Thermodynamics → how thermal, mechanical, and chemical processes affect the energy of a system

Chemical thermodynamics → no time → no kinetic energy → no vectors; ← hydrostatic eq → rocks are inviscid

4 laws

0^{th} law – a legal issue → the transitive property of equilibrium, eg $T_A = T_B$; $T_B = T_C \Rightarrow T_A = T_C$

Caratheodory ~1910 (Born) → Fowler made it a law.

1^{st} Law Clausius, 1850 → ETH processes: Q → heat

W → work

$$dU - dQ_{\underline{gained}} + \sum dW_{\underline{done}} = 0$$

internal energy

$dU_{universe} = 0$ $dU_{system} \neq 0$

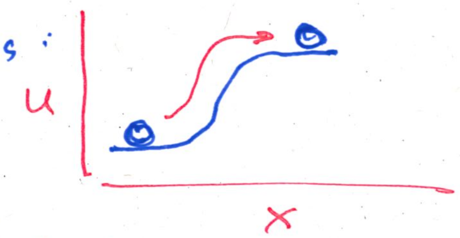
⇒ U is a state function $\oint dU = 0$ ⇒ exact differential

⇒ state variables $M_1 \dots M_\phi, V, T$ → $\oint dM = 0$

φ - kinds of mass   mechanical state   thermal state

Work !!

Mechanics:



Chemical Thermodynamics

dV ⇒ mechanical work

$M_1 | M_2$ dM_1, dM_2 ⇒ chemical work

1st law process

physics

math

$dU = -dW$

$dU = -f\,dx$

$dU = \frac{dU}{dx}\,dx = \Theta\,dx$

differential coefficient

variable

$\frac{\partial U}{\partial x} = \Theta = -f$

↑ potential

$dU = đQ - đW_{mech} - đW_{chem}$

$dU = đQ + \frac{\partial U}{\partial V}dV + \frac{\partial U}{\partial M}dM$

$dU = đQ + \underbrace{(-P)}dV + \underbrace{\mu}\,dM$

potentials for processes

$[-P(U, V, M_\phi)]$ $[\mu_1(U, V, M_{i\neq 1})]$

2022 3.2

Notation in script $\quad dU = đQ + \sum_{i}^{\lambda+1} \Theta_i \, d\Psi_i$

after Tisza $\Rightarrow$ $\quad \dfrac{\partial U}{\partial \Psi_i} = \Theta_i \Rightarrow \Psi_i$ and Θ_i are conjugate

Callen $\Rightarrow$

Hillert $\quad \dfrac{\partial U}{\partial M_1} = \mu_1 \Rightarrow M_1$ " μ_1 " "

Equilibrium - a condition were no processes are possible within the existing parts of a system $\Rightarrow$ such processes occur in response to potential variations $\Rightarrow$ ergo a necessary condition for equilibrium is the uniformity of potentials

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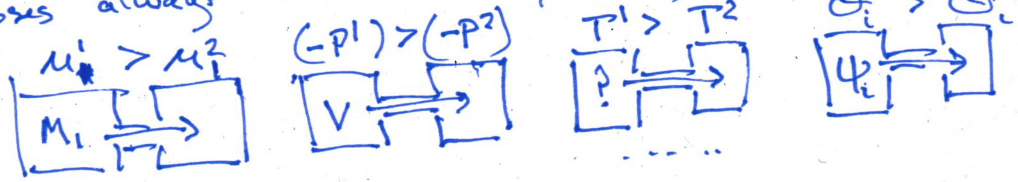
(univariate) Processes always transfer the property Ψ_i from high Θ_i to low Θ_i



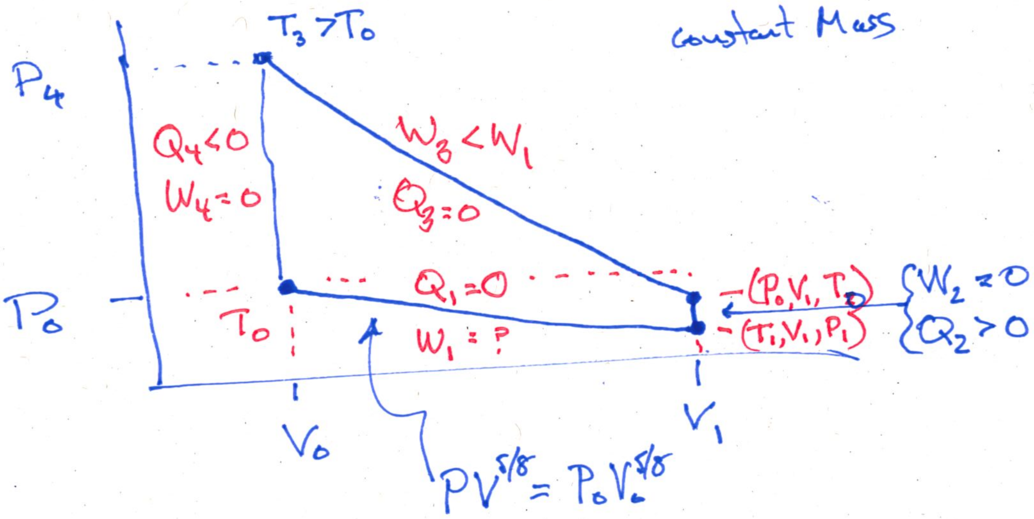
Thoughts on Exactness

if U, V, M are state functions how can Q be inexact?

$$đQ = dU + PdV - \mu dM$$

problem 1.2

constant Mass



$PV = nRT$

$\left[PV^{5/8}\right]_Q = cst$

$\downarrow$

$$P^{W1} = P_0 \left[\frac{V_0}{V}\right]^{5/8}$$

$$dW_1 = \int_{V_0}^{V_1} P^{W1} dV \Rightarrow$$

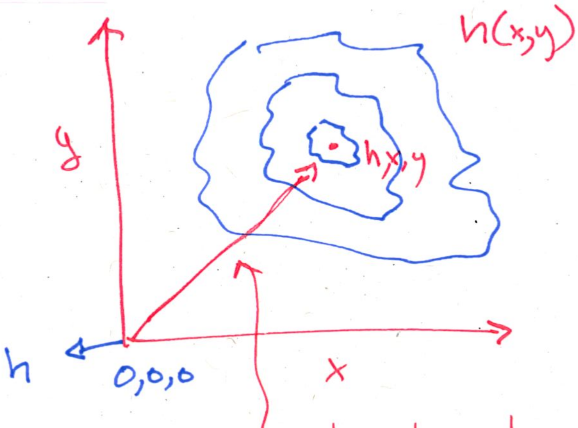
W1:= int $(P_0*(V_0/V)$^$(5/8)$, ...
V = V_0 .. V_1) assuming::
positive;
or assuming V0>0, V1>0;

$$\oint dU = 0 = \sum Q - \sum W \Rightarrow \text{it's The Law!!}$$

$$|W_3| > |W_1| \Rightarrow \sum W \neq 0$$

$$\sum Q \neq 0$$

The 1st law can also be considered to be a statement that $U(T,V,M)$ is a function



integration at constant $\frac{\partial h}{\partial x}$ $\frac{\partial h}{\partial y}$

$$dh = dW_x + dW_y$$

$$dh = \frac{\partial h}{\partial x} dx + \frac{\partial h}{\partial y} dy \quad q(x,y),\ r(x,y)$$

$$dh = q\, dx + r\, dy \Rightarrow \text{differential form}$$

integration at constant $\nabla h \Rightarrow$ cst $\frac{\partial h}{\partial x}, \frac{\partial h}{\partial y}$

$\Rightarrow$ cst q, r

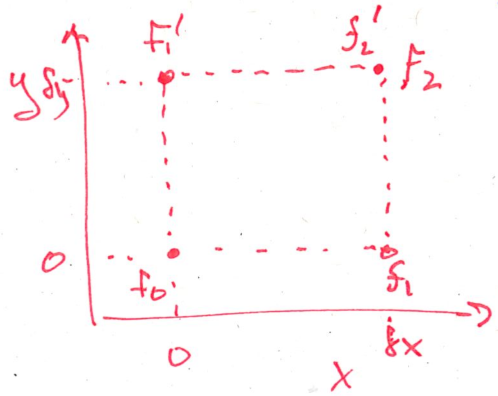
$$\int_{0,0,0}^{h,x,y} dh = h = \int_0^x q\, dx + \int_0^y r\, dy$$

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

$$= qx + ry \Leftarrow \text{Eulerian form}$$

SKIP $\Longrightarrow$

What if you can't see the mountain, ie you don't know what $U(T,V,M)$ looks like, how do you know it's exact?



Taylor Series $f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(x_0)}{n!}(x-x_0)^n$

$$n=1 \quad f(x) = f(x_0) + \left.\frac{\partial f}{\partial x}\right|_{x=x_0} \underbrace{(x-x_0)}_{\delta x}$$

$\Rightarrow$

$$f_0 \to f_1 \to f_2$$

$$f_1 = f_0 + \left.\frac{\partial f}{\partial x}\right|_{0,0} \delta x$$

$$f_2 = f_1 + \left.\frac{\partial f}{\partial y}\right|_{\delta x,0}$$

$$f_2 = f_0 + \left.\frac{\partial f}{\partial x}\right|_{0,0} \delta x + \left.\frac{\partial f}{\partial y}\right|_{\delta x,0} \delta y$$

$$f_2' = f_0 + \left.\frac{\partial f}{\partial y}\right|_{0,0} \delta y + \left.\frac{\partial f}{\partial x}\right|_{0,\delta y} \delta x$$

if $f_2 = f_2'$

$$\left.\frac{\partial f}{\partial x}\right|_{0,0} \delta x + \left.\frac{\partial f}{\partial y}\right|_{\delta x,0} \delta y = \left.\frac{\partial f}{\partial y}\right|_{0,0} \delta y + \left.\frac{\partial f}{\partial x}\right|_{0,\delta y} \delta x$$

invert

$$\left[\left.\frac{\partial f}{\partial x}\right|_{0,0} - \left.\frac{\partial f}{\partial x}\right|_{0,\delta y}\right]\delta x = \left[\left.\frac{\partial f}{\partial y}\right|_{0,0} - \left.\frac{\partial f}{\partial y}\right|_{\delta x,0}\right]\delta y$$

$$\frac{\left.\frac{\partial f}{\partial x}\right|_{0,\delta y} - \left.\frac{\partial f}{\partial x}\right|_{0,0}}{\delta y} = \frac{\left.\frac{\partial f}{\partial y}\right|_{\delta x,0} - \left.\frac{\partial f}{\partial y}\right|_{0,0}}{\delta x}$$

infinitesimal limit $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \Rightarrow$

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) \Rightarrow \text{Euler's criterion for exactness}$$

2022 3.4

$$dU_Q = (-P)\,\partial V + \mu\, dM$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial M}\right) = \frac{\partial}{\partial M}\left(\frac{\partial U}{\partial V}\right)$$

$$\frac{\partial \mu}{\partial V} = \frac{\partial(-P)}{\partial M} \Rightarrow (-P) \text{ and } \mu \text{ are not independent}$$

Euler 1707 → 10 CHF, e, Σ, f, etc catherine the great/bernoulli

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Problem 1.3 → Don't use maple

No setup script for chapter 1 problems.

Problem 1.4 will be covered next week.

The problem set for chapter 1 is not! assigned yet.

Maple configuration

Tools → options → display → Input display → Maple Not / Typesetting level → Maple Standard

Tools → options → Interface → default Format → Worksheet

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do problem 1.1 to demonstrate syntax.

ans, subs, :=, ;, .., assuming