

Memories from thermodynamics (\*Buried by time and dust\*)

Let us recall some useful thermodynamics concepts we will make use of.

The first law of thermodynamics can be seen as an energy balance equation (energy conservation) and stems from the concept of internal energy  $U$  of a system, i.e. the overall energy of a system made out of microscopic constituent particles, thus being given by the sum of conservative forces acting among these constituent units.

The variation in the internal energy  $U$  is

$$dU = TdS - pdV + \mu dN,$$

where  $T$  = temperature,  $S$  = entropy,  $p$  = pressure,

$V$  = volume,  $\mu$  = chemical potential (i.e. the energy that can be absorbed or released by a system due to

the change of particle number; if more than one

species occurs in the system,  $\sum \mu_i dN_i$ ),  $N$  = molar number).

In a closed system where only heat can be exchanged with the outer world,

$dV = 0$  and  $dN = 0 \Rightarrow \delta Q = dU = TdS \Rightarrow \delta = \delta Q/T$  for any process (be it reversible or not).

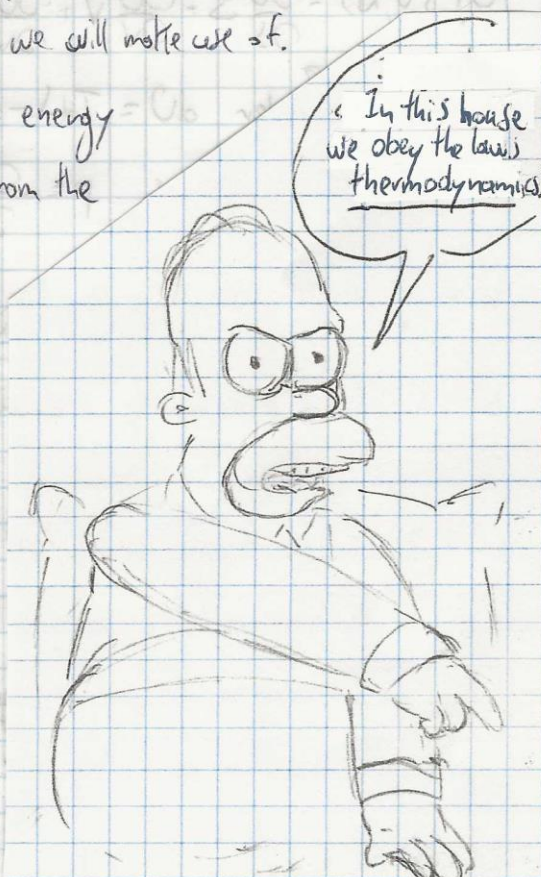
It is worth noting that  $U$  is a function of  $S, V, N$ , all of which are extensive quantity as well as  $U$ , that is

$$U(\lambda S, \lambda V, \lambda N) = \lambda \cdot U(S, V, N) \quad \forall \lambda \in \mathbb{R}^+$$

i.e.  $U$  is a homogeneous function of degree 1. Let us recall that a homogeneous function  $f(x)$  of degree  $n$  obeys the rule  $f(\lambda x) = \lambda^n f(x)$  or, given  $f(x_1, \dots, x_m)$ ,

$$\sum_{i=1}^m x_i \frac{\partial}{\partial x_i} f(x_1, \dots, x_m) = n f(x_1, \dots, x_m) \quad (\text{Euler's homogeneous function theorem}).$$

Exploiting this theorem for  $U(S, V, N)$  we get



And that's the bottom line, 'cause Homer Simpson said so.

$$U(S, V, N) = \frac{\partial U}{\partial S} S + \frac{\partial U}{\partial V} V + \frac{\partial U}{\partial N} N$$

Let us reconsider  $dU = TdS - pdV + \mu dN$ , that is to say

$$T = \frac{\partial U}{\partial S}; \quad p = -\frac{\partial U}{\partial V}; \quad \mu = \frac{\partial U}{\partial N} \quad (\text{equations of state})$$

and by comparison  $\Rightarrow$

$$U(S, V, N) = TS - pV + \mu N$$

Note 1: The internal energy per unit mass is called (Landau notation)  $\epsilon \doteq U/M$ , with  $M$  mass of the system.

Note 2: Internal energy is the first among THERMODYNAMIC POTENTIALS or thermodynamic potential energies (Duhem), also called FUNDAMENTAL FUNCTIONS (Gibbs). Thermodynamic pot. energies can be used to describe the thermodynamic state of a system, and they are obtained from  $U$  by using Legendre transforms.

Helmholtz potential (or Helmholtz free energy)  $F$

$F$  is a measure of the work that can be obtained from a closed system kept at constant  $T$ . Its expression is derived as Legendre transform of  $U$  with respect to  $S$ :

$$F \doteq U - \frac{\partial U}{\partial S} S = U - TS$$

so we go from  $U(S, V, N)$  to  $F = F(\partial U / \partial S = T, V, N)$

$$\text{Also, } F = U - TS = \underbrace{TS - pV + \mu N}_{\uparrow} - TS = -pV + \mu N$$

$$\text{and } dF = \underbrace{dU - TdS - SdT}_{\uparrow} = \underbrace{TdS - pdV + \mu dN}_{\uparrow} - TdS - SdT = -SdT - pdV + \mu dN$$

But let us demonstrate the definition of  $F$  given above. The system  $S$  is made out of constituent units permanently brought into thermal contact with an infinite heat reservoir  $R$  (a thermal bath with infinite heat capacity whose temperature  $T^R$  is constant regardless of any heat exchange with other systems). The maximum amount of work obtainable from  $S$  is

$$dW^{\max} = -dF^S, \text{ and we can prove it. Indeed}$$

$$dW = -dU^S - dU^R = -dU^S - T^R dS^R$$

The total entropy of R and S cannot decrease (only exchange  $R \leftrightarrow S$  is allowed),  $\Rightarrow$   
 $dS^S + dS^R \geq 0 \Rightarrow -dS^R \leq dS^S$   $T^R = T^S$   
 $\Rightarrow dW = -dU^S - T^R dS^R \leq -dU^S + T^R dS^S \stackrel{\downarrow}{=} -d(U^S - T^S S^S) = -dF^S$

i.e.  $dW \leq -dF^S$  which says

$$\underline{dW^{\max} = -dF^S} \quad (\text{equality is obtained for reversible processes})$$

Notes: \* As a consequence, the equilibrium state of a system communicating with a thermal bath is the state with minimum  $F$  (at equilibrium  $U$  is minimum,  $\Rightarrow$

$$dU = dU^S + dU^R = 0 \Rightarrow dF = 0);$$

\*  $F$  (as well as any other thermodynamic potential) is well defined at equilibrium - otherwise one must assume local equilibrium of subsystems (all isothermal);

\* An example of the relationship between work  $W$  and  $F$  is the molar work function of a metal; This is equal to the variation of  $F$  in a mole of electrons being extracted from the metal to the outside.

## Enthalpy $H$

$H$  is a measure of the work that can be obtained from a closed system kept at constant  $p$ .

Its expression is derived as the Legendre transform of  $U$  with respect to  $V$ :

$$H \equiv U - \frac{\partial U}{\partial V} V = U + pV$$

so we change  $U(S, V, N)$  into  $H(S, p, N)$

$$\text{Also, } H = U + pV = TS - pV + \mu N + pV = TS + \mu N$$

$$\text{and } dH = dU + pdV + Vdp = TdS - pdV + \mu dN + pdV + Vdp = TdS + Vdp + \mu dN$$

If a system is closed (no mass exchange) and kept at constant  $p$

$$dH = TdS = \delta Q_{\text{rev}} \quad (\text{heat absorbed in a reversible process is exactly the enthalpy variation})$$

This is the case for instance of phase transitions at constant  $T$ ; indeed here  $p$  is constant, the chemical potentials of the two phases are equal (we will prove it later), and the number of moles (mass) is conserved overall ( $dN^{(1)} + dN^{(2)} = 0$ )

$$\Rightarrow Vdp + \sum_{i=1}^2 \mu^{(i)} dN^{(i)} = 0$$

← The latent heat of the phase transition is the enthalpy (per unit mass) difference between the two phases.

In a similar fashion to Helmholtz's free energy, one can prove that for a system  $S$  whose parts are all kept at constant pressure  $p$  by contact with an infinite pressure reservoir, the maximum work that can be obtained from the system is the enthalpy variation:

$$dW \leq -dH^S, \quad dW^{\max} = -dH^S$$

and the equilibrium state of such system is the one with minimum enthalpy.

Note: Using Landau's notation again, the enthalpy per unit mass is called  $w \equiv H/M$ .

So  $w = \epsilon + p\upsilon = \epsilon + p/p$ , where  $\upsilon \equiv V/M$  specific volume  $\equiv 1/\rho$ ,  
 $p$  being the density.

### Gibbs free energy $G$

$G$  is a measure of the work that can be obtained from a system kept at constant  $T$  and  $p$ . Its expression is derived as the Legendre transform of  $U$  with respect to  $S$  and  $V$ :

$$G \equiv U - \frac{\partial U}{\partial S} S - \frac{\partial U}{\partial V} V = U - TS + pV$$

so  $U(S, V, N) \rightarrow G(\partial U/\partial S = T, \partial U/\partial V = p, N)$

$$\text{Also, } G = U - TS + pV = TS - pV + \mu N - TS + pV = \mu N$$

so  $\mu = G/N$ , i.e. the molar Gibbs energy is the chemical potential.

$$\begin{aligned} dG &= dU - TdS - SdT + pdV + Vdp = TdS - pdV + \mu dN - TdS - SdT + pdV + Vdp = \\ &= -SdT + Vdp + \mu dN \end{aligned}$$

Again, one can demonstrate that a closed system  $S$  in complete contact with a heat and pressure reservoir, thus resulting at constant  $T, p$  in all of its parts, can yield a maximum amount of work equal to the Gibbs free energy variation:

$$dW \leq -dG^S, \quad dW^{\max} = -dG^S$$

and the equilibrium state of such system is the one with minimum  $G$ .

Note 1: In Landau's notation,  $\phi \equiv G/M$  is the Gibbs free energy per unit mass.

Note 2: Given a system comprising two phases in equilibrium if one of the variables  $T, p$  is fixed, the other one is, too, and  $\mu^{(1)} = \mu^{(2)}$ . It is so because

$$G = \mu^{(1)} N^{(1)} + \mu^{(2)} N^{(2)} \quad \text{and} \quad dG = \mu^{(1)} dN^{(1)} + \mu^{(2)} dN^{(2)}$$

but since the total mass is unaltered (just exchange between phase (1) and (2)),  $N^{(1)} + N^{(2)} = \text{constant} \Rightarrow dN^{(1)} + dN^{(2)} = 0$

$$\Rightarrow dG = (\mu^{(1)} - \mu^{(2)}) dN^{(1)}$$

Notice that we said the phases are in equilibrium; here equilibrium  $\Leftrightarrow dG = 0$

$$\Rightarrow \mu^{(1)}(p, T) = \mu^{(2)}(p, T)$$

$\mu^{(1)}, \mu^{(2)}$  describe two different phases, so they are two separate functions of  $p, T$ ; hence this equality is an implicit relationship between  $p$  and  $T$ , and if we can say that one of them is fixed (e.g.,  $T$ : indeed constant during a phase transition), so must be the second one.

Note 3: In a thermodynamic system including more than one species/component,

$$G = \sum_i \mu^{(i)} N^{(i)} \Rightarrow dG = \sum_i \mu^{(i)} dN^{(i)} + \sum_i N^{(i)} d\mu^{(i)} \quad ; \text{ we already know}$$

$$G = U - TS + pV \Rightarrow dG = -SdT + Vdp + \sum_i \mu^{(i)} dN^{(i)}$$

$$\Rightarrow \sum_i N^{(i)} d\mu^{(i)} = -SdT + Vdp \quad \text{Gibbs-Duhem equation}$$

(describes the relationship between the  $\mu^{(i)}$  changes in the system)

Note 4: Through  $G$  we can also derive the Clausius-Clapeyron relation, i.e. the equation describing the pressure-temperature relation ( $dp/dT$ ) of the equilibrium curve between two phases of a substance at phase transition.

$$\text{Two phases at equilibrium have } G_1(p, T) = G_2(p, T);$$

$$\text{since } dG = -SdT + Vdp + \sum_i \mu^{(i)} dN^{(i)},$$

$$\frac{\partial G}{\partial T} = -S; \quad \frac{\partial G}{\partial p} = V$$

$$dG_1(p, T) = dG_2(p, T) \Rightarrow$$

$$V_1 \left( \frac{\partial G_1}{\partial p} \right) dp + \left( \frac{\partial G_1}{\partial T} \right) dT = \left( \frac{\partial G_2}{\partial p} \right) dp + \left( \frac{\partial G_2}{\partial T} \right) dT \Rightarrow$$

$$V_1 dp - S_1 dT = V_2 dp - S_2 dT$$

$$\Rightarrow \frac{dp}{dT} = \frac{S_1 - S_2}{V_1 - V_2}$$

$$\text{At constant temperature } S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} = \frac{1}{T} \int_1^2 \delta Q = \frac{\lambda M}{T}$$

where  $\lambda$  is the latent heat of transformation per unit mass, with  $M$  total mass

$$\Rightarrow \frac{dp}{dT} = \frac{\lambda}{T(V_2 - V_1)} \quad \text{Clausius-Clapeyron relation}$$

### Maxwell relations

A set of sometimes useful equations relating thermodynamical variables among them. Notice we ignore from now on the chemical potential (no mass exchange).

\* From the first law of thermodynamics,  $dU = TdS - pdV$

$$\text{while, since } U = U(S, V), \quad dU = \left. \frac{\partial U}{\partial S} \right|_{V=const.} dS + \left. \frac{\partial U}{\partial V} \right|_{S=const.} dV$$

and by comparison

$$T = \left. \frac{\partial U}{\partial S} \right|_V ; \quad p = - \left. \frac{\partial U}{\partial V} \right|_S$$

Let us take derivatives in  $V$  and  $S$  of  $T, p$ , respectively, and recall the fact that the order of differentiation, by Schwarz theorem, is unimportant:

$$\left. \frac{\partial T}{\partial V} \right|_S = \frac{\partial}{\partial V} \left( \left. \frac{\partial U}{\partial S} \right|_V \right)_S = \frac{\partial}{\partial S} \left( \left. \frac{\partial U}{\partial V} \right|_S \right)_V = - \left. \frac{\partial p}{\partial S} \right|_V$$

$$\Rightarrow \boxed{\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial p}{\partial S} \right|_V} \quad \text{I Maxwell relation}$$

\*  $dH = TdS + Vdp$ ; but  $H = H(S, p) \Rightarrow dH = \left. \frac{\partial H}{\partial S} \right|_p dS + \left. \frac{\partial H}{\partial p} \right|_S dp \Rightarrow$

$$T = \left. \frac{\partial H}{\partial S} \right|_p ; \quad V = \left. \frac{\partial H}{\partial p} \right|_S$$

Let us apply  $\frac{\partial}{\partial p} \uparrow$ ,  $\frac{\partial}{\partial S} \uparrow$  and equate the resulting expression  $\Rightarrow$

$$\boxed{\left. \frac{\partial T}{\partial p} \right|_S = \left. \frac{\partial V}{\partial S} \right|_p}$$

II Maxwell relation

$$\textcircled{*} dF = -SdT - pdV; \text{ but } F = F(T, V) \Rightarrow dF = \left. \frac{\partial F}{\partial T} \right|_V dT + \left. \frac{\partial F}{\partial V} \right|_T dV \Rightarrow$$

$$S = - \left. \frac{\partial F}{\partial T} \right|_V; \quad p = - \left. \frac{\partial F}{\partial V} \right|_T$$

Let us apply  $\partial/\partial V \uparrow$ ,  $\partial/\partial T \uparrow$  and equate;  $\Rightarrow$

$$\boxed{\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial p}{\partial T} \right|_V}$$

III Maxwell relation

$$\textcircled{*} dG = -SdT + Vdp; \text{ but } G = G(T, p) \Rightarrow dG = \left. \frac{\partial G}{\partial T} \right|_p dT + \left. \frac{\partial G}{\partial p} \right|_T dp \Rightarrow$$

$$S = - \left. \frac{\partial G}{\partial T} \right|_p; \quad V = \left. \frac{\partial G}{\partial p} \right|_T$$

Let us apply  $\partial/\partial p \uparrow$ ,  $\partial/\partial T \uparrow$  and equate;  $\Rightarrow$

$$\boxed{\left. \frac{\partial S}{\partial p} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_p}$$

IV Maxwell relation

## Specific heats

The heat capacity  $C$  of a piece of matter of mass  $M$  is the ratio between absorbed heat  $\delta Q$  and temperature increase  $dT$ :

$C \doteq \delta Q/dT$ ; we can define specific heats like

$$c = \frac{1}{M} C = \frac{1}{M} \frac{\delta Q}{dT} \quad \text{specific heat per unit mass,}$$

$$C = \frac{1}{N} C = \frac{1}{N} \frac{\delta Q}{dT} \quad \text{specific molar heat (heat capacity per mole)}$$

As a matter of fact, there is no single 'c' as it depends on the details of the heat transfer process, i.e. at constant  $p$  or  $V$ . So we define

$$c_p = \frac{1}{M} \left. \frac{\delta Q}{dT} \right|_{p=\text{const.}} \quad \left( C_p = \frac{1}{N} \left. \frac{\delta Q}{dT} \right|_{p=\text{const.}} \right) ;$$

$$c_v = \frac{1}{M} \left. \frac{\delta Q}{dT} \right|_{v=\text{const.}} \quad \left( C_v = \frac{1}{N} \left. \frac{\delta Q}{dT} \right|_{v=\text{const.}} \right)$$

- Notice that in a quasi-static process at constant volume, since  $dU = \delta Q - p dV$  we get  $dU = \delta Q$  so the specific heat at constant volume is associated to  $U$  variations.

$$c_v = \frac{1}{M} \left. \frac{\partial U}{\partial T} \right|_v = \left. \frac{\partial \mathcal{E}}{\partial T} \right|_v$$

- Similarly, in a constant- $p$  process  $dH = T ds + V dp = T ds = \delta Q \Rightarrow$

$$c_p = \frac{1}{M} \left. \frac{\partial H}{\partial T} \right|_p = \left. \frac{\partial W}{\partial T} \right|_p = \frac{T \partial S}{M \partial T} \Big|_p = T \left. \frac{\partial s}{\partial T} \right|_p \quad \text{with } s = S/M \text{ entropy per unit mass}$$

- For ideal gases,  $pV = NRT$ ;  $\Rightarrow H = U + pV = U + NRT$

and  $\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + NR$  ; dividing by  $N$  we obtain

$$\frac{1}{N} \frac{\partial H}{\partial T} = \frac{1}{N} \frac{\partial U}{\partial T} + R$$

$$C_p = C_v + R \quad (\text{a relationship between molar specific heats})$$

## Adiabatic processes

A process is adiabatic when there is no heat exchange:

$$\delta Q = 0 \Rightarrow dU + p dV = 0 \Rightarrow N C_v dT + \frac{NRT}{V} dV = 0 \quad \text{for ideal gases}$$

$$\text{and dividing by } N C_v T \rightsquigarrow \frac{dT}{T} + \frac{R}{C_v} \frac{dV}{V} = 0 \Rightarrow d(\log T) + \frac{R}{C_v} d(\log V) = 0$$

$$\Rightarrow d(\log T + \log V^{R/C_v}) = d(\log T V^{R/C_v}) = 0$$

$$\Rightarrow \log T V^{R/C_v} = \text{constant} \Rightarrow \underline{T V^{R/C_v} = \text{constant}}$$



If we define  $\gamma = C_p/C_v$ ,  $\Rightarrow \gamma = \frac{C_v + R}{C_v} = 1 + \frac{R}{C_v}$

$\Rightarrow \boxed{TV^{\gamma-1} = \text{constant}}$  equ. for an adiabatic process

Since  $pV = NRT$ , we can express equivalently this property:

$T \propto pV \Rightarrow \boxed{pV^{\gamma} = \text{constant}}$  ( $pV^{C_p/C_v} = \text{const.}$ )

$V \propto T/p \Rightarrow T \cdot (T/p)^{\gamma-1} = T^{\gamma} p^{1-\gamma} = \text{constant}$

$\Rightarrow T p^{(1-\gamma)/\gamma} = \boxed{T p^{\frac{1}{\gamma}-1} = \text{constant}}$  ( $T p^{C_p/R} = \text{const.}$ )

Let us also mention the coefficient of thermal expansion  $\beta$

$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p=\text{const.}}$  in general; for an ideal gas,  $pV = NRT \Rightarrow$

$\beta = \frac{1}{V} \underbrace{\frac{NR}{p}}_{1/T} \left( \frac{\partial T}{\partial T} \right)_p = \frac{1}{T}$  so  $\beta = 1/T$  for an ideal gas