Recap: The 1st law

processes → $dU = dQ - dW_{mech} - dW_{chem} \Rightarrow U(Q, V_{mech}, M_{chem})$

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

potentials

notation $dU = dQ + (-p(Q,V,M))\,dV + \cancel{\mu(Q,V,M)\,dM}$

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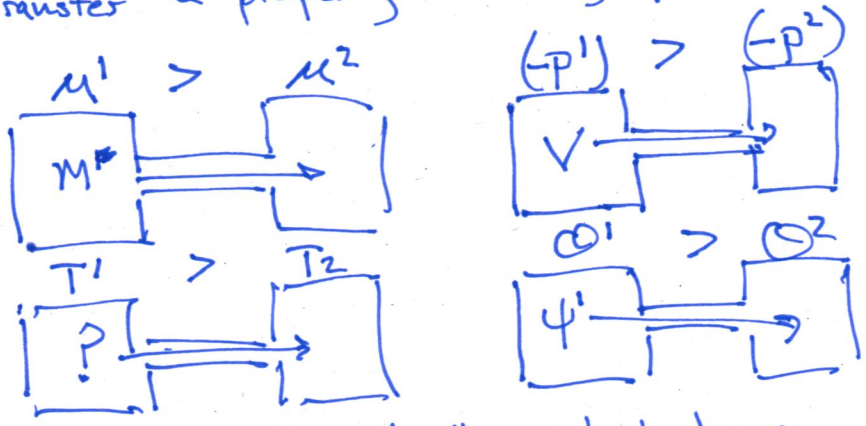
1) Equilibrium – no processes possible within the existing parts of a system

2) Processes always transfer a property from high potential to low potential



3) Ergo no processes are possible if the potentials are uniform within all parts of a system

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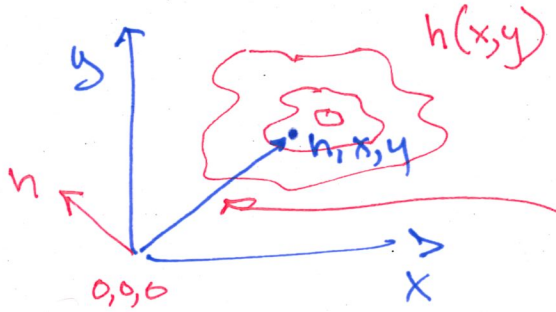
Lecture 2 notes 1.4 ⇒ problem 1.2



$dh = dW_x + dW_y$

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

$dh = q\,dx + r\,dy$ ⇒ differential form

integration along a path at constant $\nabla h \rightarrow$ cst $\frac{\partial h}{\partial x}, \frac{\partial h}{\partial y} \Rightarrow$ cst q, r

$$\int_{0,0,0}^{h,x,y} dh = h = \int_0^x q\,dx + \int_0^y r\,dy$$

$$= q\int_0^x dx + r\int_0^y dy = qx + ry = h$$

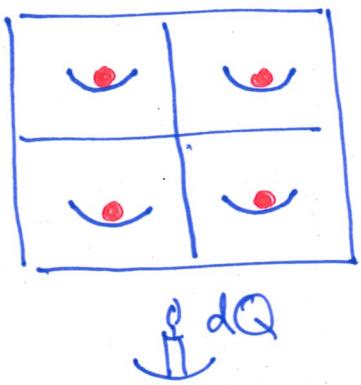
Eulerian form

$dh = q\,dx + r\,dy \Leftrightarrow dU_Q = (-P)dV + \mu dM$ Lecture 3, 2021 Z

Lecture 2 notes p 1.5 ⇒ problem 1.3 → easiest without Maple

The 2nd law $dU_w = đQ = T\,d?$ ⇒ Clausius 1875

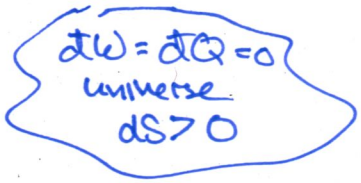
$dS \geq đQ/T$ S - a macroscopic measure of microscopic disorder



→ $dS = đQ/T$ → reversible limit, all heat converted to vibrational entropy.

Real processes → some heat is used to create damage (disorder) that cannot be drawn out again as heat.

Two uses →



→ $đQ = TdS \Rightarrow dU = TdS + (-p)dV + \mu dM$

⇒ The "Gibbs" differential, 2 uses itself

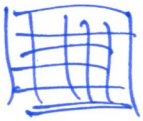
⇒ only for reversible processes

⇒ the differential coefficients must be defined ⇒ potentials must be est !!

⇒ translated to "infinitely slow" or diathermal / inviscid nonsense.

[what is T if it is not uniform ?]

Eulerian form



$U = \Sigma s_u$
$S = \Sigma s_s$
⋮

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

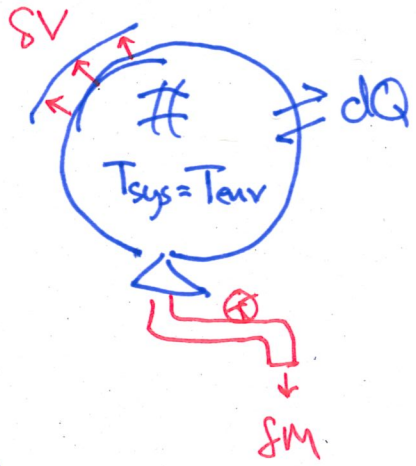
⇒ can be used for irreversible processes between equilibrium states.

$f = xy \Rightarrow df = x\,dy + y\,dx$

$dU = ?$ ⇒ Gibbs-Duhem $SdT + Vd(-P) + Md\mu = 0$

only k+1 independent potentials!!

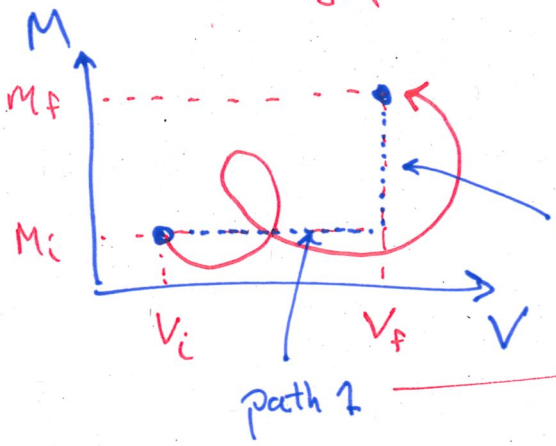
So what is so great about the G-D and exactness?



Isothermal work function

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

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



$$\Delta A = \int_{V_iM_i}^{V_fM_f} dA = \int_{V_iM_i}^{V_fM_i} (-P)dV + \int_{V_fM_i}^{V_fM_f} \mu dM$$

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 $\Rightarrow$ $M_f = M_i$, $PV = MRT$!!

$dM = 0 \Rightarrow$ $\Delta A = \int_{V_i}^{V_f} (-P)\,dV$

~~$\Delta A = \left((-P_f)V_f + \mu_f M_f\right) - \left($~~ ($M_i$)

$$\Delta A = \left((-P_f)V_f - (P_i)V_i\right) + \left(\mu_f M_i + \mu_i M_i\right)$$
$$= (\ \text{"}\ ) + \left((\mu_f - \mu_i)M_i\right)$$
$$= (\ \text{"}\ ) + \Delta\mu\, M_i$$

Gibbs-Duhem

```
simplify (ans1 - ans2);
simplify (log(R*T) - log(T))
    assuming positive;
ezalf (log(1000));
```

NO setup script is provided on the web!