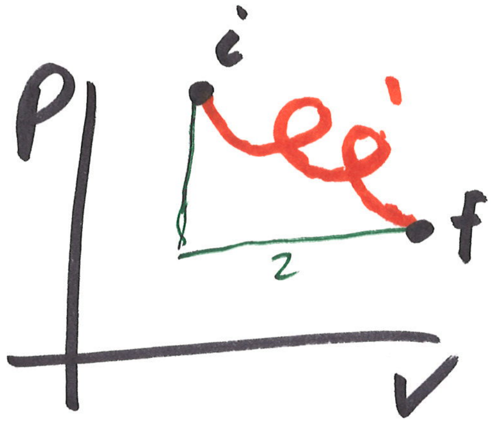


$$\Delta U = \int_i^f dU = U(f) - U(i)$$

$\uparrow$ must be integrable.

With Heat Exchange + Particle Exchange

$$\underset{\substack{\uparrow \\ \text{independent} \\ \text{of path}}}{dU} = \underbrace{\underbrace{\bar{d}W}_{\substack{\text{depends} \\ \text{on path}}} + \underbrace{\bar{d}Q}_{\substack{\text{depends} \\ \text{on path}}}}_{\text{independent of path}} + \sum_i \mu_i \, \bar{d}N_i$$

μ_i: chemical potential (Gibbs Free energy per particle

N_i: number of particles

$$dU = \bar{d}W + \bar{d}Q + \mu \, \bar{d}N$$

$\bar{d}W$: mechanical work

$\bar{d}Q$: heat "Thermal work"

$\mu \, \bar{d}N$: "chemical work"

What is an exact differential?

$$U(A,B) = A^2B^2 + 2A$$

↑ state function

$$dU = \left(\frac{\partial U}{\partial A}\right)_B dA + \left(\frac{\partial U}{\partial B}\right)_A dB$$

$$dU = (2AB^2 + 2)\,dA + (2A^2B)\,dB$$

↑ If we start here, How can we tell if dU is exact?

$$\left[\frac{\partial}{\partial B}\left(\frac{\partial U}{\partial A}\right)_B\right]_A = \left[\frac{\partial}{\partial A}\left(\frac{\partial U}{\partial B}\right)_A\right]_B$$

"no curl"

$$\frac{\partial}{\partial B}(2AB^2+2)_A \stackrel{?}{=} \frac{\partial}{\partial A}(2A^2B)_B$$

$$4AB = 4AB \checkmark$$

Inexact differential example

$$* \; \text{đ}Q = \overbrace{A}^{\left(\frac{\partial Q}{\partial A}\right)_B} dA + \overbrace{A^2}^{\left(\frac{\partial Q}{\partial B}\right)_A} dB$$

There is no function $Q(A,B)$ with this differential!

Check the mixed partial deriv.

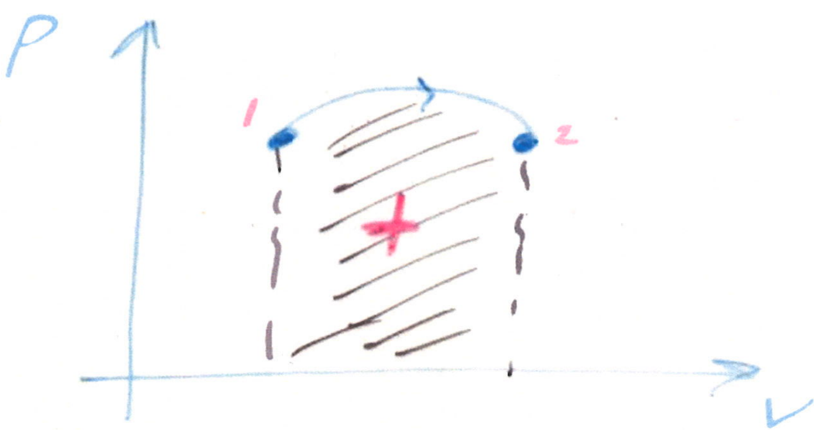
$$\frac{\partial}{\partial B}\Big[\underbrace{\left(\frac{\partial Q}{\partial A}\right)_B}_{A}\Big]_A \overset{?}{=} \Big[\frac{\partial}{\partial A}\underbrace{\left(\frac{\partial Q}{\partial B}\right)_A}_{A^2}\Big]_B$$

$$\left(\frac{\partial}{\partial B}A\right)_A \overset{?}{=} \left(\frac{\partial A^2}{\partial A}\right)_B$$

$$0 \neq 2A \qquad \forall A,B$$

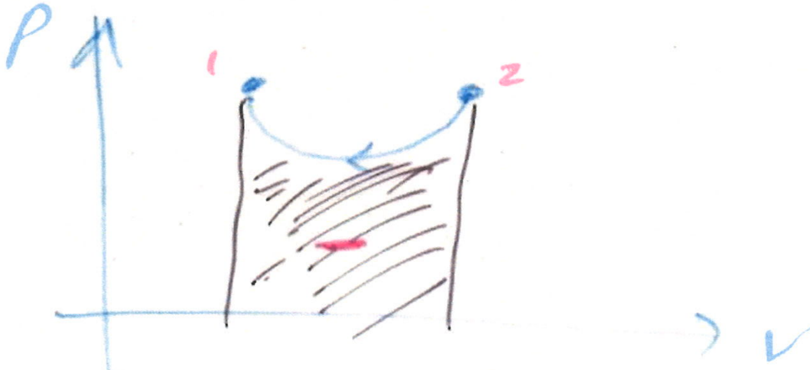
Therefore there is no $Q(A,B)$ satisfying *

Cycle for engine — 2 strokes

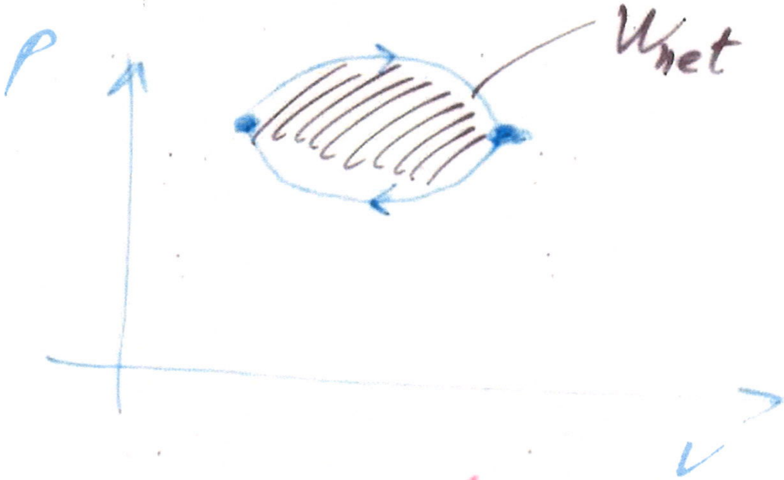


$$\int_1^2 dW = \int_1^2 P\,dV = W_{12}$$

$$\int_1^2 dU = U(2) - U(1)$$



$$\int_2^1 dW = \int_2^1 P\,dV = W_{21}$$



$$\oint dW \neq 0$$

In contrast $\oint_{1\to 2\to 1} dU = U(1) - U(1) = 0$

U is a <u>state</u> function (The system <u>has</u> internal energy U).

First Law of Thermodynamics

generalized force · chemical potential · # particles

$$dU = \sum_a J_a \, d\xi_a + T\,dS + \sum_i \mu_i \, dN_i$$

Reversible work

J_a: Mechanical work · $d\xi_a$: gen. displacement · $T\,dS$: heat $đQ$ "thermal work" · i: species · $\mu_i\,dN_i$: chemical work

$$\mu = \frac{G}{N}$$

$đq$

3-d gas:	$(-p)$	dV
2-d sheet:	σ	dA
1-d spring:	F	dx
	force, like tension	
magnet:	B	dM
	field	magnetization

magnetization: magnetic dipole moment per unit volume

extensive: If double system, these double.

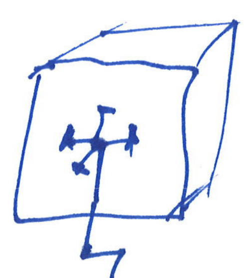
intensive: If double the system, stay same

switch extensive ⇔ intensive, Legendre transformation

$\frac{\text{ext.}}{\text{ext.}} = \text{int.}$ | $\text{int.} \times \text{ext.} = \text{ext}$ | $\text{ext}_1 \cdot \text{ext}_2 \, \cancel{\neq}$ wrong

isothermal - same temp.
isobaric - same pressure
isochoric - same volume

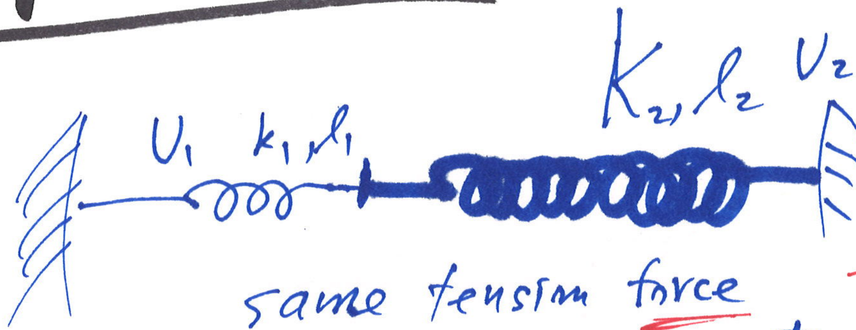
adiabatic - no heat flow



isochoric work is irreversible
"shaft work"

Equilibrium

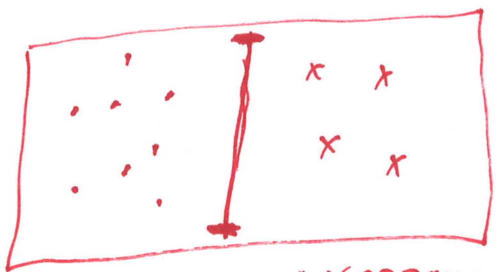
$\sum \vec{F} = \cancel{m\vec{a}} = 0$



same tension force
trade x displacement

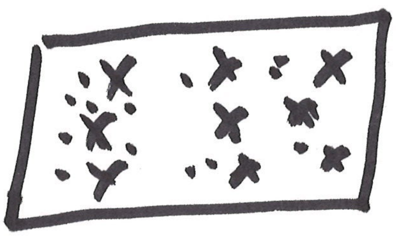
Mechanical Equilibrium

gas



same pressure
trade volume

Chemical Equilibrium



same μ chemical potential
trade number of particles N

wall is diathermal

thermal equilibrium

same Temp. T
trade entropy S