

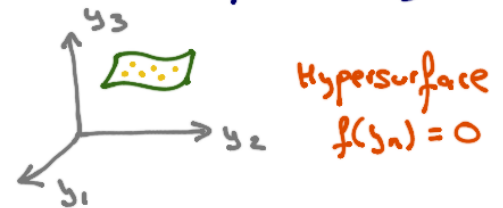
1. BASICS OF THERMODYNAMICS

I. Preliminaries

Large number of degrees of freedom

- a) A thermodynamic system is any macroscopic system
- b) Thermodynamic parameters are measurable macroscopic quantities associated with the system and defined experimentally: V, N, \dots
- c) A thermodynamic state is specified by a set of values of the thermodynamic parameters y_n
- d) Thermodynamic equilibrium: $y_n \neq y_n(t)$ (time-indep)
- e) The equation of state is a functional relationship amongst the thermodynamic parameters

$$f(y_n) = 0 \quad \Rightarrow$$



- Any point in this surface represents a state in equilibrium.

- f) **Work**: The concept of work is taken from mechanics:

$$W = \int_C \vec{F} \cdot d\vec{x} \quad \Rightarrow \quad dW = \sum_x \underbrace{X_x}_{\text{generalised force}} \underbrace{dx_x}_{\text{external parameter}} \quad [x_x \in y_n]$$

↳ path dependent

$$\text{Ex: } dW = P dV$$

↳ Pressure is the conjugate force of V

g) Heat : What is absorbed by a system if its temperature increases while no work is done

$$\Delta Q = C \Delta T \quad \left[\begin{array}{l} C_p \equiv \text{constant } P \\ C_v \equiv \text{constant } V \end{array} \right]$$

↳ heat capacity

h) A heat reservoir is a system so large that the gain or loss of any finite amount of heat does not change its temperature

i) A system is thermally isolated if no heat exchange can take place between it and the external world

j) A system is isolated if no heat or work exchange can take place

k) A thermodynamic quantity is said to be:

extensive : Proportional to the amount of substance

intensive : Independent of the amount of substance

Experimental fact : To a good approximation thermodynamic quantities are either extensive or intensive

II. The ideal gas

It is an important idealised thermodynamic system whose origin is an experimental observation: all gases behave in a universal manner when they are sufficiently dilute.

The thermodynamic parameters are P , V , T and the number of molecules N or moles n .

The equation of state is given by Boyle's law:

$$PV - kNT = 0 \quad \text{or} \quad PV - RnT = 0$$

↳ gas constant $R = 8.315 \frac{\text{joule}}{\text{deg}}$

$$\text{↳ Boltzmann's constant } k = 1.38 \times 10^{-16} \frac{\text{erg}}{\text{deg}}$$

III. The laws of thermodynamics

The laws of thermodynamics are mathematical axioms defining a mathematical model. This model does not rigorously correspond to the physical world as it ignores the atomic structure of matter. It will fail at that scale thus describing **only macroscopic** properties.

Implicit assumption : The equation of state is a regular function

* **The zeroth law** : If two systems are in thermodynamic equilibrium with a third one then they are in thermodynamic equilibrium between them.

* **The first law** : A macrostate of a system in thermodynamic equilibrium can be characterised by an state function \bar{E} called **internal energy** or **mean energy**

i) Isolated system $\Rightarrow \bar{E} = \text{cte} \quad (d\bar{E} = 0)$

ii) Interacting system $\Rightarrow d\bar{E} = \delta Q - \delta W$

not state functions $\left\{ \begin{array}{l} \delta Q = \text{Heat absorbed by the system} \\ \delta W = \text{Work done by the system} \end{array} \right.$

* **The second law** : A macrostate of a system in thermodynamic equilibrium can be characterised by an state function S called **entropy**.

i) Thermal isolated system $\Rightarrow dS \geq 0$

ii) Infinitesimal quasi-static evolution $\Rightarrow dS \geq \frac{\delta Q}{T}$
 \leftarrow reversible process

\Rightarrow Fundamental Therm. relation : $d\bar{E} = TdS - \delta W$
 \leftarrow reversible process

* The third law: The entropy of a system has a limiting value

$$T \rightarrow 0^+ \quad \text{when} \quad S \rightarrow S_0$$

where S_0 is a constant independent of all the parameters of the system.

NOTE: The quantities \bar{E} , S and T are well defined for each macrostate of the system.

NOTE: Quasi-static \equiv at any moment the system is approximately in equilibrium.

NOTE: Reversible transformation \equiv the transformation retraces its history in time when the external condition retraces its history in time.

NOTE: Reversible \Rightarrow Quasi-static

Quasi-static $\not\Rightarrow$ Reversible [freely expanding gas]

IV. Consequences of the first law

The differential $d\bar{E} = dQ - dW$ is exact. In other words, there is a state function \bar{E} whose differential is $d\bar{E}$. Equivalently, the integral

$$\int_C d\bar{E} \quad \Rightarrow \quad \text{Path independent}$$

only depends on the limits of integration. [like gravity]

Math: Given a differential $df = f_A(A, B)dA + f_B(A, B)dB$, the condition that df is exact is

$$\frac{\partial f_A}{\partial B} = \frac{\partial f_B}{\partial A}$$

Let us consider a system with thermodynamic parameters P, V, T . The equation of state allows us to express one as a function of the others so that

$$\bar{E} = \bar{E}(P, V) \Rightarrow d\bar{E} = \left(\frac{\partial \bar{E}}{\partial P}\right)_V dP + \left(\frac{\partial \bar{E}}{\partial V}\right)_P dV$$

Then the exactness of $d\bar{E}$ implies

$$\frac{\partial}{\partial V} \left[\left(\frac{\partial \bar{E}}{\partial P}\right)_V \right]_P = \frac{\partial}{\partial P} \left[\left(\frac{\partial \bar{E}}{\partial V}\right)_P \right]_V$$

• The δQ equations: Let us consider a system during an infinitesimal reversible transformation in which

$$\delta W = P \cdot dV$$

Considering $\bar{E}(P, V)$, $\bar{E}(T, P)$ and $\bar{E}(T, V)$ in the first law of thermodynamics $\delta Q = d\bar{E} + \delta W = d\bar{E} + P dV$ one finds

$$\delta Q = \left(\frac{\partial \bar{E}}{\partial P}\right)_V dP + \left[\left(\frac{\partial \bar{E}}{\partial V}\right)_P + P \right] dV$$

$$\delta Q = \left[\left(\frac{\partial \bar{E}}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P \right] dT + \left[\left(\frac{\partial \bar{E}}{\partial P}\right)_T + P \left(\frac{\partial V}{\partial P}\right)_T \right] dP$$

$$\delta Q = \left(\frac{\partial \bar{E}}{\partial T}\right)_V dT + \left[\left(\frac{\partial \bar{E}}{\partial V}\right)_T + P \right] dV$$

which are known as "dQ equations". From these equations we deduce that:

$$C_v \equiv \left(\frac{\Delta Q}{\Delta T} \right)_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_v$$

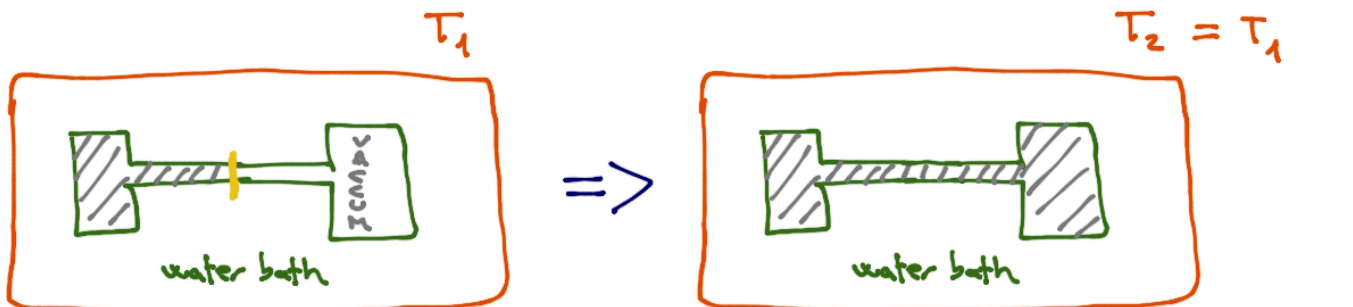
$$C_p \equiv \left(\frac{\Delta Q}{\Delta T} \right)_p = \left(\frac{\partial \bar{E}}{\partial T} \right)_p + p \left(\frac{\partial v}{\partial T} \right)_p$$

$$= \left(\frac{\partial (\bar{E} + pV)}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

with $H = \bar{E} + pV$ being the Entalpy.

• Consequences of the first law for the ideal gas.

a) Joule's irreversal free expansion:



The gas freely expands without displacing any piston or performing any work

$$\Delta W = 0 \quad \Rightarrow \quad \Delta \bar{E} = \underbrace{\Delta Q}_0 - \underbrace{\Delta W}_0 = 0$$

Thus two states with same T but different V have the same \bar{E} .

Since $\bar{E} = \bar{E}(T, v)$ is a state function we conclude that $\bar{E} = \bar{E}(T)$

b) Internal energy: Since $\bar{E} = \bar{E}(T)$, one has that

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{d\bar{E}}{dT}$$

Assuming C_V to be a constant (indep. of T) we obtain

$$\bar{E} = C_V T + \text{cte} \Rightarrow \text{linear dependence on } T$$

cte
arbitrary constant that can be set to zero

c) The quantity $C_p - C_V$: The enthalpy H is given by

$$H = \bar{E} + pV = (C_V + kN) T \Rightarrow \text{Linear dependence on } T$$

↓

$$pV - kNT = 0$$

(eq. of state)

so that

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = C_V + kN \Rightarrow C_p - C_V = kN > 0$$

⇒ It is more efficient to heat up an ideal gas keeping the volume constant than the pressure constant

$$C_V < C_p$$

V. Consequences of the second law

The entropy S is a function of state so that the differential dS is exact. Recalling the third dQ equation

$$dQ = C_v dT + \left[\left(\frac{\partial \bar{E}}{\partial v} \right)_T + P \right] dv$$

and the second law of thermodynamics $dS = \frac{dQ}{T}$ one finds

$$(1) \quad dS = \frac{dQ}{T} = \left(\frac{C_v}{T} \right) dT + \frac{1}{T} \left[\left(\frac{\partial \bar{E}}{\partial v} \right)_T + P \right] dv$$

Since dS is an exact differential one finds

$$\left(\frac{\partial}{\partial v} \right)_T \left(\frac{C_v}{T} \right) = \left(\frac{\partial}{\partial T} \right)_v \left[\frac{1}{T} \left(\frac{\partial \bar{E}}{\partial v} \right)_T + \frac{P}{T} \right]$$

Using $C_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_v$ and the exactness of $d\bar{E}$ one finds

$$0 = -\frac{1}{T^2} \left(\frac{\partial \bar{E}}{\partial v} \right)_T - \frac{1}{T^2} P + \frac{1}{T} \left(\frac{\partial P}{\partial T} \right)_v \quad (\times T^2)$$

so that ($T \neq 0$)

$$(2) \quad \left(\frac{\partial \bar{E}}{\partial v} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_v - P = \overbrace{T \frac{KN}{v}}^P - P = 0$$

↓
ideal gas $P = \frac{KNT}{v}$

→ Joule's experiment

⇒ \bar{E} being a function only of T follows from the second law !!

* TdS equations and measurable quantities :

Substituting (2) into (1) one finds

$$T dS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV \Rightarrow \text{"TdS equation"}$$

Exercise: Show that from the second dQ equation one finds another TdS equation of the form

$$T dS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP \Rightarrow \text{"TdS equation"}$$

Math: Let x, y, z be quantities satisfying $f(x, y, z) = 0$. Let w be a function of any two of x, y, z . Then

$$a) \left(\frac{\partial x}{\partial y} \right)_w \left(\frac{\partial y}{\partial z} \right)_w = \left(\frac{\partial x}{\partial z} \right)_w$$

$$b) \left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z}$$

$$c) \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \quad (\text{chain relation})$$

Let us now define three experimentally measurable quantities

- $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \Rightarrow$ Coefficient of thermal expansion

- $\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \Rightarrow$ Isothermal compressibility

- $\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \Rightarrow$ Adiabatic compressibility

Using math c) and math b) one has that

$$\left(\frac{\partial P}{\partial T} \right)_V = - \frac{1}{\left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T} = \frac{\left(\frac{\partial V}{\partial T} \right)_P}{-\left(\frac{\partial V}{\partial P} \right)_T} = \frac{\alpha}{\kappa_T}$$

so the TdS equations can be written as

$$\begin{aligned} \text{(i)} \quad T dS &= C_V dT + \frac{\alpha T}{\kappa_T} dV \\ \text{(ii)} \quad T dS &= C_P dT - \alpha T V dP \end{aligned} \quad \left. \vphantom{\begin{aligned} \text{(i)} \\ \text{(ii)} \end{aligned}} \right\} \text{ "TdS equations"}$$

Equating (i) and (ii) one has

$$(C_P - C_V) dT = \alpha T V dP + \frac{\alpha}{\kappa_T} T dV$$

and choosing $T = T(V, P)$ so that $dT = \left(\frac{\partial T}{\partial V} \right)_P dV + \left(\frac{\partial T}{\partial P} \right)_V dP$

we get

$$\left[(C_P - C_V) \left(\frac{\partial T}{\partial V} \right)_P - \frac{\alpha}{\kappa_T} T \right] dV + \left[(C_P - C_V) \left(\frac{\partial T}{\partial P} \right)_V - \alpha T V \right] dP = 0$$

From the dV piece we get

$$C_p - C_v = \frac{\alpha}{\kappa_T} T \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\alpha V} = T \frac{\alpha^2 V}{\kappa_T}$$

As a result $(C_p - C_v) > 0$ if $\kappa_T > 0$. From experience we know that $\kappa_T > 0$ for most substances but this is not implied by the laws of thermodynamics.

NOTE: For the ideal gas $C_p - C_v > 0$ was proving before using the equation of state.

VI. Thermodynamic potentials

We can introduce two additional state functions

- Helmholtz free energy : $F = \bar{E} - TS$
- Gibbs thermodynamic potential : $G = F + PV = \bar{E} - TS + PV$

* Helmholtz : In an infinitesimal reversible transformation

$$dF = \underbrace{d\bar{E}} - SdT - \underbrace{TdS} = -\delta W - SdT = -PdV - SdT$$

$$d\bar{E} = \delta Q - \delta W \quad ds = \frac{\delta Q}{T}$$

so that

$$P = - \left(\frac{\partial F}{\partial V} \right)_T, \quad S = - \left(\frac{\partial F}{\partial T} \right)_V \Rightarrow \text{Maxwell relations}$$

* Gibbs : In an infinitesimal reversible transformation

$$dG = \underbrace{dF + PdV + VdP}_{-PdV - SdT} = -SdT + VdP$$

so that

$$S = - \left(\frac{\partial G}{\partial T} \right)_P, \quad V = \left(\frac{\partial G}{\partial P} \right)_T \Rightarrow \text{Maxwell relations}$$

* Enthalpy : Recalling that $H = \bar{E} + PV$ one finds

$$dH = \underbrace{d\bar{E}} + PdV + VdP = TdS + VdP$$
$$d\bar{E} = \delta Q - \delta W = TdS - PdV$$

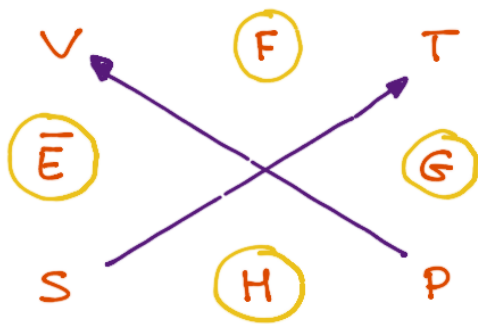
so that

$$T = \left(\frac{\partial H}{\partial S} \right)_P, \quad V = \left(\frac{\partial H}{\partial P} \right)_S \Rightarrow \text{Maxwell relations}$$

* Internal energy: Recalling $d\bar{E} = \delta Q - \delta W = TdS - PdV$ one finds

$$T = \left(\frac{\partial \bar{E}}{\partial S}\right)_V, \quad P = -\left(\frac{\partial \bar{E}}{\partial V}\right)_S \Rightarrow \text{Maxwell relations}$$

→ The eight Maxwell relations are summarised in the diagram:



⇒ The sign is determined by the orientation of the arrow.

→ Requiring the four state functions \bar{E} , H , G , F to have associated exact differentials establishes additional relations:

$$\bullet d\bar{E} = TdS - PdV \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\bullet dH = TdS + VdP \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\bullet dG = -SdT + VdP \Rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\bullet dF = -PdV - SdT \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$