Thermodynamics (TD)

TD deals with Macroscopic equilibrium states

Macroscopic state: A description of the system based macroscopic measurements (T, V, P, Mass (N), Energy U)

Macroscopic measurements have limited resolution and they do not reveal the microscopic state (Position & momenta of all the particles) of the system. Many different microscopic states can lead to the same macroscopic state.

Equilibrium state: A macroscopic state that do not change in time. There is no net transfer of energy or particles out of the system.

State function: A function of the small number of macroscopic quantities that specifies a macroscopic equilibrium state.

TD rests on the main assumption:
"For every equilibrium state there is a state function called the <u>entropy</u>."

<u>Postulates of TD</u>

1. Existence. A macroscopic system (very many particles) has equilibrium states that are characterized uniquely by a small number of extensive variables. Extensive variables provide a measure of the size of the system. They answer "how much" questions. V, U, N

For every equilibrium state there is a state function of the extensive variables called the entropy

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

"Fundamental relation"

and gives all TD information about the system.

2. Maximization: The values of the extensive variables of an isolated system in the absence of an internal constraint are those that maximize the entropy over the set of all contrained macroscopic states. $\Delta S \geq 0$

3. Additivity. The entropy of a composite system is additive over the constituent subsystems.

$$S(U_A, V_A, N_A; U_B, V_B, N_B)$$

$$= S_A(U_A, V_A, N_A) + S_B(U_B, V_B, N_B)$$

4. Continuous and differentiable.
The entropy is a continuous and differ.. function of the extensive variables.
(This can breaks down at phase transitions)

5. Extensivity: The entropy is an extensive function of the extensive variables.

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$$

This postulate breaks down if surface effects are important.

6. Monotonicity : The entropy is a monotonically increasing function of energy for equilibrium values of the energy.

$$\frac{\partial S}{\partial U}(U,V,N) \geq 0$$

Implies positive temperatures.

7. Nernst postulate:
The entropy of any physical system is non-negative.

(Only applies to Quantum mech. systems)

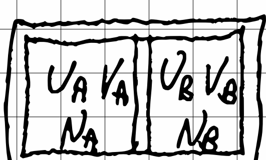
TD definition of Temperature

Temperature T is an intensive quantity and is defined in TD as

$$\boxed{\frac{\partial S}{\partial U} = \frac{1}{T}}$$

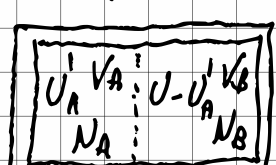
It follows from P.2 & P.3 and this def. that two subsystems in thermal contact in equilibrium share the same T.

energy can transfer between the subsystems.



$$S = S(U_A, V_A, N_A) + S(U_B, V_B, N_B)$$

when ~~removing~~ making the internal wall able to transfer energy but not particles.



$$U = U_A + U_B$$

P.2 $\Rightarrow$ U_A' is determined by maximizing S, $U_B = U - U_A'$

S is max w.r.t U_A' when

$$\frac{\partial S}{\partial U}(U_A', V_A, N_A) + \underbrace{\frac{\partial (U - U_A')}{\partial U_A'}}_{-1} \frac{\partial S}{\partial U}(\overbrace{U - U_A'}^{U_B'}, V_B, N_B)$$

$= 0$ determines U_A'

$$\Rightarrow \underbrace{\frac{\partial S}{\partial U}(U_A', V_A, N_A)}_{\frac{1}{T_A}} = \underbrace{\frac{\partial S}{\partial U}(U_B', V_B, N_B)}_{\frac{1}{T_B}}$$

$$\Rightarrow T_A = T_B$$

TD laws

Formulated long before the postulates.
But they are equivalent to the postulates
or describe "obvious facts".

0. If two systems are in equilibrium with a third system, they are also in equil. with each other.

$\boxed{A|C}$ $\quad$ $\boxed{B|C}$

$$\left.\begin{array}{l} T_A = T_C \\ T_B = T_C \end{array}\right\} T_A = T_B$$

(derivable from P.2 & P.3)

1. Heat is energy, and energy is conserved.
(obvious fact)

2. After the release of a constraint in a closed system, the entropy never decrease.
(Postulate 2)

3. The entropy of a QM system goes to a constant as $T \to 0$.
(P.7)

Small changes, Differentials

Exact and inexact differentials.

Consider a function of two vars. $f(x,y)$
The differential is

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

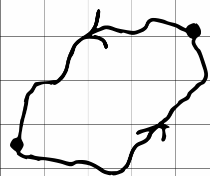
and is an <u>exact</u> differential.

An exact differential gives a unique function (up to a constant) when integrated.

$$\int_{(0,0)}^{(x,y)} df = \int_{(0,0)}^{(x,0)} \frac{\partial f}{\partial x} dx + \int_{(x,0)}^{(x,y)} \frac{\partial f}{\partial y} dy$$

$$= \cancel{f(x,0)} - f(0,0) + f(x,y) - \cancel{f(x,0)}$$
$$= f(x,y) - f(0,0)$$

This result is path-independent and the differential is therefore exact.



C

$$\oint df = \oint d\bar{l} \cdot \vec{\nabla} f = \iint d\bar{s} \cdot \underbrace{(\bar{\nabla} \times \bar{\nabla} f)}_{0}$$

Because $\dfrac{\partial}{\partial y} \dfrac{\partial f}{\partial x} = \dfrac{\partial}{\partial x} \dfrac{\partial f}{\partial y}$

But not every differential

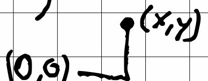
$$\delta f = f(x,y)dx + g(x,y)dy$$

is exact.

Only when $\dfrac{\partial f}{\partial y} = \dfrac{\partial g}{\partial x}$ is this differential exact.

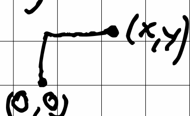
For instance the diff: $\text{đ}f = -y\,dx + x\,dy$ is not exact.

$$\int_{(0,0)}^{(x,y)} \text{đ}f = \underbrace{\int_{(0,0)}^{(x,0)} \underset{0}{\underset{\shortparallel}{-y}}\,dx}_{0} + \int_{(x,0)}^{(x,y)} x\,dy = xy$$



not equal

$$\int_{(0,0)}^{(x,y)} \text{đ}f = \underbrace{\int_{(0,0)}^{(0,y)} \underset{0}{\underset{\shortparallel}{x}}\,dy}_{0} + \int_{(0,y)}^{(x,y)} -y\,dx = -xy$$



$\Rightarrow$ $\text{đ}f$ is an inexact diff.

However, we can always find an integrating factor (not unique) so that

$$\underset{\substack{\uparrow \\ \text{exact}}}{dG} = r(x,y)\,\underset{\substack{\uparrow \\ \text{inexact.}}}{\text{đ}f}$$

for $\delta f = -y\,dx + x\,dy$, $r(x,y) = \frac{1}{x^2}$

Then

$$dG = r(x,y)\,\delta f = -\frac{y}{x^2}\,dx + \frac{1}{x}\,dy$$

$$\left.\begin{aligned} \frac{\partial}{\partial y}\left(-\frac{y}{x^2}\right) &= -\frac{1}{x^2} \\ \frac{\partial}{\partial x}\left(\frac{1}{x}\right) &= -\frac{1}{x^2} \end{aligned}\right\}$$ dG is an exact differntial.

$$\underbrace{\frac{1}{y^2}(-y)}_{-1/y}\,dx + \frac{x}{y^2}\,dy$$

$$\left.\begin{aligned} \frac{\partial\left(-1/y\right)}{\partial y} &= \frac{1}{y^2} \\ \frac{\partial\left(\frac{x}{y^2}\right)}{\partial x} &= \frac{1}{y^2} \end{aligned}\right\}$$ so $r(x,y) = \frac{1}{y^2}$ is also an interatin factor.

also $r = \frac{1}{xy}$ is an integratin factor.

This is the same integrat[ing] factor as used when solving first-order diff. eq.

say $y' = -\frac{f(x,y)}{g(x,y)} \Rightarrow \frac{dy}{dx} = -\frac{f(x,y)}{g(x,y)}$

$\Rightarrow \quad f(x,y)\,dx + g(x,y)\,dy = 0$

multiply this by the integrating factor $r(x,y)$ then

$$\underbrace{r(x,y)\,f(x,y)\,dx + r(x,y)\,g(x,y)\,dy}_{dG} = 0$$

solution are $G(x,y) = \text{const.}$

Conservation of energy

$$dU = \text{đ}Q + \text{đ}W$$

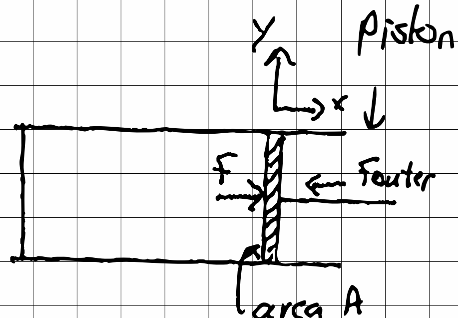
Heat added to the system

Work performed on the system.

U is a state function, so dU is exact

$\text{đ}Q$, $\text{đ}W$ are inexact. They cannot be derived by a function.

Work



Work done on the system

(dx<0)

$$\text{đ}W = \vec{F}_{outer} \cdot d\vec{x} = -F\,dx = -\underbrace{\frac{F}{A}}_{\text{Pressure } p} \cdot \overbrace{A\,dx}^{dV}$$

$$\text{đ}W = -p\,dV$$

($-\frac{1}{p}$ is an intergratg factor)