delta V + W^*$$

By pressure   other work

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0} = \frac{1}{T_0}[T_0 \Delta S - Q]$$

$$= \frac{1}{T_0}[T_0 \Delta S - (\Delta \bar{E} + p_0 \Delta V + W^*)]$$

General equilibrium conditions
8.3 System in contact with a reservoir at constant T and pressure

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0} = \frac{1}{T_0}[T_0\,\Delta S - Q]$$

$$= \frac{1}{T_0}[T_0\,\Delta S - (\Delta\bar{E} + p_0\,\Delta V + W^*)]$$

$$= \frac{1}{T_0}[\Delta(T_0 S - \bar{E} - p_0 V) - W^*]$$

$$\Delta S^{(0)} = \frac{-\Delta G_0 - W^*}{T_0}$$

Gibbs free energy $G = \bar{E} - TS + pV$

$$-\Delta G_0 \geq W^*$$

General equilibrium conditions
8.3 System in contact with a reservoir at constant T and pressure

If external paras except for V are kept fixed $W^* = 0$

$$\Delta G_0 \leq 0$$

In a system whose para is fixed except for V, is in thermal contact with a heat reservoir, the stable equilibrium condition is

$$\boxed{G_0 = \text{minimum}}$$

General equilibrium conditions
8.3 System in contact with a reservoir at constant T and pressure

$$\Delta S^{(0)} = \frac{-\Delta G_0 - W^*}{T_0}$$

$$W^* = 0$$

$$\Delta S^{(0)} = -\frac{\Delta G_0}{T_0}$$

$$S^{(0)}(y) = S^{(0)}(y_1) - \frac{G_0(y) - G_0(y_1)}{T_0}$$

$$P(y) \propto e^{S^{(0)}(y)/k}$$

$$P(y) \propto e^{-G_0(y)/kT_0}$$

General equilibrium conditions
8.4 stability conditions for a homogeneous substance

The small part is relatively small
And the rest is like a reservoir with
T_0 and p_0, then stable equil. Condi.

$$\boxed{G_0 = \bar{E} - T_0 S + p_0 V = \text{minimum}}$$

<u>* Stability against T variation</u>

$T = \tilde{T}$ when $G_0 = G_{\text{min}}$.

$\Delta T = T - \tilde{T}$,

Expanding

$$\Delta_m G_0 = G_0 - G_{\text{min}}$$

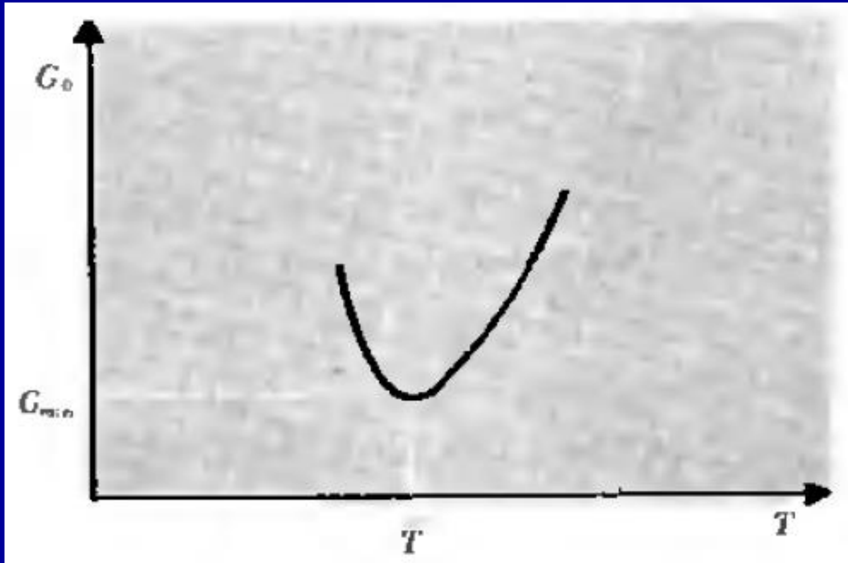
$$= \left(\frac{\partial G_0}{\partial T}\right)_V \Delta T + \frac{1}{2}\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V (\Delta T)^2 + \cdots$$

General equilibrium conditions
8.4 stability conditions for a homogeneous substance

$$\Delta_m G_0 = G_0 - G_{min}$$
$$= \left(\frac{\partial G_0}{\partial T}\right)_V \Delta T + \frac{1}{2}\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V (\Delta T)^2 + \cdots$$

$$\left(\frac{\partial G_0}{\partial T}\right)_V = 0 \qquad \text{for } T = \tilde{T}$$

$$\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V \geq 0 \qquad \text{for } T = \tilde{T}$$



General equilibrium conditions
8.4 stability conditions for a homogeneous substance

$$G_0 = \bar{E} - T_0 S + p_0 V$$

with constant V

$$\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V - T_0 \left(\frac{\partial S}{\partial T}\right)_V = 0$$

$$T\,dS = d\bar{E} + \bar{p}\,dV$$

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V$$

$$\left(\frac{\partial G}{\partial T}\right)_V = \left(1 - \frac{T_0}{T}\right)\left(\frac{\partial \bar{E}}{\partial T}\right)_V = 0$$

$$\bar{T} = T_0$$

General equilibrium conditions
8.4 stability conditions for a homogeneous substance

$$G_0 = \bar{E} - T_0 S + p_0 V$$

$$\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V = \frac{T_0}{T^2}\left(\frac{\partial \bar{E}}{\partial T}\right)_V + \left(1 - \frac{T_0}{T}\right)\left(\frac{\partial^2 \bar{E}}{\partial T^2}\right)_V \geq 0$$

$= 0$

$$\boxed{\left(\frac{\partial \bar{E}}{\partial T}\right)_V \geq 0}$$

$$\boxed{C_V \geq 0}$$

Le Chatelier principle

General equilibrium conditions
8.4 stability conditions for a homogeneous substance

fixed at $T = T_0$

$\Delta V = V - \tilde{V}$

- **Stability against volume fluctuation**

expansion gives

$$\Delta_m G_0 \equiv G_0 - G_{\min} = \left(\frac{\partial G_0}{\partial V}\right)_T \Delta V + \frac{1}{2}\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T (\Delta V)^2 + \cdots$$

$$\left(\frac{\partial G_0}{\partial V}\right)_T = \left(\frac{\partial \bar{E}}{\partial V}\right)_T - T_0\left(\frac{\partial S}{\partial V}\right)_T + p_0$$

$$G_0 = \bar{E} - T_0 S + p_0 V$$

$$T\,dS = d\bar{E} + \bar{p}\,dV$$

$$T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial \bar{E}}{\partial V}\right)_T + \bar{p}$$

$$\left(\frac{\partial G_0}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - \bar{p} - T_0\left(\frac{\partial S}{\partial V}\right)_T + p_0$$

General equilibrium conditions
8.4 stability conditions for a homogeneous substance

•**Stability against volume fluctuation**

fixed at $T = T_0$

$\Delta V = V - \tilde{V}$

$$\left(\frac{\partial G_0}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - \bar{p} - T_0\left(\frac{\partial S}{\partial V}\right)_T + p_0$$

$$\left(\frac{\partial G_0}{\partial V}\right)_T = -\bar{p} + p_0 = 0$$

$$\bar{p} = p_0$$

General equilibrium conditions
8.4 stability conditions for a homogeneous substance

•<u>Stability against volume fluctuation</u>

fixed at $T = T_0$

$$\Delta V = V - \tilde{V}$$

$$G_0 = \bar{E} - T_0 S + p_0 V$$

$$\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T = -\left(\frac{\partial \bar{p}}{\partial V}\right)_T \geq 0$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial \bar{p}}\right)_T$$

$$\kappa \geq 0$$

Le Chatelier principle

General equilibrium conditions
8.4 stability conditions for a homogeneous substance

- **density fluctuation**

equilibrium $G_0(\tilde{V}) = G_{\min}$ $V = \tilde{V}$

P(v)dV is the probability for V in [V, dV]

$$\mathcal{P}(V)\,dV \propto e^{-G_0(V)/kT}\,dV$$

ΔV is small, then

$$G_0(V) = G_{\min} - \frac{1}{2}\left(\frac{\partial \bar{p}}{\partial V}\right)_T (\Delta V)^2 = G_{\min} + \frac{(\Delta V)^2}{2\tilde{V}\kappa}$$

$$\mathcal{P}(V)\,dV \simeq B\exp\left[-\frac{(V-\tilde{V})^2}{2kT_0\tilde{V}\kappa}\right]dV$$

General equilibrium conditions
8.4 stability conditions for a homogeneous substance

• **density fluctuation**

equilibrium $G_0(\tilde{V}) = G_{\min}$ $V = \tilde{V}$

$$\boxed{\overline{(\Delta V)^2} = \overline{(V - \tilde{V})^2} = kT_0\tilde{V}\kappa}$$

$$\tilde{n} = N/\tilde{V},$$

$$\Delta n = -(N/\tilde{V}^2)\,\Delta V = -(\tilde{n}/\tilde{V})\,\Delta V.$$

$$\boxed{\overline{(\Delta n)^2} = \left(\frac{\tilde{n}}{\tilde{V}}\right)^2 \overline{(\Delta V)^2} = \tilde{n}^2\left(\frac{kT_0}{\tilde{V}}\kappa\right)}$$

General equilibrium conditions

Discussions:

$$\Delta_m G_0 = G_0 - G_{min} = \left(\frac{\partial G_0}{\partial T}\right)_V \Delta T + \frac{1}{2}\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V (\Delta T)^2 + \cdots$$

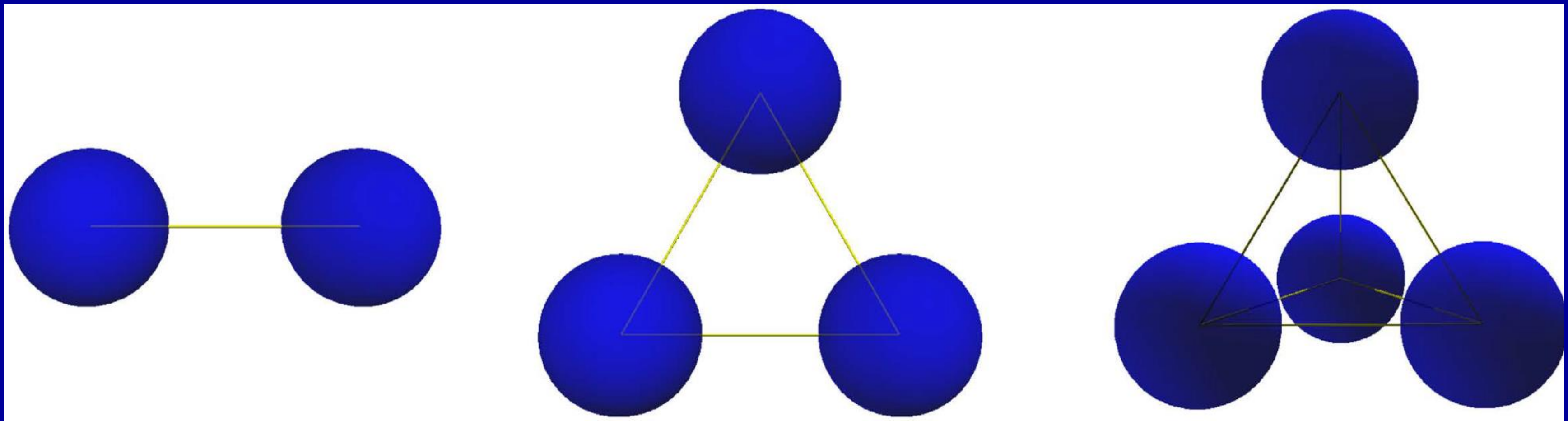
$$\Delta_m G_0 = G_0 - G_{min} = \left(\frac{\partial G_0}{\partial V}\right)_T \Delta V + \frac{1}{2}\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T (\Delta V)^2 + \cdots$$

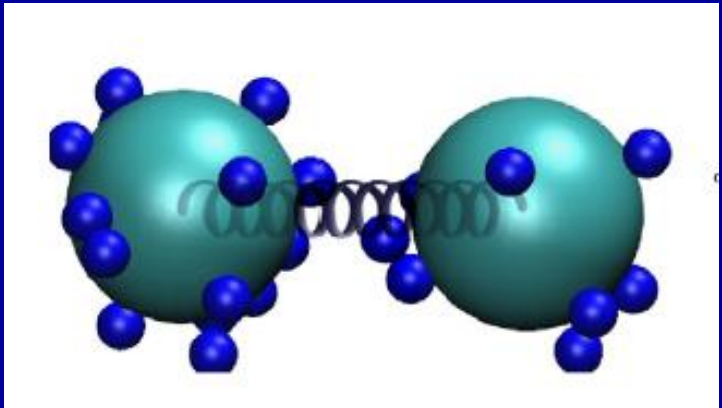
Le Châtelier's principle

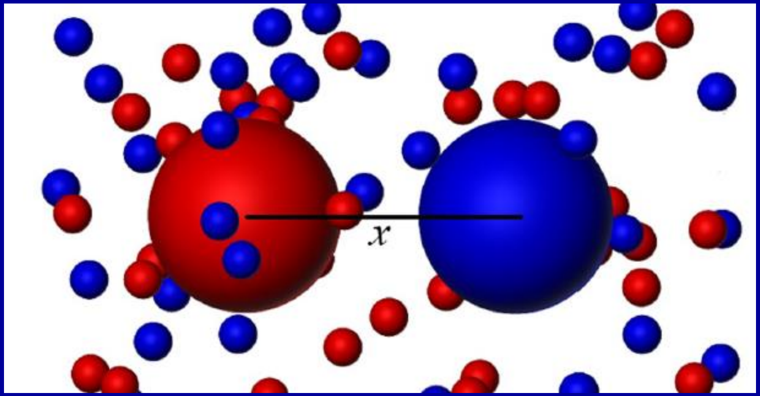
If a system is in *stable* equilibrium, then any spontaneous change of its parameters must bring about processes which tend to restore the system to equilibrium.

Attraction between like charged particles

systems



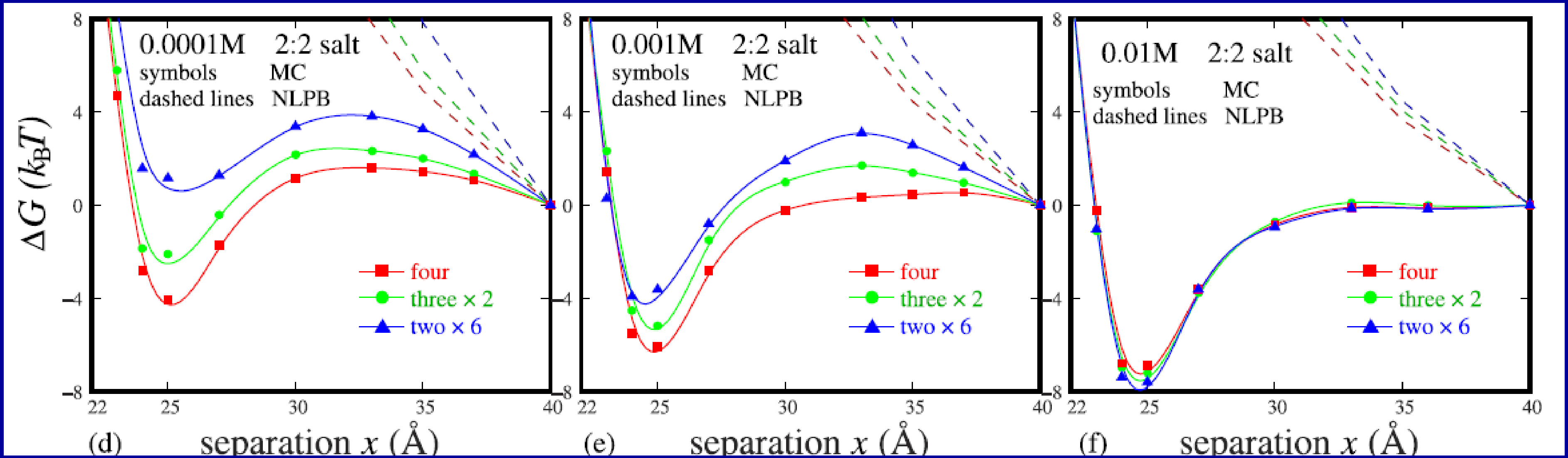




Zhang X, ...& **Tan ZJ***. Scientific Reports 6: 23434, 2016;   7: 14145, 2017

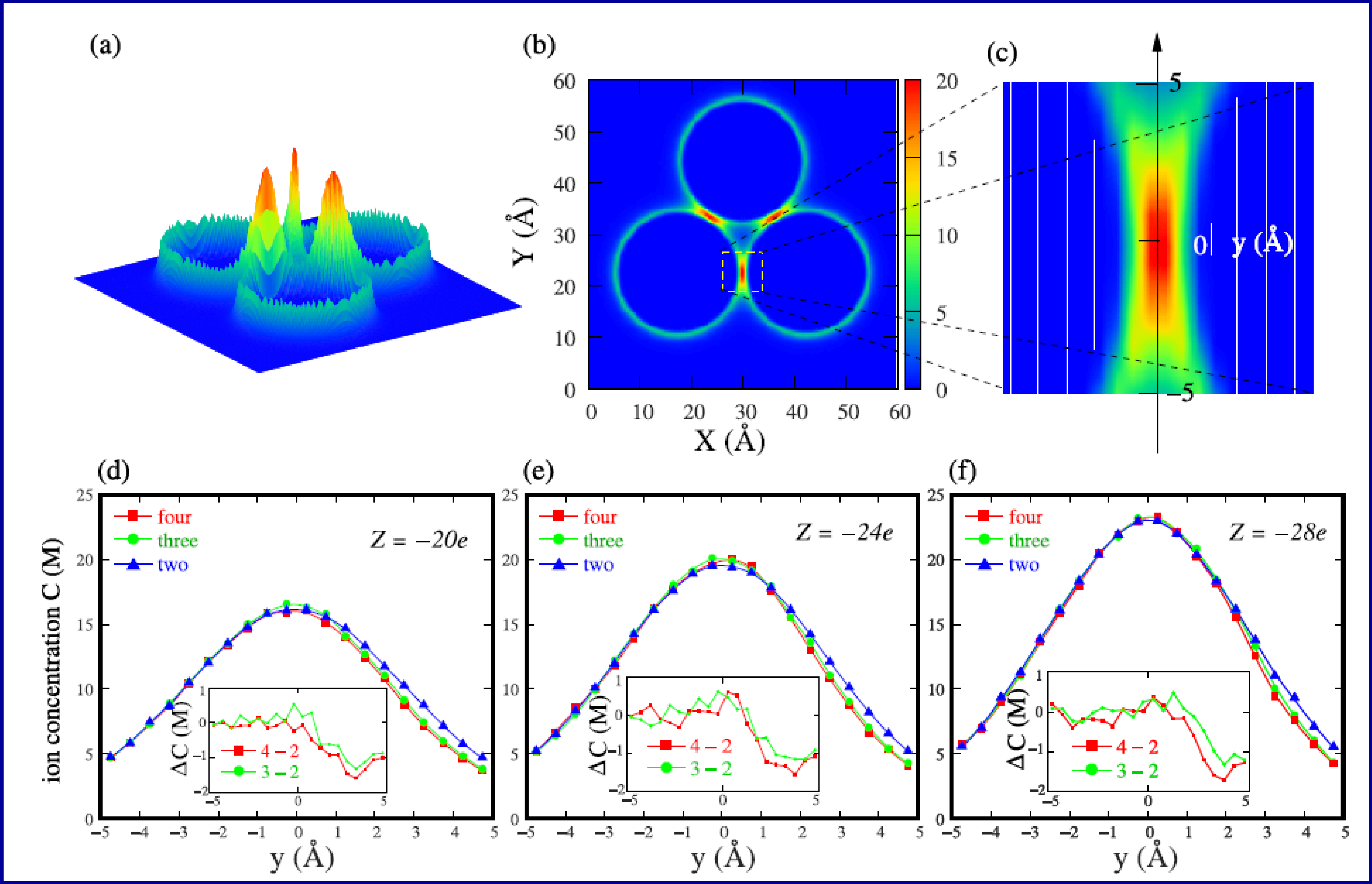
Attraction between like charged particles

Results:



Attraction between like charged particles

Analyses:



Attraction between like charged particles

Methods: thermodynamics-integration

$$Z_U = \int e^{-\beta U} (d\mathbf{r})^{3N},$$

a control variable $\lambda \in [0, 1]$,

$$G(\lambda) = -k_B T \ln Z_U(\lambda).$$

$$\frac{\partial G(\lambda)}{\partial \lambda} = k_B T \left\langle \frac{\partial (\beta U)}{\partial \lambda} \right\rangle,$$

Attraction between like charged particles

Methods: thermodynamics-integration

$$\frac{\partial G(\lambda)}{\partial \lambda} = k_B T \left\langle \frac{\partial(\beta U)}{\partial \lambda} \right\rangle,$$

a control variable $\lambda \in [0, 1]$,

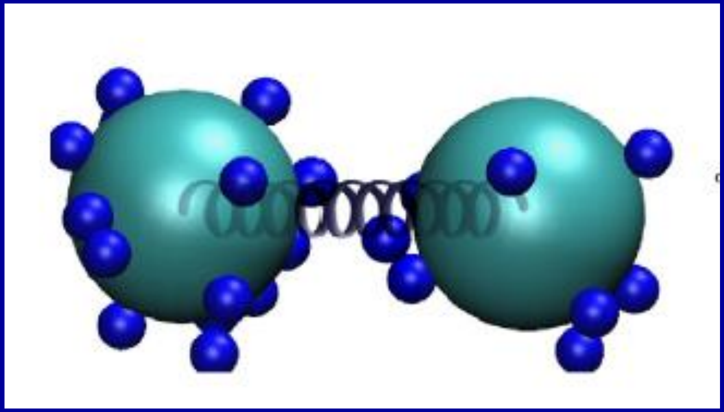
$$\Delta G = G_{\lambda=1} - G_{\lambda=0} = k_B T \int_0^1 \left\langle \frac{\partial(\beta U)}{\partial \lambda} \right\rangle d\lambda,$$

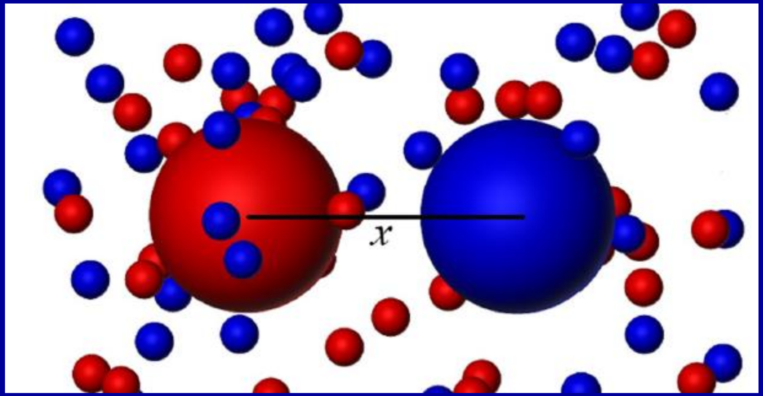
if $\beta=\lambda$

$$G_{\beta_T} = G_{\beta=0} + k_B T \int_0^{\beta_T} \langle U \rangle_\beta d\beta,$$

Attraction between like charged particles

Methods: pseudo-spring method





$$F(x) = k\Delta x,$$

$$\Delta G(x) = G(x) - G(x_{\mathrm{ref}}) = \int_{x}^{x_{\mathrm{ref}}} F(x')dx',$$

Class-work

P 326 8.1

Homework

no

Homework

$$\mathcal{P}(V,T)\, dV\, dT \propto \exp\left[-G_o(V,T)/kT_o\right] dV\, dT$$

$$G_o(V,T) = G_o(\tilde{V},\tilde{T}) + \left(\frac{\partial G_o}{\partial T}\right)_V (T-\tilde{T}) + \left(\frac{\partial G_o}{\partial V}\right)_T (V-\tilde{V}) + \frac{1}{2}\left(\frac{\partial^2 G_o}{\partial T^2}\right)_V (T-\tilde{T})^2$$
$$+ \frac{1}{2}\left(\frac{\partial^2 G_o}{\partial V^2}\right)_T (V-\tilde{V})^2 + \left(\frac{\partial^2 G_o}{\partial V\, \partial T}\right)(V-\tilde{V})(T-\tilde{T}) + \ldots$$

$$G_o(V,T) = G_o(\tilde{V}, T_o) + \frac{C_V}{2T_o}(T-T_o)^2 + \frac{1}{2\tilde{V}\kappa}(V-\tilde{V})^2$$

$$\mathcal{P}(V,T)\, dV\, dT \propto \exp\left[-\frac{Mc_V}{2kT_o{}^2}(T-T_o)^2 - \frac{\rho_o}{2M\kappa\, kT_o}(V - M/\rho_o)^2\right] dV\, dT$$