

# Lecture 9

Thermodynamic equilibrium: temperature, pressure, chemical potential

17.09.2018

# Thermal equilibrium

Thermal equilibrium of two interacting systems through *energy* exchange.

$$\Omega_{\text{total}} = \Omega_A(U_A, V_A) \cdot \Omega_B(U_B, V_B)$$

$$\begin{aligned} \frac{\partial \Omega_{\text{total}}}{\partial U_A} = 0 &\rightarrow \frac{\partial S_{\text{total}}}{\partial U_A} = 0 \\ \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0 &\rightarrow \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_B} \frac{dU_B}{dU_A} = 0 \rightarrow \frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0 \end{aligned}$$

System A and system B have the same temperature  $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \equiv \frac{1}{T}$

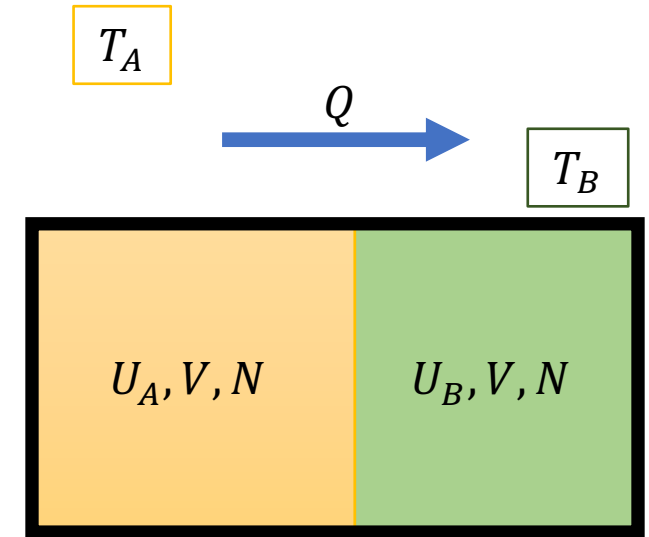
$$T = \left( \frac{\partial S}{\partial U} \right)_{V,N}^{-1}$$

*Temperature is a measure of system's ability to exchange energy*

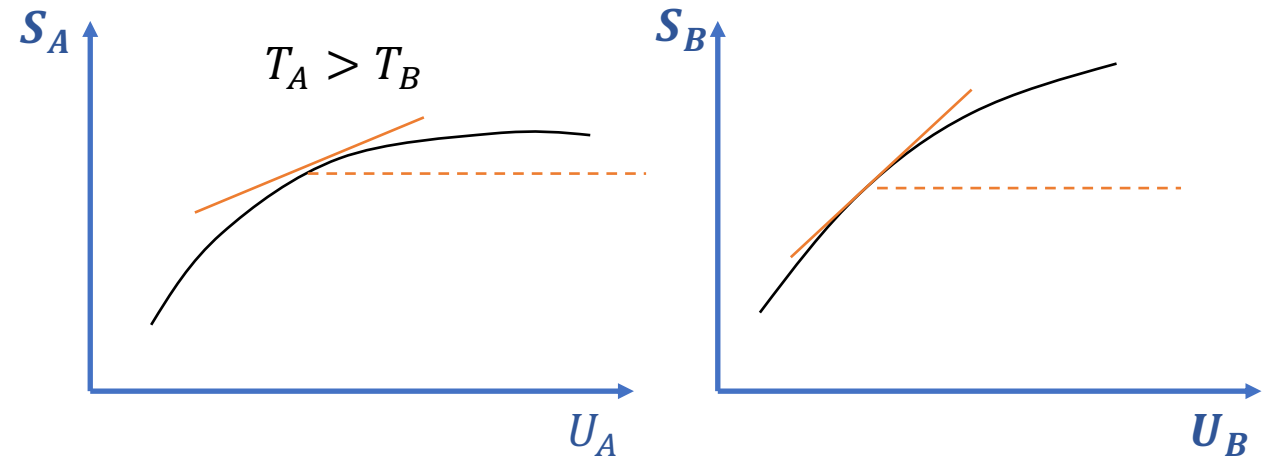
# Thermal equilibrium: Temperature

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N}$$

- ❑ The decrease  $dU_A$  balances the increase  $dU_B$ , i.e  
 $-dU_A = dU_B$
- ❑  $\frac{\partial S_A}{\partial U_A} < \frac{\partial S_B}{\partial U_B} \rightarrow -dS_A < dS_B$  **decrease in the entropy for system A is smaller than the increase in the entropy of system B, so that the total entropy increases when heat flows from A to B**
- ❑  $d(S_A + S_B) > 0$
- ❑ The system with smaller  $\frac{\partial S}{\partial U}$  (higher  $T$ ) will tend to give energy
- ❑ System with **higher  $T$  gives heat** the one with **lower  $T$**



$$\frac{\partial S_A}{\partial U_A} < \frac{\partial S_B}{\partial U_B} \rightarrow$$



# Mechanical equilibrium: What stays the same?

**Mechanical** and thermal equilibrium of two interacting systems through *energy* and *volume* exchange

$$\frac{\partial S_{total}(U_A, V_A)}{\partial U_A} = 0 \quad \text{and} \quad \frac{\partial S_{total}(U_A, V_A)}{\partial V_A} = 0$$
$$\frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = 0 \rightarrow \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_B} \frac{dV_B}{dV_A} = 0 \rightarrow \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0$$

System A and system B have the same pressure:  $T \frac{\partial S_A}{\partial V_A} = T \frac{\partial S_B}{\partial V_B} \equiv P$

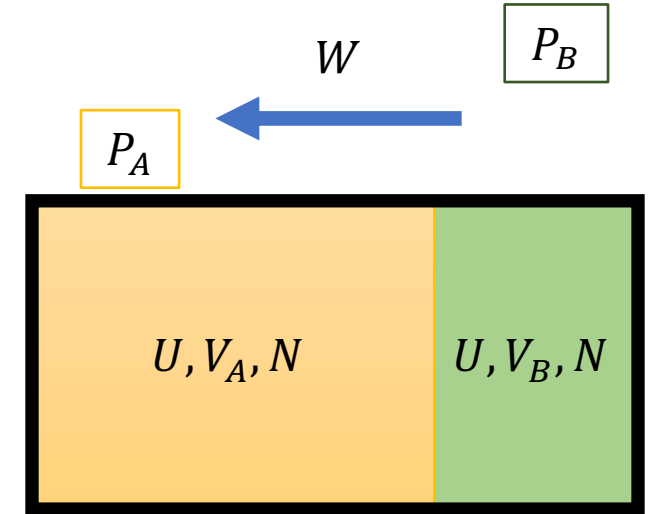
$$P = T \left( \frac{\partial S}{\partial V} \right)_{U, N}$$

*Pressure is a measure of system's ability to exchange volume*

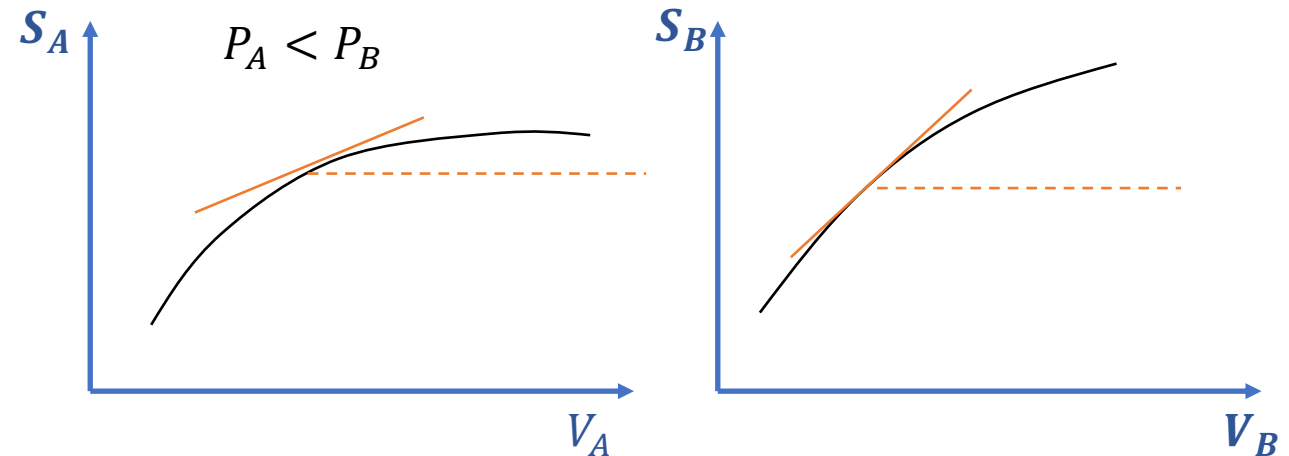
# Mechanical equilibrium: Pressure

$$P = T \left( \frac{\partial S}{\partial V} \right)_{U,N}$$

- ❑ The decrease  $dV_A$  balances the increase  $dV_B$ , i.e.  $-dV_A = dV_B$
- ❑  $\frac{\partial S_A}{\partial V_A} < \frac{\partial S_B}{\partial V_B} \rightarrow -dS_A < dS_B$  decrease in the entropy for system A is smaller than the increase in the entropy of system B, so that the **total entropy increases** when system B expands into system A
- ❑  $d(S_A + S_B) > 0$
- ❑ The system with higher  $\frac{\partial S}{\partial V}$  (higher  **$P$** ) will tend to gain volume (expand)
- ❑ System with **higher  $P$**  expands into the one with **lower  $P$**



$$\frac{\partial S_A}{\partial V_A} < \frac{\partial S_B}{\partial V_B} \rightarrow$$



# Thermodynamic identity

- Entropy computed from the multiplicity of a macrostate at fixed  $U$ ,  $V$ , and  $N$

$$S(U, V, N)$$

- Change in entropy due to *energy change* or *volume change* has a differential form

$$dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV$$

- Using the definitions for  $T$  and  $P$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

- Thermodynamic identity for  $U(S, V)$

$$dU = TdS - PdV$$

*We have derived the first law of thermodynamics for a reversible change (system goes through equilibrium states)!*

# Pressure P in the ideal gas:

- Entropy:

$$S(U, V, N) = k \ln \Omega(U, V, N) = k \left[ \ln f(N) + N \ln V + \frac{3N}{2} \ln U \right]$$

- Equation of state:

$$P = T \left( \frac{\partial S}{\partial V} \right)_{U, N} = NkT \frac{d}{dV} \ln V = \frac{NkT}{V} \rightarrow \mathbf{PV = NkT}$$

*This is now derived from counting the number of microstates for the gas particles!*

- Heat capacity  $C_P$ :

$$C_P = C_V + P \left( \frac{\partial V}{\partial T} \right)_P \rightarrow C_P = \frac{3Nk}{2} + Nk = \frac{5Nk}{2}$$

# Gas expansion: $\Delta S$

- Entropy:

$$S(U, V, N) = k \left[ \ln f(N) + N \ln V + \frac{3N}{2} \ln U \right]$$

- Isolated system ( $\Delta U = 0$ ,  $\Delta N = 0$ ) only  $V$  changes during expansion

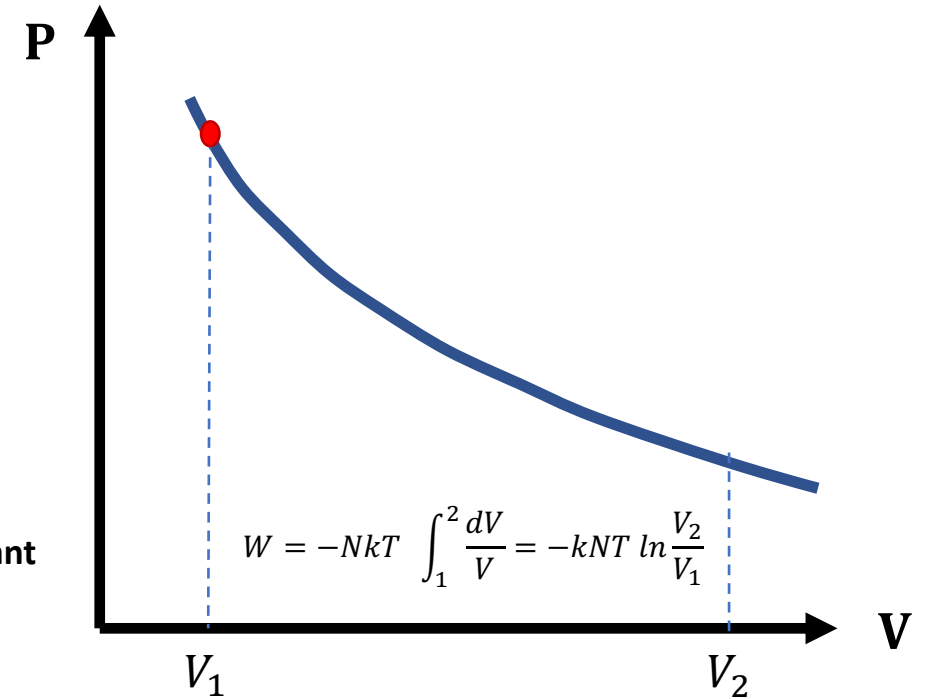
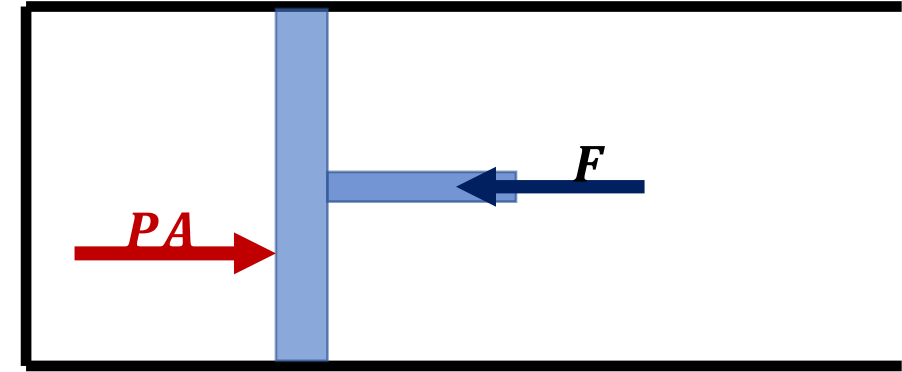
From Boltzmann's formula of  $S$ :

$$\Delta S = S_2 - S_1 = kN \ln \frac{V_2}{V_1}$$

From 1st & 2nd laws of thermodynamics: (along the isothermal path)

$$T\Delta S = Q_{\text{rev}} = -W_{\text{rev}} = kNT \ln \frac{V_2}{V_1}$$

- ❑  $\Delta S$  is related to heat during the quasistatic isothermal expansion
- ❑  $\Delta S > 0$  because of the heat absorbed by the expanding gas to keep its internal energy constant





# $\Delta S$ is path-independent

- What if we choose the path A-B (isochoric+isobaric) instead of the isothermal path?
- What will happen then?

Use the definition of entropy from heat  $dS = \frac{\delta Q_{rev}}{T}$

The entropy change  $\Delta S = S_2 - S_1$  is then  $\Delta S = \int_{A \rightarrow B \text{ path}} \frac{\delta Q_{rev}}{T}$

$$\Delta S = \int_{\text{path}_{\text{isochoric}}} \frac{\delta Q_{rev}}{T} + \int_{\text{path}_{\text{isobaric}}} \frac{\delta Q_{rev}}{T} = \int_{\text{path}_{\text{isochoric}}} \frac{dU}{T} + \int_{\text{path}_{\text{isobaric}}} \frac{dU + PdV}{T}$$

$$\Delta S = C_V \int_a^b \frac{dT}{T} + C_P \int_b^c \frac{dT}{T} = C_V \int_a^b \frac{dT}{T} + C_P \int_b^c \frac{dT}{T}$$

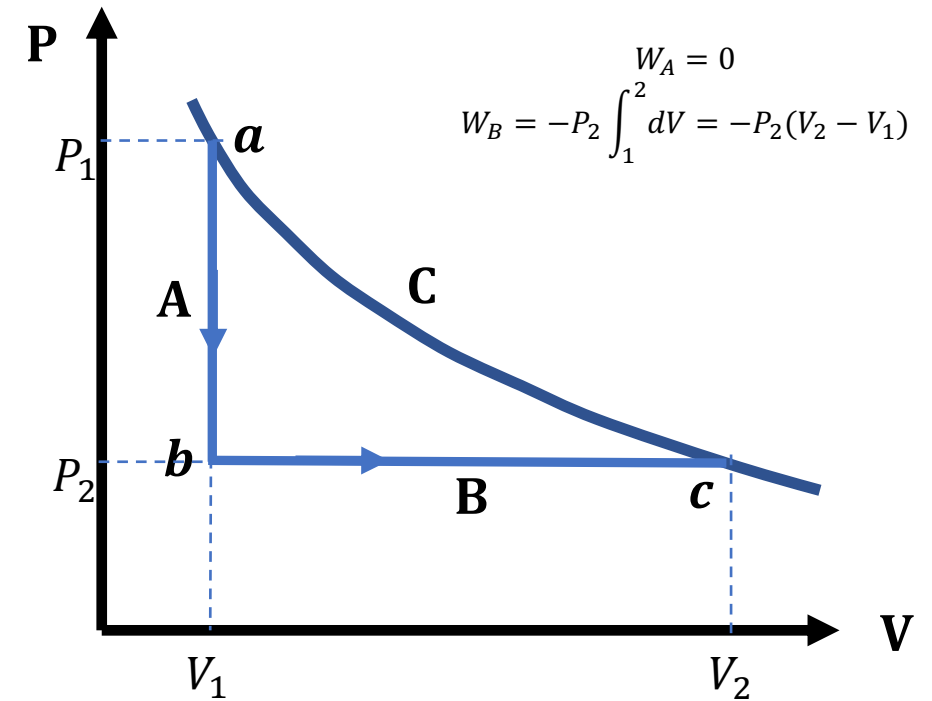
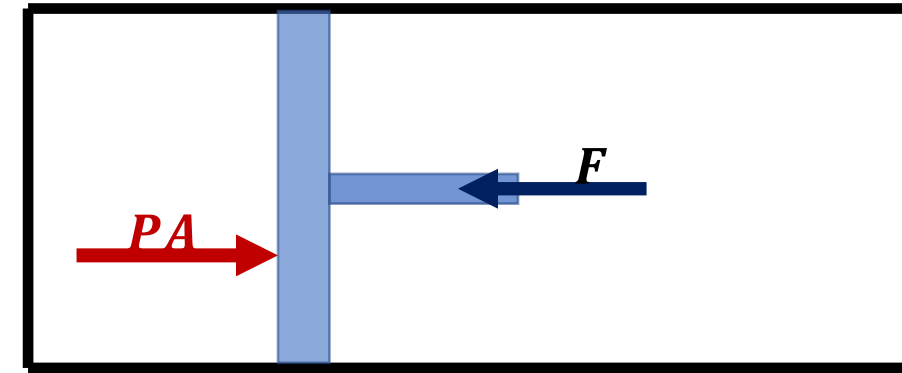
$$\Delta S = C_V \ln \frac{T_b}{T_a} + C_P \ln \frac{T_c}{T_b} = C_V \ln \frac{P_2 V_1}{P_1 V_1} + C_P \ln \frac{P_2 V_2}{P_2 V_1}$$

$$\Delta S = C_V \ln \frac{P_2}{P_1} + C_P \ln \frac{V_2}{V_1} = C_V \ln \frac{T_2/V_2}{T_1/V_1} + C_P \ln \frac{V_2}{V_1}$$

$$\Delta S =_{(T_1=T_2)} C_V \ln \frac{V_1}{V_2} + (C_V + Nk) \ln \frac{V_2}{V_1} = Nk \ln \frac{V_2}{V_1}$$

□ Entropy change is the same as on the isobaric path

□ Moral: Choose the simplest path between the states to compute  $\Delta S$



# Free gas expansion: $\Delta S$

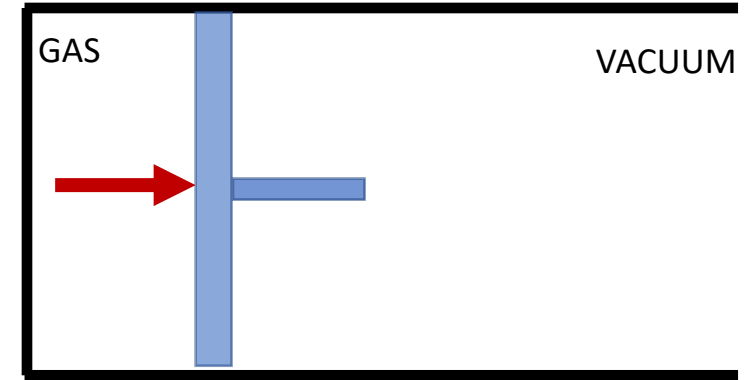
- Irreversible expansion with no heat, no work

$$\Delta U = Q + W = 0 + 0 = 0$$

- As the gas expands freely into the vacuum, **its entropy changes because of volume change**
- **The multiplicity of a state with higher volume is larger, hence the entropy increases**

$$\Delta S = kN \ln \frac{V_{final}}{V_{initial}} > 0, \quad \text{since } V_{final} > V_{initial}$$

This is a spontaneous expansion



# Diffusive equilibrium: What stays the same?

**Diffusive**, mechanical and thermal equilibrium of two interacting systems through *particle*, *energy* and *volume* exchange

$$\frac{\partial S_{total}(U_A, V_A, N_A)}{\partial U_A} = 0, \quad \frac{\partial S_{total}(U_A, V_A, N_A)}{\partial V_A} = 0 \text{ and } \frac{\partial S_{total}(U_A, V_A, N_A)}{\partial N_A} = 0$$
$$\frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_A} = 0 \rightarrow \frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_B} \frac{dN_B}{dN_A} = 0 \rightarrow \frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B} = 0 \quad \text{at } U_A, V_A \text{ fixed}$$

System A and system B have the same **chemical potential**:  $T_A \left( \frac{\partial S_A}{\partial N_A} \right)_{U_A, V_A} = T_B \left( \frac{\partial S_B}{\partial N_B} \right)_{U_B, V_B} \equiv -\mu$

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U, V}$$

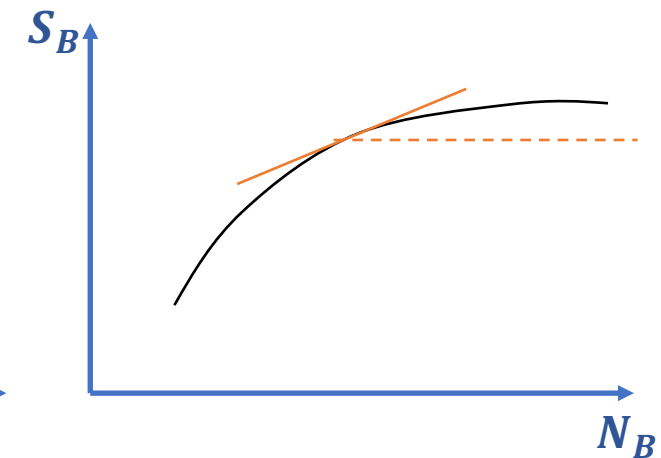
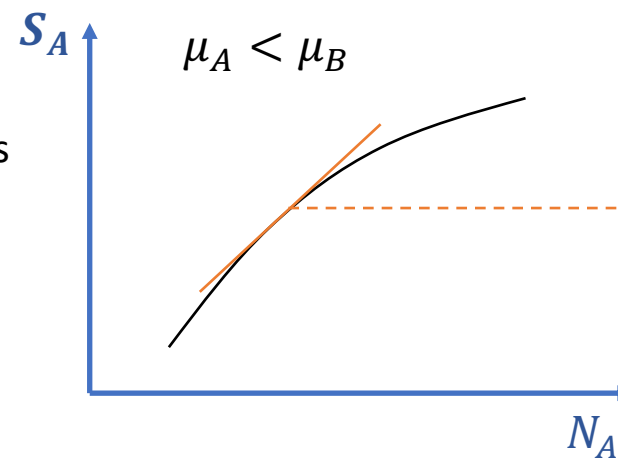
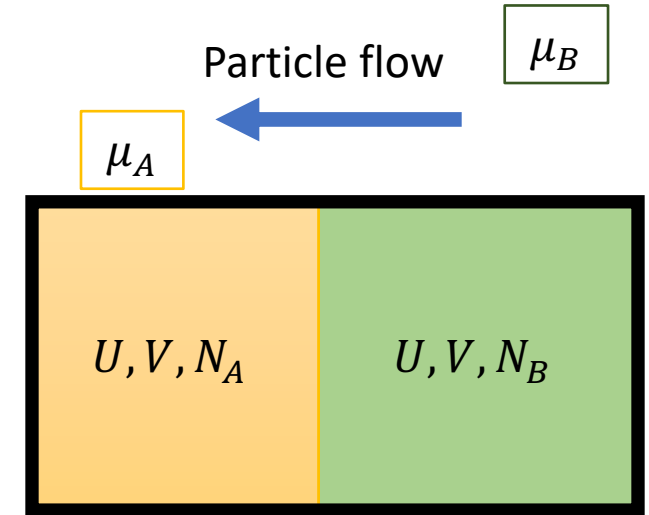
*Chemical potential is a measure of system's ability to exchange particle*

# Diffusive equilibrium: chemical potential

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V}$$

- ❑ The increase  $dN_A$  balances the decrease  $dN_B$ , i.e  $dN_A = -dN_B$
- ❑  $\frac{\partial S_A}{\partial N_A} > \frac{\partial S_B}{\partial N_B} \rightarrow dS_A > -dS_B$  increase in entropy for system A is larger than the decrease in entropy of system B, so that the total entropy increases when particles flow from B to A
- ❑  $d(S_A + S_B) > 0$
- ❑ The system with higher  $\frac{\partial S}{\partial N}$  (smaller  $\mu$ ) will tend to gain particles
- ❑ Particles flow from the system with higher  $\mu$  to the one with smaller  $\mu$

$$\frac{\partial S_A}{\partial N_A} > \frac{\partial S_B}{\partial N_B} \rightarrow$$



# Thermodynamic identity

- Entropy computed from the multiplicity of a macrostate at fixed  $U$ ,  $V$ , and  $N$

$$S(U, V, N)$$

- Change in entropy due to *energy change, volume change or particle number changes* has a differential form

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

- Using the definitions for  $T$ ,  $P$  and  $\mu$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

- Thermodynamic identity for  $U(S, V, N)$

$$dU = TdS - PdV + \mu dN$$

Chemical work



# Chemical potential $\mu$

- In a process with fixed internal energy  $U$  and volume  $V$

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V}$$

- In a process with fixed entropy  $S$  and volume  $V$ :

$$dU = TdS - PdV + \mu dN \rightarrow dU = \mu dN$$

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}$$

- ❑  $\mu$  has units of energy
- ❑  $\mu$  is the change in the internal energy by bring in or taking out a particle at *fixed entropy and volume*
- ❑ *When a particle is added, entropy typically increases. Hence, to keep  $S$  constant some energy may be removed*
- ❑ *thus, typically  $\mu < 0$*

# Ideal gas: chemical potential $\mu$

- From  $S(U, V, N) = kN \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi m U}{3h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]$

- The chemical potential is  $\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U, V}$

$$\mu = -kT \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi m U}{3h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] + NkT \cdot \frac{5}{2N}$$

$$\mu = -kT \ln \left( \frac{V}{N} \left( \frac{4\pi m U}{3h^2} \right)^{\frac{3}{2}} \right) \rightarrow \mu(T, V, N) = -kT \ln \left( \frac{V}{N} \left( \frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}} \right)$$

□  $\mu(T, V, N) < 0$  when  $\frac{V}{N} \left( \frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}} > 1 \rightarrow \left( \frac{V}{N} \right)^{1/3} > \sqrt{\frac{h^2}{2\pi m kT}}$

□ typical distance between particles is larger than thermal wavelength  $\Lambda = \sqrt{\frac{h^2}{2\pi m kT}}$

□ thermal wavelength is very small at room temperatures, but increases with cooling the system and then the chemical potential can change sign

□ something fundamental happens with the ideal gas at sufficiently small temperature! (stay tuned to find out)

# Einstein crystal: chemical potential $\mu$

- From  $S(q, N) = k[(N + q) \ln (N + q) - q \ln q - N \ln N]$
- The chemical potential is  $\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U, V}$

$$\mu = -kT [\ln(N + q) - \ln N] = -kT \ln \left( 1 + \frac{q}{N} \right)$$

- ❑ *Energetic limit:*  $q \gg N \rightarrow \mu \approx -kT \ln \left( \frac{q}{N} \right) < -kT$  entropy increases more when a particle with no energy is added
- ❑ *Dense limit:*  $N \gg q \rightarrow \mu \approx -kT \frac{q}{N}$  very small entropy increase when a new particle with no energy is added
- ❑ In energetic limit, the system can take in more particles to gain entropy, while in the dense limit is more saturated in its entropy already.



# Recap

- 1st law of thermodynamics:

Energy cannot be created or destroyed, it can be transformed

A *change* in the internal energy (energy of a state) of a system is equal to heat *exchange* or work *exchange (energies in action)* with its surroundings

$$dU = \delta Q + \delta W$$

A *change* in the internal energy (energy of a state) of a system on a **reversible path**

$$dU = TdS - PdV$$

# Recap

- Entropy is a state variable (path-independent)

$$S(U, V, N) = k_B \ln \Omega(U, V, N)$$

- S is maximum for the thermodynamic state that is the most likely one (highest probability, maximum number of microstates)
- When the system is in a state that has a lower probability, it will spontaneously go into the most likely state. This is the free relaxation to equilibrium

# Recap

- 2nd law of thermodynamics:

Entropy of an isolated system can be created, but never destroyed

$$dS \geq 0$$

On a reversible path, entropy change is due to heat exchange between the system and its surroundings at a given temperature  $T$

$$TdS = \delta Q_{rev}$$

Mechanical analogue to heat and entropy: volume change due to reversible work at a given pressure

$$-PdV = \delta W_{rev}$$

On an irreversible path, not all heat gives rise to entropy change or available work (some of it is lost or dissipated into the environment)

$$dS \geq \frac{\delta Q}{T}$$

$$dU \leq TdS - PdV$$

# Recap

- Thermodynamic identity:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{P} dN \leftrightarrow dU = TdS - PdV + \mu dN$$

$$T = \left( \frac{\partial S}{\partial U} \right)^{-1}_{V,N}, \quad P = T \left( \frac{\partial S}{\partial V} \right)_{U,N}, \quad \mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V}$$

- 2nd law implies that

- Heat flows from **hot** to **cold**
- Volume expansion happens from **high pressure** to **low pressure**
- Particle migration is from **high chemical potential** to **low chemical potential**