Recap: The 1st law

processes → $dU = \delta Q - \delta W_{mech} - \delta W_{chem}$

math + physics → $dU = \delta Q + \left(\frac{\partial U}{\partial V}\right)dV + \left(\frac{\partial U}{\partial M}\right)dM \Rightarrow U(Q,V,M)$

potentials

notation → $dU = \delta Q + (-p(Q,V,M))dV + \mu(Q,V,M)dM$

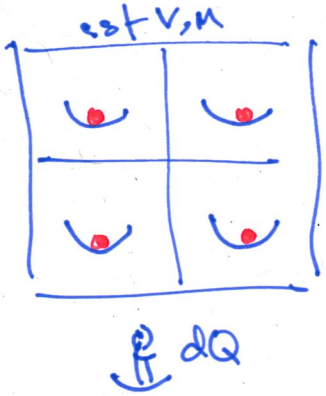
$\oint_{V,T,M} dU = 0 \Rightarrow U(T,V,M)$ $\quad \oint_{VTM} \delta Q \neq 0$ (problem 1.2)

The 2nd law

$dU_w = \delta Q = T dP \Rightarrow$ Clausius 1875

$dS \geq \delta Q/T$

S - a macroscopic measure of microscopic disorder ⇒ Thermodynamic def of $T \equiv \frac{\partial U}{\partial S}$



→ $dS = dQ/T$ → reversible limit → all heat converted to vibrational energy

Real processes → some heat is used to create damage (disorder) that cannot be drawn out again as heat → $dS > \delta Q/T$

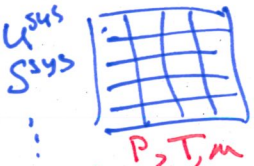
Two uses → isolated systems ($\delta W_s = \delta Q = 0$), eg the universe → $dS \geq 0$

- $\delta Q = TdS \Rightarrow dU = TdS + (-p)dV + \mu dM$ $U(S,V,M)$
  - ⇒ The "Gibbs" differential (2 uses itself)
  - ⇒ only for reversible processes
  - ⇒ differential coefficients must be defined
  - ⇒ potentials must be uniform
  - ⇒ translated to "infinitely slow" or diathermal / rigid (infinitely fast transport)

[what is T if it is not uniform] ←

Integration of the Gibbs differential:

1) U, S, M, V are metrical properties ⇒ extensive properties



$U^{sys} = \sum \delta U_i$

$S^{sys} = \sum \delta S_i$

Potentials are ratios of differentials of extensive properties ⇒ intensive ⇒ intensities

conservative properties are by definition extensive (U, M)

V is metrical by continuity

S is metrical at a point in time (no processes) or in an equilibrium system.

2) at constant -P, T, μ

$$\int_0^U dU = T\int_0^S dS + (-P)\int_0^V dV + \mu\int_0^M dM$$

The Eulerian form ⇒

$$U = TS + (-P)V + \mu M$$

⇒ can be used to evaluate irreversible processes between equilibrium states

3) The Gibbs-Duhem relation

if $f = xy$ ⇒ $df = x\,dy + y\,dx$

so if ~~$dU = TdS + (-P)dV + \sum_k \mu_i dM_i$~~

$$U = TS + (-P)V + \sum_k \mu_i M_i$$

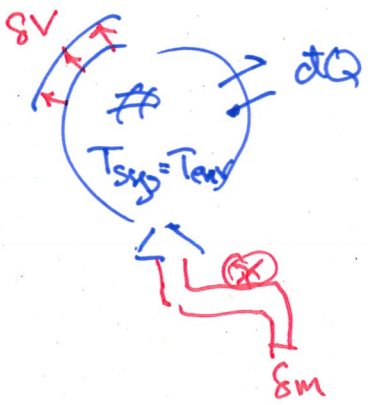
what is dU?

if the Gibbs differential is correct (and it IS the combined statement of the 1st & 2nd laws) then

$$SdT + Vd(-P) + \sum_k M_i d\mu_i = 0$$

only $k+1$ independent potentials

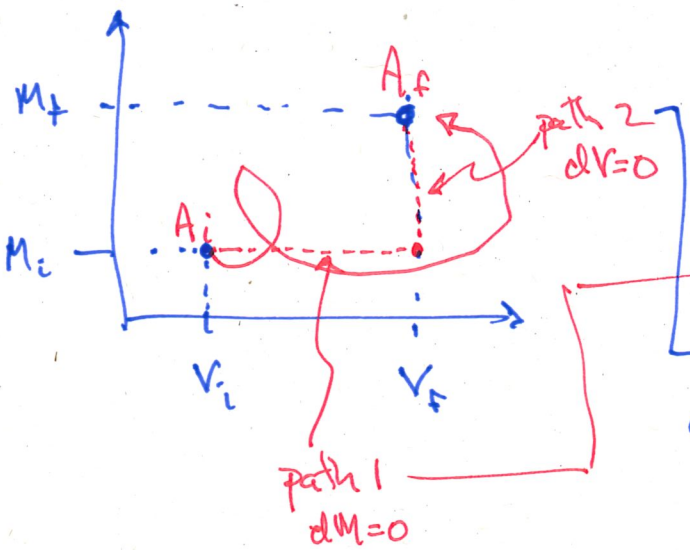
So what's so great about the GD and exactness



an isothermal work function

$$dA \equiv dU - dQ \rightarrow \text{reversible limit} \rightarrow$$
$$= dU - TdS$$
$$= (-P)dV + \mu dM \Leftarrow \text{differential form}$$

$$A = (-P)V + \mu M \Leftarrow \text{Eulerian form}$$



$$\Delta A = \int_{V_i M_i}^{V_f M_f} dA = \int_{V_i M_i}^{V_f M_f} (-P)dV + \int_{V_f M_i}^{V_f M_f} \mu dM$$

or $\Delta A = A_f - A_i$

$$= \left((-P_f)V_f + \mu_f M_f\right) - \left((P_i)V_i + \mu_i M_i\right)$$

Problem 1.4 $\Rightarrow$ $M_f = M_i$; $PV = MRT$ $\leftarrow$ P(V)

differential: $dM = 0 \Rightarrow \int dA = \Delta A_1 = \int_{V_i}^{V_f} (-P)\,dV$

Euleran: $\Delta A = \left((-P_f)V_f - (-P_i)V_i\right) + \left(\mu_f M_f - \mu_i M_i\right)$

$= (\ \ ) + (\mu_f - \mu_i) M_i$

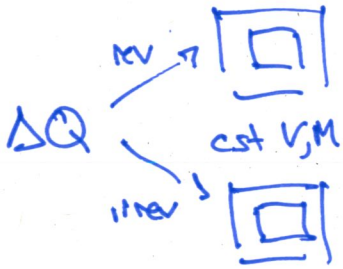
$= (\ \ ) + \Delta\mu\, M_i$

↑ Gibbs-Duhem

simplify (ans1 - ans2)
simplify (log(R·T) - log(T)) ...
assuming positive;
evalf(log(1000));

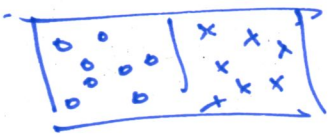
illustrate maple page 3.4 of previous notes.

irreversible processes: some examples



$$U_{rev} = T_f S_f + (-P_f) V_0 + \mu_f M_0$$
$$U_{irrev} = T_i S_i + (-P_i) V_0 + \mu_i M_0$$
$$\Delta U_{rev-irrev} = \Delta T \Delta S + (-\Delta P) V_0 + \Delta\mu M_0 = ?$$

ideal gas – non-interacting particles $U(S, V, M_0, M_x)$



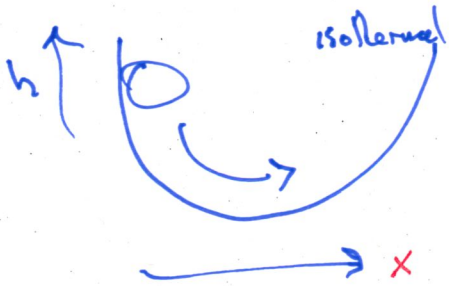
$\Delta T = \Delta P = \Delta M_0 = \Delta M_x = \Delta V = 0$

$\Delta U = ?$

$$\Delta U = 0 = T\Delta S + \Delta\mu_0 M_0 + \Delta\mu_x M_x$$

$T\Delta S > 0$; $\Delta\mu_x M_x < 0$

mixing lowers [dissipates] the net potential for useful mechanical and chemical work



$E = \frac{1}{2} M v^2 + Mgh$ [+TS]

$v(x)$, $h(x)$

$E(M, x, S)$

you cannot do any real process without creating entropy ⇒ damage ⇒ lowering the quality of the systems energy, i.e., the potential to do useful work

Rheology

elastic → reversible → no damage = thermodynamic

viscous, plastic → irreversible → damage ↔ permanent

3rd Law - Nernst's Law - it is impossible to reach 0K

→ a real process is possible if S can increase

→ no process is impossible at 0K

→ ergo all states of matter at 0K must have the same S

→ might as well define that S to be 0.

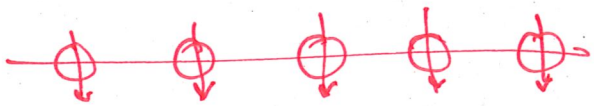
Exception 1

"vibrational" disorder = 0
configurational order →
like damage ≠ 0

→ leads to the "perfect crystal" qualification

Exception 2 quantum gas on a coin $\frac{\partial U}{\partial S} = T \quad \frac{\partial S}{\partial U} = \frac{1}{T}$

OK



$\delta U_{spin} << \delta U_{electronic}$

$+\delta U \quad \frac{\delta S}{\delta U} > 0 \Rightarrow \frac{1}{T} > 0$

δS is purely configurational (up/down)

C.P. Snow → Geologist (crystallographer) → Scientific philosopher

→ Novelist (The Affair) ⇒ 0 - you must play
1 - you can't win
2 - you must lose
3 - you can't quit