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Thermodynamics: an introduction

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Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all.

The second time you go through it, you think you understand it, except for one or two small points.

The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more.

(Attributed to Arnold Sommerfeld)



Definitions :

- Thermodynamic system : important to define what the system is :
Vessel + gas? Gas ?
- Constraints :
 - isolated system: *does not exchange energy or matter with the exterior*
 - Closed system: *does not exchange matter*
 - Open system: *exchanges matter*
 - Adiabatic wall: *does not allow exchange of heat*
- Thermodynamic equilibrium : does not evolve with time at the macroscopic level
- Out of equilibrium: when a constraint is suppressed, the system is out of equilibrium

State variables and equation of state: $f(N, V, U)$

- Extensive variables: $X = N_X$ examples: N, V, U, M (*magnetic moment*)...
- Intensive variables: $Y(n_1) = Y(n_1+n_2)$ examples: $T, P, H \dots$

State functions and exact differentials: state functions admit exact differentials

(see $dE, \delta W, \delta Q$ later on)

- Transformations: the system evolves after the suppression of a constraint, or due to exchanges with the exterior:

State A  **State B**



- *Quasi-static transformation : close to the equilibrium at all stages*
- *Isothermal: $T=Cst$ Isobaric: $P=Cst$ Isochoric: $V=Cst$ Adiabatic: $dQ=0$*

Partial derivatives :

$\left(\frac{\partial V}{\partial P}\right)_T$ = variation of V associated with a variation of P, at constant T

Analytical identities:

a) Let us consider 3 variables x, y, z related through $f(x,y,z) = 0$; then

$$\left(\frac{\partial x}{\partial y}\right)_z = \left[\left(\frac{\partial y}{\partial x}\right)_z\right]^{-1}$$

b) Two of the three variables are independent; therefore the expression of some physical parameter can be expressed as $u=u(x,y)$, or $u=u(x,z)$, ...

$$\left(\frac{\partial u}{\partial y}\right)_x = \left[\left(\frac{\partial u}{\partial z}\right)_x\right]^{-1} = \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial z}{\partial u}\right)_x = \left(\frac{\partial z}{\partial y}\right)_x$$

c) From the relation $f(x,y,z) = 0$ we get: $df = 0 = \left(\frac{\partial f}{\partial x}\right)dx_{y,z} + \left(\frac{\partial f}{\partial y}\right)dy_{x,z} + \left(\frac{\partial f}{\partial z}\right)dz_{x,y}$

hence, after a simple calculation setting $dx=0$, $dy=0$ and $dz=0$: $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

Thermodynamic coefficients:

Isobaric thermal expansion coefficient

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Pressure thermal coefficient at constant volume

$$\beta = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V$$

Isothermal compressibility

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

The existence of a State Equation $f(P, V, T) = 0$ allows us to write:

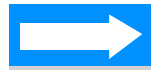
$$\left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial P}{\partial V} \right)_T = -1 \quad \text{and then} \quad \alpha = P\beta\chi_T$$

Example: for the ideal gas $\alpha = \beta = \frac{1}{T} \quad \chi_T = \frac{1}{P}$

II) First Principle – Internal Energy

1) Properties of the internal energy:

Microscopic view: $E = \sum_i k_i + \sum_{i,j} V_{i,j} + \sum_i V_i$ (sum of kinetic, potential and interaction energies of microscopic particles)



The energy can be calculated by the laws of mechanics

Macroscopic view : Thermodynamics postulates the existence of a magnitude U the “*internal energy*”.

- U is conserved for an isolated system
- U is a state variable
- U is an extensive variable

2) Exchange of energy by Work

- Elementary work: gas in a cylinder with a piston

For a displacement dl , the work made on the gas by the external force $F = P.S$ is

$$\delta W_{qs} = F dl = P S dl = - P dV$$

The subscript mean “quasi-static”. This expression is valid for any thermodynamic system, of any shape.

- Finite transformation : for a finite quasi-static transformation between two equilibrium states A and

B, the system receives a work $W_{qs} = - \int_A^B P dV$

- If the transformation is NOT quasi-static, but if the *external* pressure is always well defined, one can calculate the work done by the external force : $\delta W = -P_{ext} dV$
- The process MUST be quasi-static to be able to define the “pressure” of the gas
- Remarks:
 -
 - the variables P (intensive) and V (extensive) are called “conjugated”
 - We write δW and not dW to indicate that this is not a total differential: the Work **W characterizes the transformation, but it is not a state function!**

3) Exchange of energy by Heat

We consider an elementary transformation between two macroscopic states. The expression $dU = \delta W + \delta Q$ **defines** the heat received by the system.

Heat is not a function of state.

Heat and Temperature: giving Heat to a system does not necessarily increase its Temperature (example of ice-water equilibrium at 0 C even when heat is applied)

Temperature is an intensive magnitude, which plays for heat exchanges the same role as pressure for energy exchange by work.

Heat Capacity

We consider a closed system containing one kind of molecules, with a volume V .

Heat capacity is defined as $C_\alpha = \frac{\delta Q}{dT}$

where δQ is the heat received by the system, and dT the temperature increase.

C is an extensive magnitude.

The index α indicates the kind of process of the transformation : C_P or C_V ...

Useful formula: for a closed system with 3 variables (P,V,T) and two are independent, then

$$\delta Q = C_V dT + L dV \quad (\text{variables T and V}), \text{ or } \delta Q = C_P dT + h dV \quad (\text{variables T and P}).$$

Isothermal transformation : $dT = 0$ and $\delta Q = L dV = h dP$ (latent heat)

Using these relations : $\frac{h}{L} = \left(\frac{\partial V}{\partial P} \right)_T = -V \chi_T$ and $C_P - C_V = L \left(\frac{\partial V}{\partial T} \right)_P = \alpha V L$

4) Using the First Principle

First principle of Thermodynamics: We postulated the existence of state function “internal energy” the variation of which is given by $dU = \delta W + \delta Q$

Therefore, $\delta W + \delta Q$ is an exact differential.

Since $\delta W = -P dV$ and $\delta Q = C_V dT + L dV$ then $dU = C_V dT + (L - P) dV$ for a simple, closed, system.

And hence

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \qquad L = P + \left(\frac{\partial U}{\partial V} \right)_T$$

Also, $\delta W = -P dV$ and $\delta Q = C_P dT + h dP$ then $dU = C_P dT + h dP - P dV$ for a simple, closed, system.

We define a new State Function, the *Enthalpy* H:

$$H = U + PV$$

$$dH = C_P dT + (h + V) dP$$

And hence

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad \text{and} \quad h = -V + \left(\frac{\partial H}{\partial P} \right)_T$$

If one uses variables T and V, then U is suitable; for T and P, better choose H!

5) Ideal gas:

The internal energy U does NOT depend on the volume V .
It depends on T : $U = U(T)$; and therefore $H=H(T)$

One can show easily that $L = P$ and $h = -V$

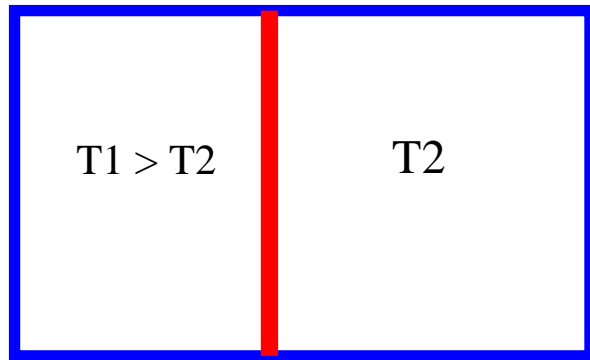
$$\text{and using } PV=NRT : \quad C_P - C_V = R$$

Ideal gas: case of adiabatic processes ($\delta Q = 0$), with $\gamma = C_P / C_V$,

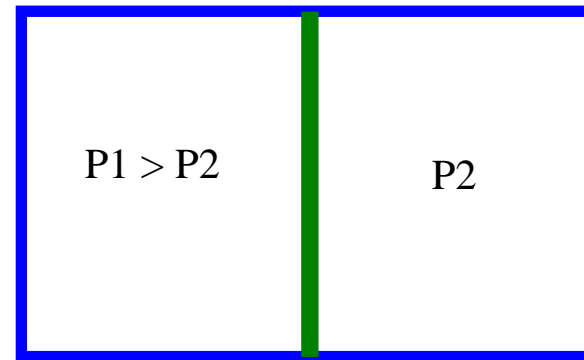
One can show that $TV^{\gamma-1} = \text{Const}$ and $PV^\gamma = \text{Const}$

III) Second Principle – Entropy

1) Notion of evolution of a system after releasing a constraint.



Heat flows if we suppress the adiabatic wall



Pressures change if the piston moves (Work)

Note: in Mechanics, there is no preferred direction of evolution (time reversal).

2) In Thermodynamics, we postulate that there exists a State Function, extensive, called Entropy (S), which obeys a principle of evolution: the evolution of an isolated system can only be done with an increase of its Entropy; the equilibrium corresponds to the maximum Entropy.

For an isolated system, the entropy remains constant if the evolution is quasi-static. The entropy increases if the evolution is irreversible.

3) **Fundamental equations** (we consider a simple, isolated system, characterized by U, V, and N)

The function $S = S(U, V, N)$ gives all the thermodynamic information on the system.

Therefore $U = U(S, V, N)$ (“Internal Energy fundamental equation”)

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

We define $T = \left(\frac{\partial U}{\partial S} \right)_{V,N}$ (Temperature, intensive)

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

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

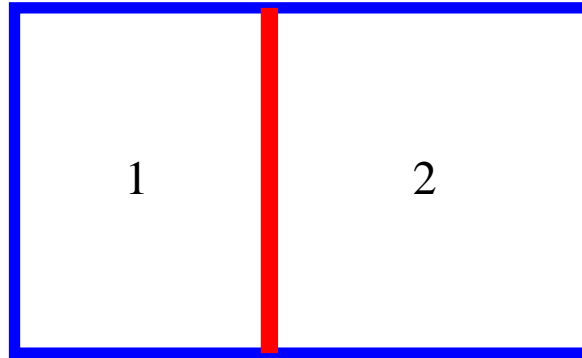
$$dU = T dS - P dV + \mu dN$$

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

There exists a function, the *Entropy*, that can be written in terms of the extensive variables of the system.

4) Temperature and Pressure: equilibrium

The temperature T and the pressure P defined previously have the properties we expect:



The wall is initially rigid and adiabatic. The entropy is maximum.

We imagine then that we allow a heat transfer from 1 to 2, with variation of volumes and internal energies:

$$dV = dV_1 = -dV_2 \quad dU = dU_1 = -dU_2 \quad \text{therefore} \quad dS = dS_1 + dS_2 = dU \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + dV \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right)$$

Maximising S corresponds to $dS = 0$ and this requires that

$$T_1 = T_2 \quad \text{and} \quad P_1 = P_2 \quad \text{the usual equilibrium condition !}$$

One can show, for a membrane that allows flow of matter, that equilibrium corresponds to $\mu_1 = \mu_2$

5) Heat and Entropy

For any transformation at constant N , we have $dU = T dS - P dV + \cancel{\mu dN}$

If the transformation is quasi-static, $\delta W = -P dV$ and since $dU = \delta W + \delta Q$, then

$$\delta Q_{q.s.} = T dS$$

N.B. : for an adiabatic, quasi-static transformation, $\delta Q = 0$ and $dS = 0$, and $S = \text{Const}$
(isoentropic transformation)

N.B. : For a non-quasi-static transformation, irreversibility gives rise to an additional entropy and

$$dS \geq \frac{\delta Q_{q.s.}}{T} \quad (\text{Clausius inequality})$$

N.B. : $dU =$ Energy $T dS$ heat gained $-$ $P dV$ work done $+$ μdN chemical work (for a quasi-static transformation!)

Determination of the calorimetric coefficients

Using the fact that $f(P,V,T)=0$ (equation of state) one can show that

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad \text{and} \quad L = T \left(\frac{\partial S}{\partial V} \right)_T$$

And after some more work, that $L = T \left(\frac{\partial P}{\partial T} \right)_V$ and $\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$

These 2 last equations allow the determination of the latent heat L from the equation of state, and to determine C_V (up to a function of T)

Analogously, one can show that $C_P = T \left(\frac{\partial S}{\partial T} \right)_P$ and $h = T \left(\frac{\partial S}{\partial P} \right)_T$

And after some more work, that $h = -T \left(\frac{\partial V}{\partial T} \right)_P$ and $\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$

For the ideal gas, $PV = NRT$, and $L = P$, $h = -V$ and hence $dU = C_V dT$ and $dH = C_P dT$
 U and H only depend on T !

III) Third Principle

Defining the temperature as $\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N}$ we assume that S is a continuous and derivable function of the internal energy U .

For « normal » systems, T is positive: S is a monotonous, increasing function of U .

$$\delta Q_{q.s.} = T dS, \text{ therefore } S(B) - S(A) = \int_A^B \frac{\delta Q_{q.s.}}{T}$$

Can we know only variations of entropy???

Thermodynamics *postulates* that as $T \rightarrow 0$, $S \rightarrow 0$ (Nernst postulate)

N.B. : some expressions (ideal gas!) do not obey this Law. One can only use them for the calculation of entropy differences, in their validity range!

One can show that this implies that $T \rightarrow 0$, $C \rightarrow 0$, as well as the thermoelastic coefficients.
One cannot reach the absolute Zero of temperature in a finite number of operations...

IV) Fundamental Equations – Thermodynamic Potentials

1) The fundamental equations contain all the information available on the system

$$U = U(S, V, N) \quad dU = T dS - P dV + \mu dN$$

$$S = S(U, V, N) \quad dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

From the first derivatives:

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

From these equations, eliminating the Entropy, one obtains the Equation of State : $f(P, V, N, T) = 0$

We can also obtain $S(T, V, N)$, $S(T, P, N)$

Note that we never needed to integrate the functions: no additive (unknown constant).

From $S = S(U, V, N)$ we get : $\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$ $\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}$ $\left(\frac{\partial S}{\partial N}\right)_{U,V} = \frac{\mu}{T}$

We have therefore $T = T(U, V, N)$ or $T = T(S, V, N)$
 $P = P(U, V, N)$ or $P = P(S, V, N)$
 $\mu = \mu(U, V, N)$ or $\mu = \mu(S, V, N)$

These “equations of state” of the system contain also all the available information.

2) Other fundamental equations

From $U(S,V,N)$, find other fundamental equations, with other variables)
Lagrange multipliers!

- Free Energy (Helmholtz potential) F (sometimes called A) $F = F(T,V,N)$

$$F = U - T S \quad T = \left(\frac{\partial U}{\partial S} \right)_{V,N} \quad dF = -S dT - P dV + \mu dN$$

- Enthalpy H $H = H(S,P,N)$

$$H = U + PV \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S,N} \quad dH = T dS + V dP + \mu dN$$

- Free Enthalpy (Gibbs free energy) G $G = G(T,P,N)$

$$G = U + PV - T S \quad dG = -S dT + V dP + \mu dN$$

For a given problem, choose the potential with the adapted variables, and the corresponding fundamental equation.

One can show that $U + PV - TS - \mu N$ is identically 0 (homogeneity of the function) Therefore

$$G = \mu N \quad \text{and} \quad Nd\mu = -S dT + V dP \quad (\text{Gibbs - Duhem relations})$$

<i>Internal Energy</i>	<i>U</i>	<i>S, V, N</i>	$dU = T dS - P dV + \mu dN$
<i>Enthalpy</i>	<i>H</i>	<i>S, P, N</i>	$dH = T dS + V dP + \mu dN$
<i>Free Energy</i>	<i>F</i>	<i>T, V, N</i>	$dF = -S dT - P dV + \mu dN$
<i>Free Enthalpy</i>	<i>G</i>	<i>T, P, N</i>	$dG = -S dT - V dP + \mu dN$

The chemical potential:

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

Internal Energy *U*

Helmholtz free energy $F = U - T S$

Enthalpy $H = U + P V$

Gibbs free enthalpy $G = U + P V - T S$

Grand Potential $\Phi_G = U - T S - \mu N$

Maxwell relations: obtained with the Schwartz condition

$$\frac{\partial}{\partial x_j} \left(\frac{\partial \Phi}{\partial x_i} \right) = \frac{\partial}{\partial x_i} \left(\frac{\partial \Phi}{\partial x_j} \right)$$

$$\begin{aligned} \left(\frac{\partial T}{\partial V} \right)_S &= - \left(\frac{\partial p}{\partial S} \right)_V &&= \frac{\partial^2 U}{\partial S \partial V} \\ \left(\frac{\partial T}{\partial p} \right)_S &= + \left(\frac{\partial V}{\partial S} \right)_p &&= \frac{\partial^2 H}{\partial S \partial p} \\ \left(\frac{\partial S}{\partial V} \right)_T &= + \left(\frac{\partial p}{\partial T} \right)_V &&= - \frac{\partial^2 A}{\partial T \partial V} \\ \left(\frac{\partial S}{\partial p} \right)_T &= - \left(\frac{\partial V}{\partial T} \right)_p &&= \frac{\partial^2 G}{\partial T \partial p} \end{aligned}$$

The Maxwell equations can be generalized for an open system : $\left(\frac{\partial \mu}{\partial p} \right)_{SN} = \left(\frac{\partial V}{\partial N} \right)_{Sp} = \frac{\partial^2 H}{\partial p \partial N}$

(additional relations appear, where μ plays an important role)

V) Equilibrium Conditions

Two systems are in thermal equilibrium when their temperatures are the same.

Two systems are in mechanical equilibrium when their pressures are the same.

Two systems are in diffusive equilibrium when their chemical potentials are the same.

For a system at constant entropy and volume, $\Delta U = 0$ at equilibrium. Minimum internal energy.

For a completely isolated system, $\Delta S = 0$ at equilibrium. Maximum Entropy.

For a system at constant entropy and pressure, $\Delta H = 0$ at equilibrium. Minimum enthalpy.

N.B. the variation of H in a constant pressure transformation gives the heat transferred!

For a system at constant temperature and volume, $\Delta F = 0$ at equilibrium. Minimum Free energy.

N.B. the variation of F in a constant temperature transformation gives the work done!

For a system at constant temperature and pressure, $\Delta G = 0$ at equilibrium. Minimum Gibbs free enthalpy.

These relationships can be derived by considering the differential form of the Thermodynamic potentials

References

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