Ten Introductions to Workshops on Thermodynamics

Based on Lectures for Year 1, held by Tim Veal, University of Liverpool

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October 2021 – January 2022

Liverpool, 5.10.2021

from T. Veal
L1a, 1b.

Intro 5.10.21

Heat: energy in transit

$J = kg\, m^{-2} s^{-2} = Ws$

Fourier: $\frac{dQ}{dt} = -kA \frac{dT}{dx}$

heat/time   temperature gradient

$Q = C \cdot \Delta T$

heat capacity   change of temperature

$dQ = C \cdot dT$ differential.

$c = \frac{C}{m}$ specific heat capacity

$= \frac{dQ}{m\, dT}$. also molar: $\frac{1}{n} \frac{dQ}{dT}$

$n =$ total mass / molar mass

heat transfer including phase change:

$m \cdot c \cdot \Delta T + m \cdot L$

specific latent heat

$dQ = C\, dT$

$\frac{dQ}{dt} = C \frac{dT}{dt} = -hA\Delta T$ Newton

heat transfer

$\frac{d\Delta T}{dt} = -\frac{hA}{C} \Delta T$ time const. $t_0 = \frac{C}{hA}$

$\frac{d\Delta T}{\Delta T} = -\frac{1}{t_0} dt$

$\ln \Delta T = -\frac{t}{t_0} + \alpha \rightarrow \Delta T = \underbrace{e^{\alpha}}_{\Delta T(0)} \cdot e^{-t/t_0}$

$\Delta T = \Delta T(0) \cdot e^{-t/t_0}$

Exercises on
Heat Transfer

October 5, 2021

ideal gas equation

$$p\cdot V = nRT.$$

$$p = \frac{RT}{V/n} = \frac{RT}{V_m}$$

many particles, pressure due to impact of particles. neglect: volume of molecules, internal forces. elastic collisions with wall.

units

$[p] = Nm^{-2} = Pa$ [Blaise Pascal]

$[pV]: Nm$

$[n] = mol$ $\quad R = 8.314\ J\cdot K^{-1}\, mol^{-1}$

$[nRT] = mol\cdot J\cdot K^{-1}\cdot mol^{-1}\cdot K = J$

$J = Kg\, m^2 s^{-2} = N\cdot m$

Van der Waals [Nobel 1910]

- molecules have finite radius → b = co-volume

$p = \dfrac{RT}{V_m - b}$ $\quad$ Volume of sphere: $\frac{4\pi}{3} r^3 = V_s$

occupies $\frac{4\pi}{3}(2r)^3 = 8V_s$

halved through collision → $b \approx \underbrace{4 V_s}_{\text{effective}} \cdot N_A$

- extra pressure from wall exerted to adjacent particles
↳ proportional to density $\rho = \dfrac{N_A}{V_m}$ ← Avogadro # particles/mol.

# of particles in surface layers also proportional to ρ

→ $p + a'\rho^2 = p + \dfrac{a}{V_m^2}$ [square due to Laplace]

$$\left(p + \frac{a}{V_m^2}\right)\cdot(V_m - b) = RT. \qquad n\cdot V_m = V$$

[page 19, lecture 2a

$$\left(p + \frac{an^2}{V}\right)(V - nb) = nRT$$

molecular gas constant: $R = N_A \cdot k_B$

Amadeo Avogadro (1811): R the same for different ideal gases, $\neq f(m)$.
÷ Berzelius.

Exercises on
Gas Laws and
Kinetic Gas Theory

October 12, 2021

Intro 19.10.21

Heat: energy in transit

$\boxed{Q = C \cdot \Delta T}$

↑ heat capacity.

$\boxed{C = \frac{dQ}{dT}}$ specific C/m

molar C/n

$J = kg\, m^{-2} s^{-2} : Ns$

n = number of moles

$N_A = 6 \cdot 10^{23}$ particles. Avogadro

$pV = nRT$, $R = 8.3\ JK^{-1} mol^{-1}$

or $pV = N \cdot k_B T$

$k_B = \frac{R}{N_A} = 1.4 \cdot 10^{-23}\ JK^{-1}$

Boltzmann

Planck: $E = h \cdot \nu$ $[\hbar = 1.05\ 10^{-34}\ Js]$ $E = \hbar\omega$

$v^2 = \frac{3k_BT}{m} \rightarrow E_{Kin} = \frac{3}{2} k_B T$. per atom/mole.

equipartition: $\boxed{\frac{1}{2} k_B T}$ for any "quadratic" dof.

translation (3), rotation (2+0), vibration (2) : $\frac{7}{2} k T_B$

kin + pot

depends on T

1st Law of Thermodynamics: Clausius 1850

In a thermodyn. process involving a closed system, the increment in the internal energy (ΔU) is equal to the difference between the heat accumulated by the system (Q) and the work done by it (W): $\Delta U = Q - W$

Planck, IUPAC: $\boxed{\Delta U = Q + W}$ [here W work done on the system]

energy conservation. ↳ $\boxed{W = -\int_{V_\alpha}^{V_\beta} p\, dV}$

Rotation energy: classic.

$E_{rot} = \frac{1}{2} I\omega^2$, $L = I\omega$ angular momentum + velocity

↑ inertia

$E_{rot} = \frac{L^2}{2I}$ Quantum $\frac{L^2}{2I} = \boxed{\frac{1}{2I} \cdot n(n+1)\hbar^2 = E_{n,rot}}$

↑ azimuthal quantum number.

QM: $L^2\psi = \hbar^2 n(n+1)\psi$ → quantization of L, energy levels.

Exercises on First Law of Thermodynamics

October 19, 2021

$Q = C\Delta T$

$pV = nRT$ cf also V d Waals.

$k_B = \frac{R}{N_A}$

$E_{kin} = \frac{3}{2} k_B T$

$= 3 \cdot \frac{1}{2} k_B T \quad f=3$

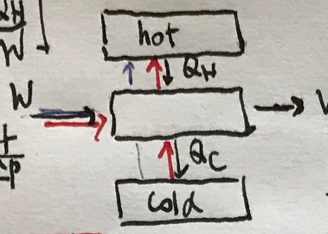
$\Delta U = Q + W$

$W = -\int_{V_\alpha}^{V_\beta} p\,dV$

1st law of T. dyn.

"η = benefit/cost"

$[\eta = \frac{Q_H}{W}]$



heat pump or refrigerator

$[\eta_R = Q_C/W]$

heat (steam) engine

$[Q_H \to W]$

$\eta = \frac{W}{Q_H} \leq 1.$

adiabatic:

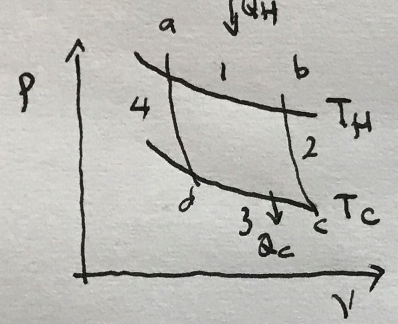
$pV^\gamma = \text{const.}$

$\gamma = C_p/C_V = f+2/f$

$pV = \alpha T \to TV^{\gamma-1} = \text{const.}$

atom: $f=3$: $\gamma = 5/3$

diatom: f=5 : $\gamma = 7/5$



Carnot cycle

[Sadi Carnot 1824.]

1. isothermal expansion (absorb Q_H, expand V)
2. adiabatic expansion (V expands: $T_H \to T_C$ no heat transfer, entropy const)
3. isothermal compression (V compressed, delivers Q_C, T_C = const)
4. adiabatic compression (V compressed and $T_C \nearrow T_H$).

1. $\Delta U = 0$: $Q_H = -W = \int_a^b p\,dV = nRT_H \ln(V_b/V_a)$
2. $T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}$
3. $Q_C = nRT_C \ln V_c/V_d$
4. $T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1}$

$\Rightarrow \boxed{\frac{Q_H}{Q_C} = \frac{T_H}{T_C}}$

maximum efficiency (of a steam engine)

$\eta_C = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H} \to 1$ for $T_C \ll T_H$.

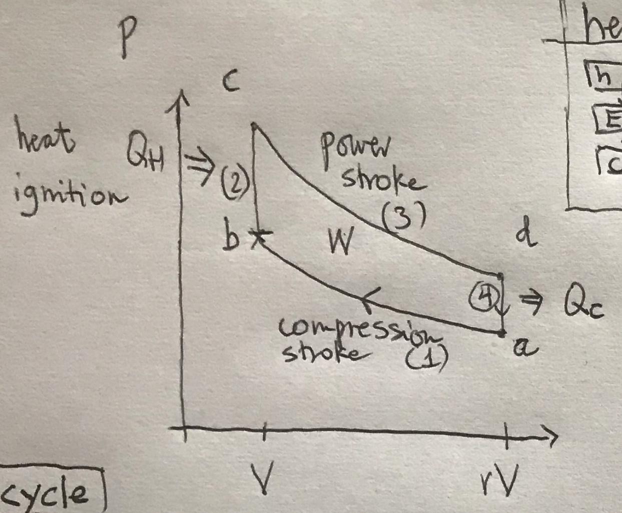
2nd law: no transfer of heat from cold to hot (Clausius)

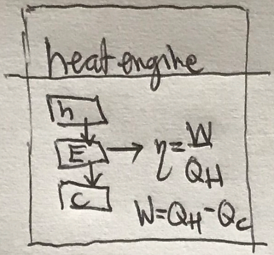
(Kelvin Planck) there is no complete conversion of heat into work

Exercises on Heat Engine and Carnot Cycle

October 26, 2021

Otto cycle





cycle

(1) piston moves up, adiabatic compression, no heat flow

↓

(2) spark plug ignites mixture ⇒ Q_H in / burning

↓

(3) fuel combusts, piston moves down → work
adiabatic expansion

↓

(4) → cooling of exhaust gases ⇒ Q_c out. / exhaust valve open
closes

piston down – subpressure – intake of fuel / valve open

Diesel: fuel ignited by heat from compression of air in combustion chamber into which fuel is then injected.

Thermodynamics

- $pV = nRT \rightarrow \left(\frac{pV}{T}\right)_a = \left(\frac{pV}{T}\right)_b \cdots$ ideal gas law.
- adiabatic process: $TV^{\gamma-1} = \text{const}$, $\gamma = c_p/c_v = \frac{f+2}{f}$. f diatom dof. = 7
  $c_p/c_v = 1.4$.
- $\eta = 1 - \frac{Q_c}{Q_H} = 1 - r^{1-\gamma}$ $\quad r = 10: \eta = 0.60.$ / friction, heat loss, turbulences ⇢ $\eta \leq 0.4$
- $Q_c = Q_H(1-\eta)$
- $W = Q_H - Q_c$

interesting history

Nicolaus August Otto (1832–1891)
Dr. hc

first motor factory ⇢ DEUTZ AG
1872

technical directors: Gottlieb Daimler
Wilhelm Maybach

4 stroke motor: Christian Reithmann 1860
Alphonse Beau de Rochas, 1862

...

1818–1909 watch maker

handed patent over to Otto...

Intro 2.11.21

Exercises on
Otto Motor + Cycle

November 2, 2021

$\boxed{\text{stress: } \sigma = \frac{F}{A} \quad [Pa, N/m^2]}$

F can be $F = m \cdot a$

[tensile or compressive] a gravitation $9.81\, ms^{-2}$

$\boxed{\text{strain [deformation]: } \varepsilon = \frac{\Delta L}{L}}$

thermal: $\boxed{\frac{\Delta L}{L} = \alpha \Delta T}$ linear expansivity

elastic - plastic - fracture

$\boxed{\text{Young modulus: } Y = \frac{\sigma}{\varepsilon}}$

high Y: large stress ↳ little deformation

Cfibre: 1000 GPa
rubber: 0.1 GPa

$\boxed{\text{Hooke law: } \sigma = \varepsilon \cdot Y = Y \cdot \frac{\Delta l}{l} \quad : F = k \cdot x}$

Robert Hooke: 1635-1702

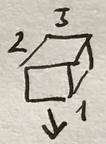
÷ Newton, London. Royal Society

strain (deformation) energy:

$U = \int F dx = \frac{1}{2} k x^2 = \frac{1}{2} F x$

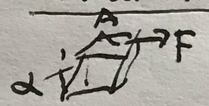
density: $\boxed{u = \frac{U}{V}} = \int \frac{F dx}{A \cdot L} = \int \sigma \, d\varepsilon = \int Y \varepsilon \, d\varepsilon$

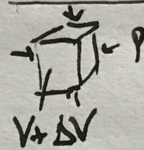
$\rightarrow \boxed{u = \frac{1}{2} Y \varepsilon^2}$

Poisson number/ratio:  $\boxed{\frac{\Delta l_{2,3}}{l_{2,3}} = -\nu \frac{\Delta l_1}{l_1}}$

rubber $\nu \simeq .5$
cork $\nu \simeq 0$
diamond $\nu = 0.21$
$0 < \nu < .5$: Volume reduces under tensile stress
enlarges compressive

$-1 < \nu \leq 0.5$

shear stress:  : $\boxed{\tau = \frac{F}{A} \quad (\text{like } \sigma) \quad \text{rigidity: } \frac{\tau}{\alpha} = G}$

hydrostatic stress:  : $\boxed{\text{bulk modulus: } B = K = -V \frac{dP}{dV}}$

$\downarrow$

relations: $G = \frac{Y}{2(1+\nu)}$, $K = \frac{Y}{3(1-2\nu)}$ $\boxed{\kappa = \frac{1}{K} = -\frac{d \ln V}{dp}}$ compressibility

Exercises on Mechanical Properties of Solids (stress, strain..)

November 9, 2021

partial differentiation.

$\boxed{z = z(x,y)}$

- $dz = \frac{\partial z}{\partial x} \cdot dx + \frac{\partial z}{\partial y} dy$
- reciprocal rule: $\left.\frac{\partial x}{\partial y}\right|_z = \frac{1}{\partial y / \partial x|_z}$.

e.g. $z = \frac{x}{\ln y}$, $x = z \cdot \ln y$, $y = e^{x/z}$

$\left.\frac{\partial x}{\partial y}\right|_z = \frac{z}{y}$. $\left.\frac{\partial y}{\partial x}\right|_z = \frac{y}{z} = 1/{z/y}$.

- cyclic: $\left.\frac{\partial y}{\partial z}\right|_x \cdot \left.\frac{\partial z}{\partial x}\right|_y \cdot \left.\frac{\partial x}{\partial y}\right|_z = -1$.

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

$$= \frac{\partial x}{\partial y}\left[\frac{\partial y}{\partial x} dx + \frac{\partial y}{\partial z} dz\right] + \frac{\partial x}{\partial z} dz$$

$$dx = dx\Bigg[\underbrace{\frac{\partial x}{\partial y} \cdot \frac{\partial y}{\partial x}}_{1}\Bigg] + \Bigg[\underbrace{\frac{\partial x}{\partial y}\frac{\partial y}{\partial z} + \frac{\partial x}{\partial z}}_{0}\Bigg] dz$$

- **chain**: $f = y(\phi(x))$: $\frac{df}{dx} = \frac{dy}{d\phi}\frac{d\phi}{dx}$

$f = \sin(x^2)$: $\frac{df}{dx} = \cos(x^2) \cdot 2x$.

- exact differential: $dz = A(x,y)dx + B(x,y)dy$

if $A = \left.\frac{\partial z}{\partial x}\right|_y$ & $B = \left.\frac{\partial z}{\partial y}\right|_x$ then $\left.\frac{\partial A}{\partial y}\right|_x = \left.\frac{\partial B}{\partial x}\right|_y$.

because $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$.

differentials in Thermodynamics – a preview.

Gibbs potential or free energy

Josiah W Gibbs (1839–1903) statistical mechanics with Boltzmann, Maxwell

$$G = \underbrace{U + pV}_{\text{enthalpy}} - T \cdot \underbrace{S}_{\text{entropy}}$$

2nd law of thermodynamics: free energy minimal

U, S, V all $\sim N$ $\Rightarrow$ $G = N \cdot \phi$.

$$dG = dU - TdS - SdT + pdV + Vdp$$

amount of free energy to do some work, eg pdV if only V changes

identity: $dU = \mu dN + TdS - pdV$ – due to first law of t.dyn.

μ chemical potential.

$$\to dG = \mu dN - SdT + Vdp$$

[also $\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_N$]

$\mu = \left.\frac{\partial G}{\partial N}\right|_{T,p}$ $S = -\left.\frac{\partial G}{\partial T}\right|_{N,p}$ $V = \left.\frac{\partial G}{\partial p}\right|_{N,T}$

$= \phi \Rightarrow G(N,p,T) = N \cdot \mu(p,T)$

[Charles Kittel: "Thermal Physics", NY Wiley & Sons (1969)]

16.11.21

Exercises on Differentiation

With a Preview on Gibbs Potential

November 16, 2021

• heat $\boxed{dQ = mC\cdot dT}$

• energy $\boxed{U=\frac{3}{2}nRT}$ (mono-atomic)

• work $\boxed{dW=-p\,dV ,\quad p=\frac{nRT}{V}}$

$$dQ = dU - dW = nR\left[\frac{3}{2}dT + \frac{T}{V}dV\right]$$

non-exact: $\frac{\partial}{\partial V}(3/2) \neq \frac{\partial}{\partial T}\left(\frac{T}{V}\right)$.

• entropy: $dS := \frac{1}{\phi}dQ$

$$dS = nR\cdot\left[\frac{3}{2\phi}dT + \frac{T}{V\phi}dV\right]$$

$\frac{\partial}{\partial V}\left(\frac{3}{2\phi}\right) := \frac{\partial}{\partial T}\left(\frac{T}{V\phi}\right)$ to determine ϕ

assume $\phi(T,V)=\phi(T)$. integrating factor ϕ^{-1}.

$$\frac{\partial}{\partial V}\left(\frac{3}{2\phi}\right) = 0 = \frac{1}{V}\left[\frac{1}{\phi} + T\frac{\partial}{\partial T}\left(\frac{1}{\phi}\right)\right]$$

$$\rightarrow \frac{1}{\phi} = -T\cdot\left(-\frac{\partial\phi/\partial T}{\phi^2}\right)$$

$$\hookrightarrow \frac{\partial T}{T} = \frac{\partial\phi}{\phi} \rightarrow \phi = T \rightarrow \boxed{dS = \frac{dQ}{T}}$$

exact differential.

body

reservoir (surrounding)

• Q res → body:

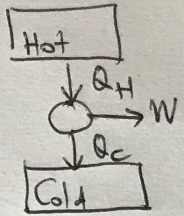
$$\Delta S = mc\int_{T_i}^{T_f}\frac{dT}{T}$$

$$\boxed{\begin{aligned}&\Delta S_b = mc\cdot\ln\left(\frac{T_f}{T_i}\right)\\ &\Delta S_r = -mc\,\Delta T/T_{res}\end{aligned}}$$

• phase transition

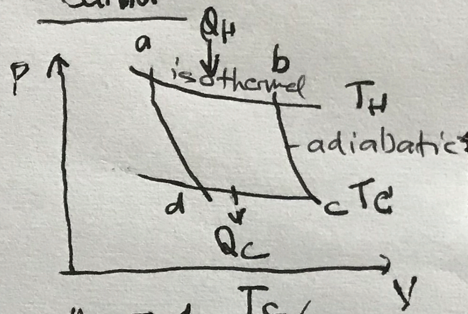
$$\boxed{\begin{aligned}&\Delta S_b = \frac{m_b L_b}{T_b}\\ &\Delta S_{res} = -\frac{m_b L_b}{T_{res}}\end{aligned}}$$

• heat engine (reverse: heatpump)



$$\eta = W/Q_c = 1 - \frac{Q_H}{Q_H}$$

• Carnot



$$\left\{\begin{aligned}&TV^{\gamma-1} = \text{const}\\ &\gamma = C_p/C_V = \frac{f+2}{f}\end{aligned}\right.$$

$$\eta_c = 1 - T_c/T_H = 1 - \frac{Q_c}{Q_H}$$

"Reminder on preview" (from last week.)

$G = U + pV - TS$ free energy, Gibbs potential

$$dG = \mu\,dN - S\,dT + V\,dp$$

[from $dG = dU + p\,dV + V\,dp - T\,dS - S\,dT$
and inserting $dU = \mu\,dN + \underbrace{T\,dS}_{dQ} \underbrace{- p\,dV}_{dW}$!
approaching Gibbs ..]

Exercises on Entropy

November 23, 2021

1st law of T.dyn:

internal energy = heat accumulated ⊕ work done on the system (Planck/Clausius).

$dU = dQ + dW.$

$dW = -\,p\,dV$

$U = \frac{3}{2} nRT \;,\; p = \frac{nRT}{V}$

$\boxed{\text{for } V = \text{const}: \; dU = dQ = C_V \cdot dT, \quad C_V = \frac{\partial U}{\partial T}\Big|_V}$

$dQ = nR\left[\frac{3}{2} dT + \frac{T}{V} dV\right]$

$dS := \frac{dQ}{\phi} \;,\; \phi = T$

$\rightarrow T\,dS = dQ$ $\boxed{C_V = T \frac{\partial S}{\partial T}\Big|_V}$

└ entropy

$\boxed{dU = T\,dS - p\,dV}$

"central equation"

$T = \frac{\partial U}{\partial S}\Big|_V \;,\; -p = \frac{\partial U}{\partial V}\Big|_S$

$\Rightarrow \boxed{\frac{\partial T}{\partial V}\Big|_S = -\frac{\partial p}{\partial S}\Big|_V}$ Maxwell 1st equ. −U−

2nd law of T.dyn

- no heat transfer from cold to hot. (Clausius)
- no complete conversion of heat into work (Planck/Kelvin)
- closed system approaching equilibrium: $dS \geq 0$: entropy rise and free energy G min.

$\boxed{\begin{array}{ll} G = U + pV - TS & \text{Gibbs} \\ H = U + pV & \text{enthalpy} \\ F = U - TS & \text{Helmholtz} \end{array}}$

$dH = dU + p\,dV + V\,dp$: enthalpy

$= T\,dS - p\,dV + p\,dV + V\,dp$

$dH = T\,dS + V\,dp$

$\boxed{\text{for } p = \text{const}: \; dH = dQ = T\,dS = C_p \cdot dT \;\; \hookrightarrow C_p = \frac{\partial H}{\partial T}\Big|_p = T\frac{\partial S}{\partial T}\Big|_p}$

$T = \frac{\partial H}{\partial S}\Big|_p \quad V = \frac{\partial H}{\partial p}\Big|_S$

$\Rightarrow \boxed{\frac{\partial T}{\partial p}\Big|_S = \frac{\partial V}{\partial S}\Big|_p}$ Maxwell 2nd eq. −H−

Helmholtz and Gibbs

$dF = \underbrace{dU - T\,dS}_{-p\,dV} - S\,dT$ · Helmholtz

$\Rightarrow \boxed{\frac{\partial p}{\partial T}\Big|_V = \frac{\partial S}{\partial V}\Big|_T}$ Maxwell 3rd eq. −F−

$dG = dH - T\,dS - S\,dT$

$dG = V\,dp - S\,dT \; [+ \mu\, dN]$

$V = \frac{\partial G}{\partial p}\Big|_{T,N} \;,\; S = -\frac{\partial G}{\partial T}\Big|_{N,p} \;,\; \left[\mu = \frac{\partial G}{\partial N}\Big|_{T,p} \quad G = N \cdot \mu\right]$

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

Maxwell 4th eq. −G−

partition function [cf Finn T.dyn]

$Z = \sum g_i\, e^{-E_i/kT} \;,\; F = -RT \ln Z$

two levels: $Z = 1 + e^{-\varepsilon/kT}$, $R = Nk$

$\rightarrow F = -NkT \ln(1 + e^{-\varepsilon/kT})$

$S = -\frac{\partial F}{\partial T}\Big|_V = Nk\left[\ln(1 + e^{-\varepsilon/kT}) + \frac{\varepsilon}{kT}\,\frac{1}{1 + e^{\varepsilon/kT}}\right]$

$T \rightarrow 0: \; S = 0$

$kT \gg \varepsilon: \; S \rightarrow Nk \ln 2 = R \ln 2.$

Exercises on Maxwell Equations

November 30, 2021

Intro 30.11.21

- 1st law of T.dyn.

$dU = dQ - pdV$

$\boxed{dU = TdS - pdV}$ $\quad [dS = \frac{dQ}{T}]$

- 2nd law of Tdyn.

$G = U + pV - TS$

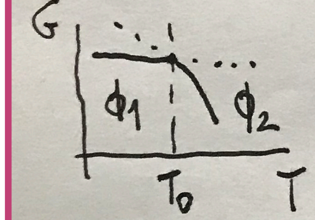
$dG = TdS - pdV + pdV + Vdp - TdS - SdT$

$\boxed{dG = Vdp - SdT}$

Paul (1880-1933)

- Ehrenfest: 1st order phase transition

eg. $p = \text{const}$



$\left.\frac{\partial G}{\partial T}\right|_p = -S$

discontinuous at $\phi_1 \to \phi_2$.

$G_1 = G_2$ at T_0.

- Émile Clapeyron (1799–1864)

$dG_1 = dG_2 |_{T_0}$

$\Rightarrow \boxed{\frac{dp}{dT} = \frac{S_2 - S_1}{V_2 - V_1}}$ 1834

$\Delta S = \frac{\Delta Q}{T} = \frac{L}{T}$ phase trans.

$\boxed{\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}}$

Claudius-Clapeyron

vaporisation $V_2 \gg V_1$

$\frac{dp}{dT} = \frac{L}{TV} = \frac{l}{Tv}$ specific L, specific V

Units

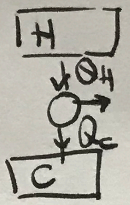
$J = Nm$

$Pa = \frac{N}{m^2}$

$1\,atm = 1.01 \cdot 10^5\,Pa = 1.01\,bar$

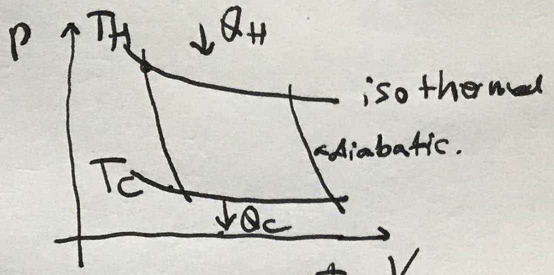
$\Rightarrow$ problem 1.

- Heat Engine



$\eta = \frac{W}{Q_c} = 1 - \frac{Q_c}{Q_H}$

. Carnot



$\eta_{carnot} = 1 - T_c / T_H$

$\rightarrow \boxed{\frac{T_c}{T_H} = \frac{Q_c}{Q_H}}$

→ problem 2: sequential (composite) heat engine.

heat transfer (ΔS) negative for away direction!

Exercises on
Claudius-Clapeyron-Eqn.
and on
Combined Heat Engine

December 7, 2021

Intro 7.12.21