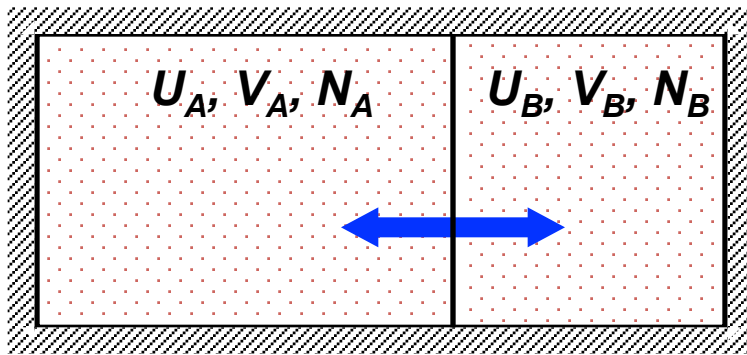# Mechanical Equilibrium and Pressure

Let's fix U_A, N_A and U_B, N_B , but allow V to vary (the membrane is insulating, impermeable for gas molecules, but its position is not fixed). Following the same logic, spontaneous "exchange of volume" between sub-systems will drive the system towards mechanical equilibrium (the membrane at rest). The equilibrium macropartition should have the largest (by far) multiplicity Ω (U, V) and entropy S (U, V).

In mechanical equilibrium:

$$\frac{\partial S_{AB}}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0 \qquad \Longrightarrow \qquad \boxed{\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}}$$

The volume-per-molecule should be the same for both sub-systems, or, if T is the same, P must be the same on both sides of the membrane.

$$\text{for ideal gas} \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{kN}{V} = \frac{P}{T}$$

Relation between entropy and pressure:

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

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

This definition implies that you are holding both the internal energy and the number of particles constant in taking the derivative. This can be applied to the expression for the entropy of a monoatomic ideal gas:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

$$P = T \frac{\partial}{\partial V} (Nk \ln V) = \frac{NkT}{V}$$

This relationship is just the ideal gas law! But the ideal gas law can be obtained from just Newton's laws, which give an expression for average pressure of a gas. That along with the kinetic temperature gives the form of the gas law. So, looking at it from the other direction, the ideal gas law offers confirmation of the relationship between pressure and entropy.

We have finally derived the equation of state of an ideal gas from first principles!

Thermodynamic identity

Let's assume N is fixed:
$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV$$

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

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

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

$$\boxed{dU = TdS - PdV}$$

This useful summary relationship called the thermodynamic identity makes use of the power of calculus and particularly partial derivatives. It may be applied to examine processes in which one or more state variables is held constant, e.g., constant volume, constant pressure, etc. The thermodynamic identity holds true for any infinitesmal change in a system so long at the pressure and temperature *are well defined*. It is presumed that the number of particles is constant (i.e., you are dealing with the same system before and after the change).

Thermodynamic Identity
$$dU = TdS - PdV$$

Constant V

$$dU = TdS = Q$$
$$dS = \frac{Q}{T}$$

Macroscopic entropy

Constant V

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

A definition of temperature

Constant U

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

Consistency with ideal gas law

Constant S

$$dU = -PdV$$

Adiabatic process

$$dU = dQ - dW$$

First law of thermodynamics

Quasistatic Processes

$$\boxed{dU = TdS - PdV}$$ $\Longleftrightarrow$ $$\boxed{dU = \delta Q + \delta W}$$

(*quasistatic* processes with fixed *N*)   (*all* processes)

Thus, for *quasistatic processes* :

$$\delta Q = TdS \qquad dS = \frac{\delta Q}{T}$$

We see that the above relation is valid even if the work is being done, provided that the pressure is well-defined and uniform throughout the system. In particular, for the adiabatic process

$$\delta Q = 0 \quad \Longrightarrow \quad \text{adiabatic + quasistatic = isentropic}$$

Comment on State Functions :

$$dS = \frac{\delta Q}{T}$$ is an exact differential (*S* is a state function). Thus, the factor $1/T$ converts δQ into an exact differential for quasi-static processes.

$$\Delta S = 0$$
$$\Delta Q \neq 0$$
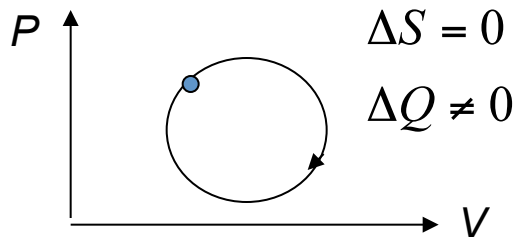
From the Sackur-Tetrode equation for an isentropic process :

$$\Delta S = 0 \quad \Longrightarrow \quad VT^{f/2} = const \quad \longrightarrow \quad VT^{\frac{1}{\gamma-1}} = const$$

Example

Bacterias of mass M with heat capacity (per unit mass) C, initially at temperature $T_0+\Delta T$, arebrought into thermal contact with a heat bath at temperature T_0.

(a) Show that if $\Delta T << T_0$, the increase ΔS in the entropy of the entire system (body+heat bath) when equilibrium is reached is proportional to $(\Delta T)^2$.

(b) Find ΔS if the body is a bacteria of mass 10^{-15}kg with $C=4$ kJ/(kg·K), $T_0=300$K, $\Delta T=0.03$K.

(c) What is the probability of finding the bacteria at its initial $T_0+\Delta T$ for Δt $=10^{-12}$s over the lifetime of the Universe (~10^{18}s).

(a)

$$\Delta S_{body} = \int_{T_0+\Delta T}^{T_0} \frac{\delta Q}{T'} = \int_{T_0+\Delta T}^{T_0} \frac{CdT'}{T'} = C\ln\left(\frac{T_0}{T_0+\Delta T}\right) < 0$$

$$\Delta S_{heat\ bath} = \frac{\delta Q}{T_0} = \frac{-\int_{T_0+\Delta T}^{T_0} CdT'}{T_0} = \frac{C\Delta T}{T_0} > 0$$

$$\Delta S_{total} = \Delta S_{body} + \Delta S_{heat\ bath} = C\frac{\Delta T}{T_0} - C\ln\left(\frac{T_0+\Delta T}{T_0}\right)$$

$$\approx \left[\ln(1+\alpha) = \alpha - \frac{\alpha^2}{2} + \frac{\alpha^3}{3} - ...\right] = \frac{C}{2}\left(\frac{\Delta T}{T_0}\right)^2 > 0$$

(b)

$$\Delta S_{total} = \frac{C}{2}\left(\frac{\Delta T}{T_0}\right)^2 = \frac{4\cdot10^3 \times 1\cdot10^{-15}\ J/K}{2}\left(\frac{0.03}{300}\right)^2 = 2\cdot10^{-20}\ J/K$$

(c)

Ω for the (non-equilibrium) state with $T_{bacteria} = 300.03$K is greater than Ω in the equilibrium state with $T_{bacteria} = 300$K by a factor of

$$\frac{\Omega_{T_0}}{\Omega_{T_0+\Delta T}} = \exp\left(\frac{\Delta S_{total}}{k_B}\right) = \exp\left(\frac{2\cdot10^{-20}\ J/K}{1.38\cdot10^{-23}\ J/K}\right) \approx e^{1450} \approx 10^{630}$$

Thus, the probability of the event happening in 10^{30} trials:

$$(\#\ events)(probability\ of\ occurrence\ of\ an\ event) = 10^{30} \times 10^{-630} \rightarrow 0$$