1st Law $du = dq - dw$

2nd Law $\Delta S_u \geq 0$

Stability (closed) $dq \leq Tds$ { Helmholtz / Gibbs.

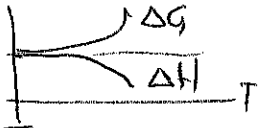
" (open) $U = U(S, V, N)$

| $T_1$ $P_1$ $V_1$ $U_1$ $N_1$ |
|---|
| $T_2$ $P_2$ $V_2$ $U_2$ $N_3$ |

$ds = 0$

thermal $T_1 = T_2$ chem $\mu_1 = \mu_2$ mech $P_1 = P_2$

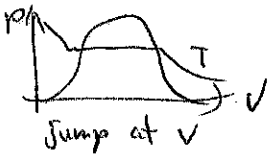
3rd Law At absolute zero, isothermal & isobaric $T < \varepsilon$ $\varepsilon \ll 1$

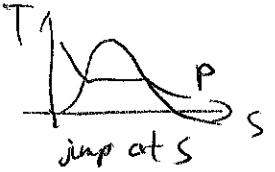



$G = H - TS$

Equilibrium state of sys at absolute zero has zero entropy so as heat capacity.

phase transition (below Cp) $P, T$ = constant $dq = dh$ $T\Delta S = L$ (measurable)



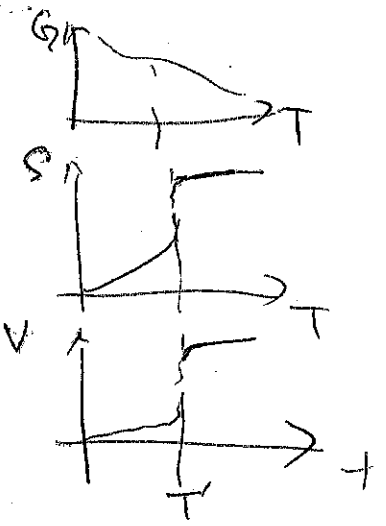




$dg = -sdT + vdp$

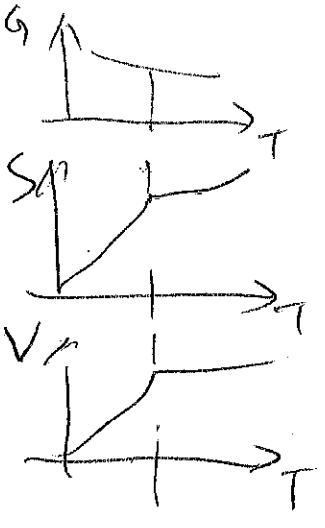
(1st) $\left(\frac{\partial g}{\partial T}\right)_p = -s$ $\left(\frac{\partial g}{\partial p}\right)_T = V$ (2nd) $\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\left(\frac{\partial S}{\partial T}\right)_p = -\frac{C_p}{T}$

(above Cp)


continuous chang in V(S)

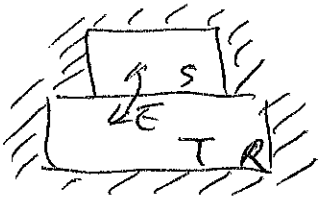



cont' for derivative of S, V at 1st order




jump for derivative of S, V at 2nd order.

## Canonical Ensemble



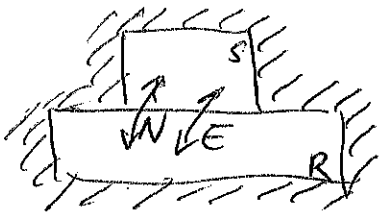

$$P_s = \frac{e^{-E_s/kT}}{Z} \qquad Z = \sum_s e^{-E_s/kT}$$

$$\langle E \rangle = \sum_s E_s e^{-E_s/kT}/Z = -\frac{\partial}{\partial \beta} \ln Z \qquad \beta = \frac{1}{kT}$$

$$C_v = \frac{\partial \langle E \rangle}{\partial T}$$

$$F = -kT \ln Z$$

## Grand Canonical Ensemble




V fixed
Equilibrium at $T$ & $\mu$

$$P_s = \frac{e^{-\beta(E_s - \mu N_s)}}{Z_G} \qquad Z_G = \sum_s e^{-\beta(E_s - \mu N_s)}$$

Landau Potential $\Omega_L = F - \mu N$

$$\Omega_L = -kT \ln Z_G$$

$\Omega(E)$ # of microstate w/ energy $E$

$\Gamma(E)$ # of microstate w/ energy $\leq E$

$g(E)\Delta E$ # of microstate between $E$ & $E + \Delta E$

$g(E)$ Density of states

| | Fixed Microstate | Prob dist | Thermal Properties |
|---|---|---|---|
| Microcanonical | $E, V, N$ | $P_s = \frac{1}{\Omega}$ | $S = -k \ln \Omega$ |
| Canonical | $T, V, N$ | $P_s = e^{-\beta E}/Z$ | $F = -kT \ln Z$ |
| Grand Canonical | $T, V, \mu$ | $P_s = e^{-\beta(E_s - \mu N_s)}/Z_G$ | $\Omega_L = -kT \ln Z_G$ |

**1st Law** $Q_{in} \xrightarrow{\geq 0} (sys) \rightarrow W_{out} \geq 0$

Temp change $dU = dQ - dW$

$U = U(T,V)$ $U = U(S,V)$

Phase trans. $H = U + PV$

Process well describe using ideal gas model $U = U(T)$ under Joule's exp


Induced properties (Heat Cap)

temp raise: $C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{dS}{dT}\right)_V$

phase trans: $C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial h}{\partial T}\right)_P = T\left(\frac{dS}{dT}\right)_P$

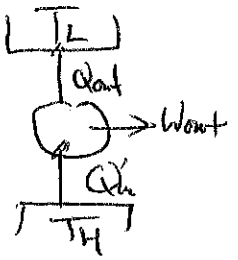
Equipartition thm. $K_{tot} = \frac{f}{2}NK_BT = \frac{f}{2}nRT$ ex - diatomic - solid

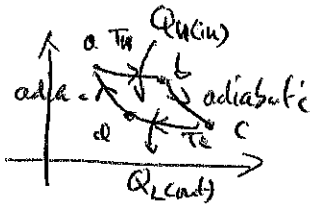
Isothermal process $PV = const$

adiabatic process $TV^{\gamma-1} = const$ or $PV^{\gamma} = const$ ideal gas.

$W_{adiabatic} = -C_V\Delta T = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$

Work efficiency Ideal Carnot cycle




$\eta = \frac{W_{out}}{Q_{in}} = 1 - \frac{T_L}{T_H}$

from which we have $\eta_{actual} \leq \eta_{carnot} \Rightarrow \oint \frac{dQ}{T} = 0 \Rightarrow \oint \frac{dQ}{T} \leq 0$

**2nd Law** $\Delta S_u \geq 0$ entropy of universe can only be non-negative definite

available energy. (free E) $W_{lost} = T\Delta S$ (universe, low temp)

$\frac{T_H}{T_L}$ (Q) $\Delta S_u = \Delta S_H + \Delta S_L = -\frac{Q}{T_H} + \frac{Q}{T_L}$

$W_{lost} = T_L\Delta S_u$

---

Maxwell Relation $U = TS - PV$

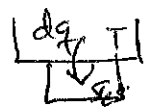
$H = U + PV$

$F = U - TS$

$G = U - TS + PV$

## Stability & Equilibrium (Closed Sys)

Helmholtz $F(T,V)$ free energy relation to available work under thermal contact $T$.




$dq \leq TdS$

$dW \leq -dF$ max. free energy available for work

at equilibrium $T, V = \text{const}$, $0 \leq -dF$

Thus $F_{min}$ at equilibrium but maximize for available work as $F$ decreases.

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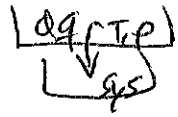
Gibbs $G(T,P)$ free energy relation to spontaneous reaction (ie chem. change & phase trans.) under const $T, P$.




$dq \leq TdS$

$dG \leq 0$

spontaneous reaction occurs as $G$ decreases

---

Stability at equilibrium.

1st Law $dS = \frac{1}{T}dU + \frac{P}{T}dV = S_U dU + S_V dV$

need $S_{UU} < 0 \Rightarrow C_V = \left(\frac{dQ}{dT}\right)_V > 0$ thermal stability

$S_{UU}S_{VV} - S_{UV}^2 > 0 \Rightarrow K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T > 0$ mech. stab.

---

(Open Sys) allow matter exchanges in sys $\rightarrow \boxed{\mu dN}$

realization $U = U(S, V, N)$

$dU = TdS - PdV + \mu dN$ $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$ chemical potential

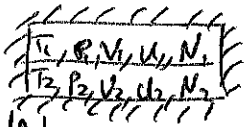
Apply Euler's thm $\lambda U = U(\lambda S, \lambda V, \lambda N)$

then $U = TS - PV + \mu N$

$G = \mu N$ (Gibbs' physical def.)

$dG = \mu dN$

Now equilibrium for two contacting system




1st law $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$

$dS = 0 \Rightarrow$ thermal $T_1 = T_2$ $\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2}$

chemical $\mu_1 = \mu_2$ $-T_1\frac{\partial S_1}{\partial N_1} = -T_2\frac{\partial S_2}{\partial N_2}$

Mech. $P_1 = P_2$ $T_1\frac{\partial S_1}{\partial V_1} = T_2\frac{\partial S_2}{\partial V_2}$

Note Conserved quantities mass, vol. energy.