



Lecture 7. Thermodynamic Identities (Ch. 3)

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

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

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

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

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

Diffusive Equilibrium and Chemical Potential

Let's fix V_A and V_B (the membrane's position is fixed), but assume that the membrane becomes permeable for gas molecules (exchange of both U and N between the sub-systems, the molecules in A and B are the same).

For sub-systems in diffusive equilibrium: $\left(\frac{\partial S_{AB}}{\partial U_A} \right)_{V_A, N_A} = 0 \quad \left(\frac{\partial S_{AB}}{\partial N_A} \right)_{U_A, V_A} = 0$

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

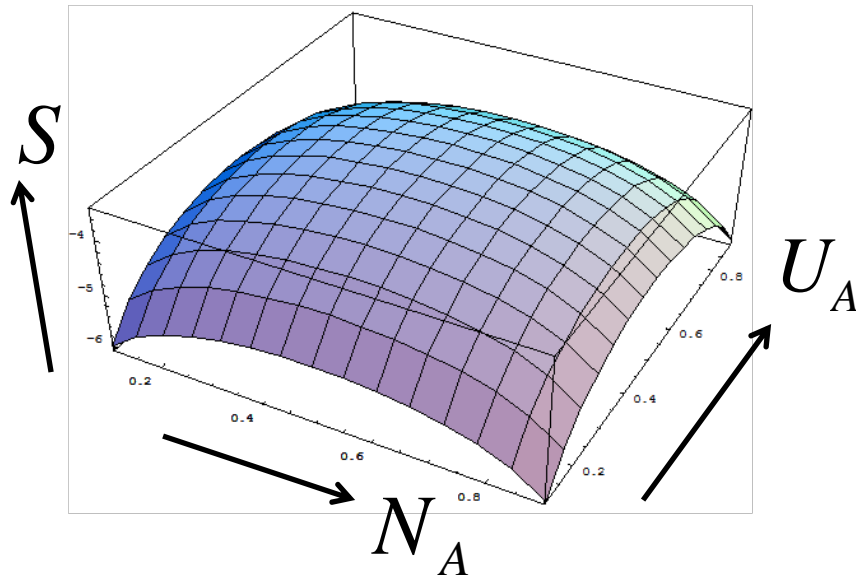
In equilibrium,

$$T_A = T_B$$

$$\mu_A = \mu_B$$

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

- the chemical potential



Sign “-”: out of equilibrium, the system with the larger $\partial S / \partial N$ will get more particles. In other words, particles will flow from a high μ/T to a low μ/T .

Chemical Potential: examples

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

Einstein solid: consider a small one, with $N = 3$ and $q = 3$.

$$\Omega(N = 3, q = 3) = \frac{(q + N - 1)!}{q!(N - 1)!} = 10 \quad S(N = 3, q = 3) = k_B \ln 10$$

let's add one more oscillator: $S(N = 4, q = 3) = k_B \ln 20$

$$\mu \equiv \left(\frac{\partial U}{\partial N} \right)_S \Leftrightarrow dS = \frac{1}{T} dU - \frac{\mu}{T} dN \quad \text{To keep } dS = 0, \text{ we need to } \mathbf{decrease} \text{ the energy, by subtracting one energy quantum.}$$

Thus, for this system
$$\mu = \left(\frac{\Delta U}{\Delta N} \right)_S = -\varepsilon$$

Monatomic ideal gas:
$$S(N, V, U) = N k_B \left\{ \ln \left[V \left(\frac{4\pi m}{3h^2} U \right)^{3/2} \right] - \ln N^{5/2} + \frac{5}{2} \right\}$$

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V} = -k_B T \ln \left[\frac{V}{N} \left(\frac{2\pi m}{h^2} k_B T \right)^{3/2} \right] = -k_B T \ln \left[g(m) \frac{VT^{3/2}}{N} \right]$$

At normal T and P , $\ln(\dots) > 0$, and $\mu < 0$ (e.g., for He, $\mu \sim -5 \cdot 10^{-20} \text{ J} \sim -0.3 \text{ eV}$).

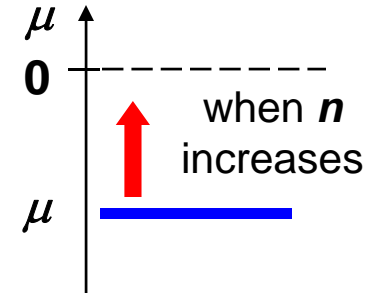
Sign “-”: usually, by adding particles to the system, we increase its entropy. To keep $dS = 0$, we need to subtract some energy, thus ΔU is negative.

The Quantum Concentration

$$\mu = -k_B T \ln \left[\frac{V}{N} \left(\frac{2\pi m}{h^2} k_B T \right)^{3/2} \right] = k_B T \ln \left[n \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right] = k_B T \ln \left(\frac{h^3}{(2\pi m)^{3/2}} \cdot \frac{P}{(k_B T)^{5/2}} \right)$$

$n=N/V$ – the concentration of molecules

The chemical potential increases with the density of the gas or with its pressure. Thus, the molecules will flow from regions of high density to regions of lower density or from regions of high pressure to those of low pressure .



$$\mu = k_B T \ln \left[n \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right] = k_B T \ln \left(\frac{n}{n_Q} \right) \quad \text{when } n \rightarrow n_Q, \mu \rightarrow 0$$

$$n_Q = \left(\frac{2\pi m}{h^2} k_B T \right)^{3/2}$$

- the so-called **quantum concentration** (one particle per cube of side equal to the thermal de Broglie wavelength). When $n_Q \gg n$, the gas is in the classical regime.

$$\lambda_{dB} = \frac{h}{p} \propto \frac{h}{\sqrt{mk_B T}} \quad n_Q = \frac{1}{\lambda_{dB}^3} \propto \left(\frac{mk_B T}{h^2} \right)^{3/2}$$

At $T=300\text{K}$, $P=10^5 \text{ Pa}$, $n \ll n_Q$. When $n \rightarrow n_Q$, the quantum statistics comes into play.

Entropy Change for Different Processes

The partial derivatives of **S** play very important roles because they determine how much the entropy is affected when **U**, **V** and **N** change:

Type of interaction	Exchanged quantity	Governing variable	Formula
thermal	energy	temperature	$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N}$
mechanical	volume	pressure	$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{U,N}$
diffusive	particles	chemical potential	$\frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{U,V}$

The last column provides the connection between statistical physics and thermodynamics.

Thermodynamic Identity for $dU(S,V,N)$

$S = S(U, V, N) \Rightarrow$ if monotonic as a function of U (“quadratic” degrees of freedom!), may be inverted to give $U = U(S, V, N)$

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

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

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

pressure

chemical potential

μ shows how much the system's energy changes when one particle is added to the system at fixed S and V . The chemical potential units – J .

$$dU = T dS - P dV + \mu dN$$

- the so-called **thermodynamic identity** for U

This holds for **quasi-static processes** (T , P , μ are well-defined throughout the system).

Thermodynamic Identities

With these abbreviations:

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

- the so-called
thermodynamic identity

μ shows how much the system's energy changes when one particle is added to the system at fixed **S** and **V**. The chemical potential units – **J**.

μ is an **intensive** variable, independent of the size of the system (like **P**, **T**, density). **Extensive** variables (**U**, **N**, **S**, **V** ...) have a magnitude proportional to the size of the system. If two identical systems are combined into one, each extensive variable is doubled in value.

The thermodynamic identity holds for the **quasi-static processes** (**T**, **P**, μ are well-defined throughout the system)

The 1st Law for quasi-static processes (**N** = const):

$$dU = TdS - PdV$$

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

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

This identity holds for small changes ΔS provided **T** and **P** are well defined.

The coefficients may
be identified as:

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

The Equation(s) of State for an Ideal Gas

Ideal gas:
(fN degrees of freedom)

$$\Omega(U, V, N) = g(N) V^N U^{fN/2}$$
$$S(U, V, N) = Nk_B \ln \left[g(N) V U^{f/2} \right]$$

The “energy” equation of state ($\mathbf{U} \leftrightarrow \mathbf{T}$):

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N} = \frac{f}{2} N k_B \frac{1}{U}$$
$$U = \frac{f}{2} N k_B T$$

The “pressure” equation of state ($\mathbf{P} \leftrightarrow \mathbf{T}$):

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

- we have finally derived the equation of state of an ideal gas from first principles!
In other words, we can calculate the thermodynamic information for an isolated system by counting all the accessible microstates as a function of \mathbf{N} , \mathbf{V} , and \mathbf{U} .

Ideal Gas in a Gravitational Field

Pr. 3.37. Consider a monatomic ideal gas at a height z above sea level, so each molecule has potential energy mgz in addition to its kinetic energy. Assuming that the atmosphere is isothermal (not quite right), find μ and re-derive the barometric equation.

$$U = U_{kin} + Nmgz$$

note that the U that appears in the Sackur-Tetrode equation represents only the kinetic energy

$$dU = T dS - P dV + \mu dN$$

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} = \mu(z) + mgz = -k_B T \ln \left[\frac{V}{N(z)} \left(\frac{2\pi m}{h^2} k_B T \right)^{3/2} \right] + mgz$$

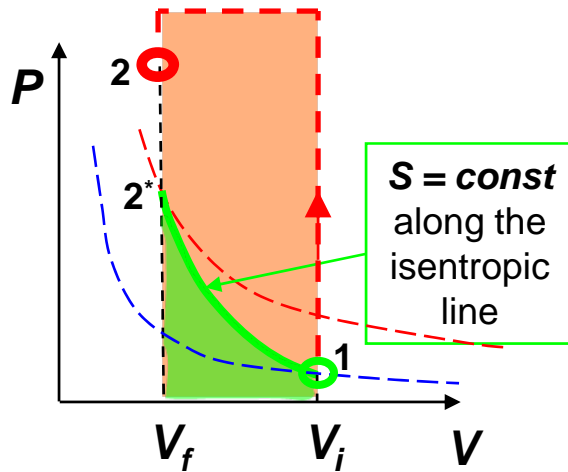
In equilibrium, the chemical potentials between any two heights must be equal:

$$-k_B T \ln \left[\frac{V}{N(z)} \left(\frac{2\pi m}{h^2} k_B T \right)^{3/2} \right] + mgz = -k_B T \ln \left[\frac{V}{N(0)} \left(\frac{2\pi m}{h^2} k_B T \right)^{3/2} \right]$$

$$k_B T \ln N(z) + mgz = k_B T \ln N(0) \qquad N(z) = N(0) e^{-\frac{mgz}{k_B T}}$$

An example of a non-quasistatic adiabatic process

Caution: for non-quasistatic adiabatic processes, ΔS might be non-zero!!!



Pr. 3.32. A non-quasistatic compression. A cylinder with air ($V = 10^{-3} \text{ m}^3$, $T = 300\text{K}$, $P = 10^5 \text{ Pa}$) is compressed (very fast, non-quasistatic) by a piston ($A = 0.01 \text{ m}^2$, $F = 2000\text{N}$, $\Delta x = 10^{-3}\text{m}$). Calculate δW , δQ , ΔU , and ΔS .

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

holds for **all processes**,
energy conservation

$$\Delta U = T\Delta S - P\Delta V$$

quasistatic, T and P are well-defined for any intermediate state

quasistatic adiabatic \equiv isentropic

$\delta Q = 0$ for both

non-quasistatic adiabatic

$$\begin{aligned} \delta W &= \int_{V_i}^{V_f} P(V) dV = [PV^\gamma = \text{const}] = P_i V_i^\gamma \int_{V_i}^{V_f} \frac{1}{V^\gamma} dV \\ &= \frac{P_i V_i^\gamma}{\gamma - 1} \left[\frac{1}{V_f^{\gamma-1}} - \frac{1}{V_i^{\gamma-1}} \right] = \frac{P_i V_i}{\gamma - 1} \left[\left(\frac{V_i}{V_f} \right)^{\gamma-1} - 1 \right] \\ &= \frac{P_i V_i}{\gamma - 1} \left[\left(1 + \frac{\Delta x}{x} \right)^{\gamma-1} - 1 \right] \\ &\approx P_i V_i \frac{\Delta x}{x} = 1 \cdot 10^5 \text{ Pa} \times 10^{-3} \text{ m}^3 \times 10^{-2} = 1 \text{ J} \end{aligned}$$

$$\begin{aligned} \delta W &= -P \int_{V_i}^{V_f} dV = P [V_i - V_f] \\ &= 2 \cdot 10^5 \text{ Pa} \times 10^{-2} \text{ m}^2 \times 10^{-3} \text{ m}^2 \\ &= 2 \text{ J} \end{aligned}$$

The non-quasistatic process results in a higher T and a greater entropy of the final state.

Direct approach: $S(U, V, N) = N k_B \ln V + \frac{f}{2} N k_B \ln U + k_B \ln f(N)$

adiabatic quasistatic \equiv isentropic

$$\delta Q = 0 \quad \Delta U = \delta W \quad \frac{f}{2} N k_B \Delta T = -P \Delta V$$

$$\frac{f}{2} N k_B \Delta T = -\frac{N k_B T}{V} \Delta V$$

$$V T^{f/2} = \text{const}$$

$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f} \right)^{2/f}$$

$$\Delta S = N k_B \ln \frac{V_f}{V_i} - \frac{f}{2} N k_B \frac{2}{f} \ln \frac{V_f}{V_i} = 0$$

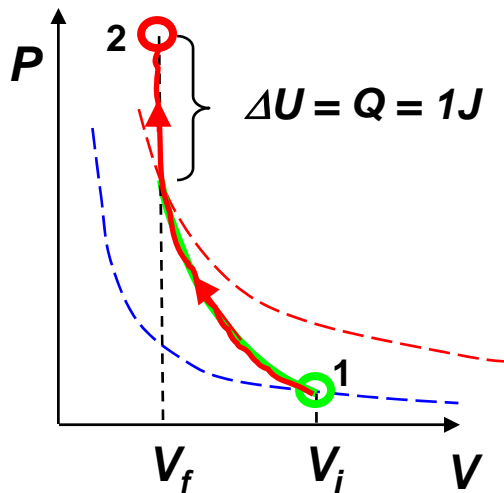
adiabatic non-quasistatic

$$\Delta S = N k_B \ln \frac{V_f}{V_i} + \frac{f}{2} N k_B \ln \frac{U_f}{U_i} \approx N k_B \frac{V_f - V_i}{V_i} + \frac{f}{2} N k_B \frac{U_f - U_i}{U_i}$$

$$= \frac{P_i}{T_i} \Delta V + \frac{1}{T_i} \Delta U = \frac{\Delta U + P_i \Delta V}{T_i} = \frac{-P \Delta V + P_i \Delta V}{T_i}$$

$$= \frac{(P - P_i)(-\Delta V)}{T_i} = \frac{(2 \times 10^5 - 10^5) \times 10^{-5}}{300} = \frac{1}{300} \text{ J/K}$$

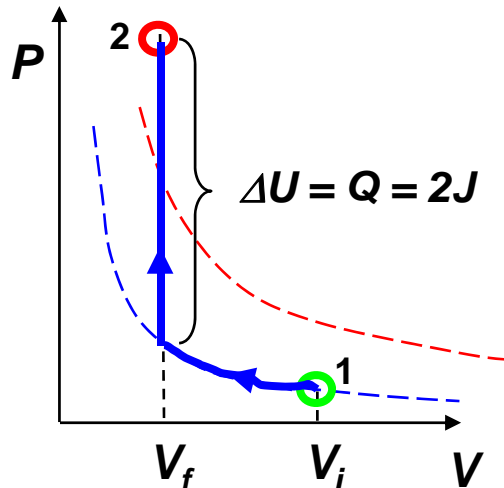
$$\frac{\Delta V}{V} = 10^{-2} \quad \Delta U = W = 2 \text{ J} \quad U_i = \frac{f}{2} N k_B T_i = \frac{5}{2} P_i V_i = \frac{5}{2} \times 10^5 \text{ Pa} \times 10^{-3} \text{ m}^3 = 250 \text{ J}$$



To calculate ΔS , we can consider any **quasistatic** process that would bring the gas into the final state (S is a state function). For example, along the red line that coincides with the adiabat and then shoots straight up. Let's neglect small variations of T along this path ($\Delta U \ll U$, so it won't be a big mistake to assume $T \approx \text{const}$):

$$\Delta S \approx 0 \text{ (adiabata)} + \frac{Q}{T} = \frac{2J - 1J}{300K} = \frac{1}{300} \text{ J/K}$$

The entropy is created because it is an **irreversible, non-quasistatic** compression.



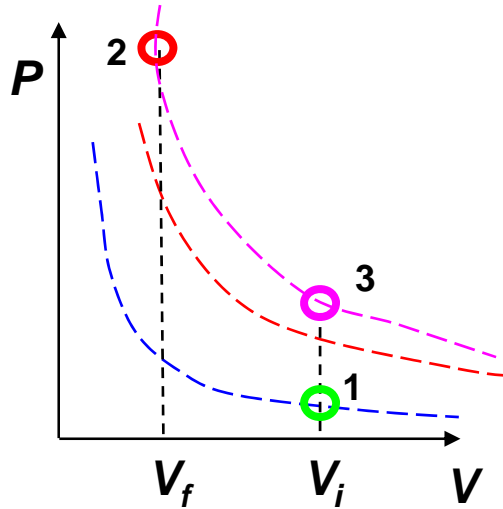
For **any** quasi-static path from 1 to 2, we must have the same ΔS . Let's take another path – along the isotherm and then straight up:

isotherm:
$$\Delta S = \frac{1}{T} \int_{V_i}^{V_f} P(V) dV = \frac{P_i V_i}{T} \int_{V_i}^{V_f} \frac{dV}{V} = \frac{P_i V_i}{T} \ln\left(\frac{V_f}{V_i}\right)$$

$$\approx \frac{P_i V_i}{T} \frac{\Delta x}{x} = -\frac{10^5 \text{ Pa} \times 10^{-3} \text{ m}^3 \times 10^{-2}}{300K} = -\frac{1}{300} \text{ J/K}$$

“straight up”:
$$\Delta S = \frac{\Delta U}{T} = \frac{Q}{T} \approx \frac{2J}{300K} = \frac{2}{300} \text{ J/K}$$

Total gain of entropy:
$$\Delta S \approx -\frac{1}{300} \text{ J/K} + \frac{2}{300} \text{ J/K} = \frac{1}{300} \text{ J/K}$$



The inverse process, sudden expansion of an ideal gas (2 – 3) also generates entropy (**adiabatic** but not **quasistatic**). Neither heat nor work is transferred: $W = Q = 0$ (we assume the whole process occurs rapidly enough so that no heat flows in through the walls).

Because U is unchanged, T of the ideal gas is unchanged. The **final** state is identical with the state that results from a **reversible** isothermal expansion with the gas in thermal equilibrium with a reservoir. The work done on the gas in the **reversible** expansion from volume V_f to V_i :

$$W_{rev} = N k_B T \ln \frac{V_f}{V_i}$$

The work done on the gas is negative, the gas does positive work on the piston in an amount equal to the heat transfer into the system

$$Q_{rev} = -W_{rev} > 0 \quad \Delta S = \frac{Q_{rev}}{T} = \frac{-W_{rev}}{T} = N k_B \ln \frac{V_i}{V_f} \approx \frac{P_i V_i}{T_i} \frac{\Delta V}{V_i} = \frac{1}{300} \text{ J/K}$$

Thus, by going $1 \rightarrow 2 \rightarrow 3$, we will increase the gas entropy by $\Delta S_{1 \rightarrow 2 \rightarrow 3} = \frac{2}{300} \text{ J/K}$