The fundamental thermodynamic relation

First Law ; $dE = \delta Q + \delta W$

$$\delta W = p\,dV$$
$$\delta Q = T\,dS \qquad \text{(quasistatic reversible process)}$$

$$dE = T\,dS - p\,dV \qquad = \text{"heat + work"}$$

if particle number can change: μ: energy change per particle

$$\boxed{dE = T\,dS - p\,dV + \mu\,dN} \implies E(S,V,N) \qquad T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \quad \mu = \left(\frac{\partial E}{\partial N}\right) \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$$

$$\boxed{dS = \frac{1}{T}\,dE + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN} \implies S(E,V,N)$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}, \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

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example: ideal gas

$E = \frac{3}{2}NkT \qquad PV = NkT$ assume fixed N

$$\frac{1}{T} = \frac{3Nk}{2E} \qquad \frac{P}{T} = \frac{Nk}{V}$$

$$dS = \frac{3Nk}{2}\frac{dE}{E} + Nk\frac{dV}{V}$$

$$S(E,V) = \frac{3}{2}Nk\ln\frac{E}{E_0} + Nk\ln\frac{V}{V_0}$$

E_0, V_0 arbitrary constants

often needed: $S(T,V) = \frac{3}{2}Nk\ln\frac{T}{T_0} + Nk\ln\frac{V}{V_0}$

$$\boxed{\Delta S(1\to 2) = \frac{3}{2}Nk\ln\left(\frac{T_2}{T_1}\right) + Nk\ln\left(\frac{V_2}{V_1}\right)}$$

Gibbs-Duhem relation

$S = S(E,V,N)$ maximum at fixed E,V,N

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$ thermo pot.

$$\boxed{dE = T\,dS - P\,dV + \mu\,dN}$$ (I. Law)

$E = E(S,V,N)$ extensive state function

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

extensivity: $E(\lambda S, \lambda V, \lambda N) = \lambda E(S,V,N)$, $\forall \lambda$ (hom. function of the first order)

differentiate with respect to λ:

$$\frac{\partial E}{\partial(\lambda S)} \cdot \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial E}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial E}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = E(S,V,N)$$

$$\frac{\partial E}{\partial(\lambda S)} S + \frac{\partial E}{\partial(\lambda V)} V + \frac{\partial E}{\partial(\lambda N)} N = E(S,V,N)$$

then set $\lambda = 1$

$$\boxed{E(S,V,N) = TS - PV + \mu N}$$

$$dE = T\,dS + S\,dT - p\,dV - V\,dp + \mu\,dN + N\,d\mu$$

compare with first law: $\Rightarrow$ $$\boxed{S\,dT - V\,dp + N\,d\mu = 0}$$ Gibbs-Duhem relation

The Third Law of Thermodynamics

$$\boxed{\lim_{T\to 0} S = 0}$$ (with exceptions) Consequences:

quasistatic changes: $\frac{\delta Q}{T} = dS$

at constant volume: $\delta Q = C_V(T)\,dT$

$$\int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{\delta Q}{T} = \int_{T_1}^{T_2} \frac{C_V(T)}{T}\,dT$$

$$S(T_2,V) - S(T_1,V) = \int_{T_1}^{T_2} \frac{C_V(T)}{T}\,dT$$

$$S(T_2,V) = \lim_{T_1\to 0} \int_{T_1}^{T_2} \frac{C_V(T)}{T}\,dT \quad \Rightarrow \quad \lim_{T\to 0} C_V(T) = 0$$

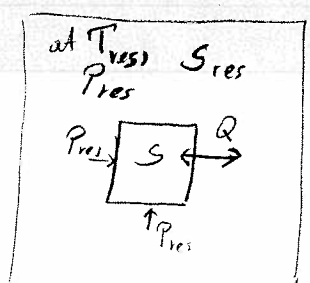
since $S(T_2,V)$ must be finite

similarly, one can repeat the same for constant P

$$\lim_{T\to 0} C_P(T) = 0$$

Generalized Thermodynamical Potentials

(equilibrium with constraints)



$$S_{composite} = S + S_{res}$$

$$\Delta S_{comp} = \Delta S + \Delta S_{res} \geq 0$$

system of our interest

$S_{comp} = \max.$ in equilibrium

find a (property) function of the system alone which is characterized by max. or min.

(S is max. for an isolated unconstrained system – II. Law)

$$\Delta S_{res} = -\frac{Q}{T_{res}}$$ Q transferred from reservoir to system

$$\Delta S_{composite} = \Delta S - \frac{Q}{T_{res}}$$

$$\Delta E = Q + W = Q - P_{res}\Delta V$$ if W due to work by res.

$$\Delta S_{comp} = \Delta S - \frac{Q}{T_{res}} = \Delta S - \frac{\Delta E + P_{res}\Delta V}{T_{res}} \geq 0$$ (II. Law)

$$\boxed{\Delta E + P_{res}\Delta V - T_{res}\Delta S \leq 0}$$

(I.) $T = T_{res}$, $\Delta V = 0$ (V fixed) (N = fixed) $\Rightarrow$ $\boxed{\Delta E - T\Delta S \leq 0}$

$$\boxed{F = E - TS}$$ Helmholtz free energy

minimized at constant T, V, N

$$dF = dE - TdS - SdT$$
$$= TdS - pdV + \mu dN - TdS - SdT =$$
$$= -SdT - pdV + \mu dN$$

$F(T, V, N)$ (T, V, N are the natural variables of F)

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

(II.) Gibbs free energy $T = T_{res}$ $P = P_{res}$

$$\Delta E + P\Delta V - T\Delta S \leq 0$$

$G = E + PV - TS$ minimum at fixed T, P, N

$$dG = TdS - \cancel{pdV} + \mu dN + \cancel{pdV} + Vdp - \cancel{TdS} - SdT =$$
$$= -SdT + Vdp + \mu dN$$ $G(T, P, N)$

Legendre Transformation

$E(S,V,N)$ $\qquad T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

$$F = E - S\left(\frac{\partial E}{\partial S}\right)_{V,N} = E - TS$$

F is the Legendre tr. of E

$$dF = dE - T\,dS - S\,dT =$$

$$= \cancel{T\,dS} - P\,dV + \mu\,dN - \cancel{T\,dS} - S\,dT = -S\,dT - P\,dV + \mu\,dN$$

$F(T,V,N)$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

Legendre tr replaced the extensive variable S by its intensive conjugate thermodyn. variable T

$$E(S,V,N) \xrightarrow[F = E - S\left(\frac{\partial E}{\partial S}\right)_{V,N}]{\mathcal{L}.\ tr.} F(T,V,N)$$

T, P intensive
N extensive $\Big\} \Downarrow$

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \qquad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \qquad \left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu$$

$$G(T,P,N) = N \cdot g(T,P)$$

$$\left.\begin{aligned}\left(\frac{\partial G}{\partial N}\right)_{T,P} &= \mu = g(T,P)\\ G &= \mu N\end{aligned}\right\}$$ Gibbs free energy per particle

μ: chemical potential

$$dg = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP = -s\,dT + v\,dP$$

where $s = \frac{S}{N}$ $\quad v = \frac{V}{N}$

$$\boxed{dg = -s\,dT + v\,dP}$$

Mathematical Note:

$$E = E(S,V,N) \qquad \text{extensive variables}$$

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S,V,N)$$ homogeneous function of the first order

differentiate with respect to λ

$$\frac{\partial E}{\partial(\lambda S)} S + \frac{\partial E}{\partial(\lambda V)} V + \frac{\partial E}{\partial(\lambda N)} N = E$$

$$\lambda = 1: \quad \boxed{TS - PV + \mu N = E} \Rightarrow \text{Gibbs-Duham:}$$

$$S\,dT - V\,dP + N\,d\mu = 0$$

$$G = E + PV - TS = (TS - PV + \mu N) + PV - TS = \mu N$$

$$G(T,P,N) = \mu(T,P) \cdot N$$

$$g(T,P) = \frac{G(T,P,N)}{N} = \mu(T,P)$$

similarly: $F = E - TS = -PV + \mu N$

III Landau or Grand thermodynamic potential

Use notation $\Phi(T,V,\mu)$

$$\Phi(T,V,\mu) = F - \mu N \qquad = \text{min. at fixed } T, V, \mu$$

$$d\Phi = dF - \mu dN - N d\mu =$$
$$= -SdT - PdV + \mu dN - \mu dN - N d\mu =$$
$$= -SdT - PdV - N d\mu$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} \qquad P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} \qquad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

using Gibbs-Duhem:

$$\Phi(T,V,\mu) = F - \mu N = \boxed{E - TS - \mu N} = \underbrace{(TS - PV + \mu N) - TS - \mu N}_{= -PV}$$

$\Phi(T,V,\mu) = -PV$ useful to obtain equation of state

Thermodynamic Response Functions

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V$$

$$H = E + PV$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{isothermal compressibility}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{thermal expansion coefficients}$$

Are they independent?

Maxwell Relations and Applications

$E(S, V, N)$ $\qquad dE = T\,dS - P\,dV + \mu\,dN$

assume $N =$ constant $\qquad \boxed{dE = T\,dS - P\,dV}$

$$T = \left(\frac{\partial E}{\partial S}\right)_V \qquad P = -\left(\frac{\partial E}{\partial V}\right)_S$$

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V} - \left(\frac{\partial P}{\partial S}\right)_V$$

example 1. $\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$

$$dF = -S\,dT - P\,dV$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial V \partial T} = -\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial P}{\partial T}\right)_V$$

example 2. $\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$ $\qquad$ *

other examples: $dG = -S\,dT + V\,dP \implies \boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$

$dH = T\,dS + V\,dP \implies \boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$

Application: Relationship between c_p, c_v, K_T, and α

$$C_p = C_v + \left(\frac{\partial V}{\partial T}\right)_p \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] \qquad \text{(from earlier)}$$

$$dE = TdS - p\,dV \qquad \text{(fix } N\text{)}$$

$$\Downarrow$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T + P$$

$$C_p = C_v + \left(\frac{\partial V}{\partial T}\right)_p \cdot T\left(\frac{\partial S}{\partial V}\right)_T$$

using (*) (Maxwell relation, example 2)

$$C_p = C_v + \left(\frac{\partial V}{\partial T}\right)_p T\left(\frac{\partial P}{\partial T}\right)_V$$

use identity: $\left(\frac{\partial V}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial P}\right)_V \cdot \left(\frac{\partial P}{\partial V}\right)_T = -1$ (follows from the existence of eq. o. st $P = P(V,T)$)

$$C_p = C_v - T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p^2$$

similarly: $C_p = C_v - T\left(\frac{\partial P}{\partial T}\right)_V^2 \left(\frac{\partial V}{\partial P}\right)_T$

using definitions:

$$\boxed{C_p = C_v + VT\frac{\alpha^2}{K_T}}$$

$$K_T > 0$$

$$\boxed{C_p > C_v}$$

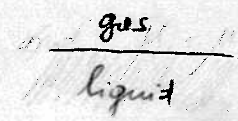
Thermodynamic Processes

- Joule (free expansion) process $\quad \delta Q = 0, \ \delta W = 0 \Rightarrow dE = 0$

- Joule-Thomson process $\quad dH = 0$

Equilibrium between Phases (Phase Coexistence)

in equilibrium: $T_1 = T_2$, $P_1 = P_2$



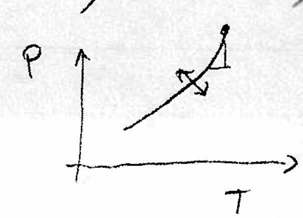
$G(T,P,N)$ $\quad g = \frac{G}{N} = g(T,P)$ $\quad G = Ng$

$G = N_1 g_1 + N_2 g_2$ $\quad N = N_1 + N_2 = \text{const}$ $\quad dN_2 = -dN_1$

$dG = g_1 dN_1 + g_2 dN_2 = (g_1 - g_2) dN_1 = 0$ at equilibrium

$\Rightarrow g_1(T,P) = g_2(T,P)$, i.e. $\mu_1(T,P) = \mu_2(T,P)$

The Clausius - Clapeyron equation



along the coexistence curve: $\Delta g_1 = \Delta g_2$

$-s_1 \Delta T + v_1 \Delta P = -s_2 \Delta T + v_2 \Delta P$ $\quad$ where $s = S/N$, $v = V/N$

C-C: $\boxed{\frac{\Delta P}{\Delta T} = \frac{s_2 - s_1}{v_2 - v_1}}$

at the first order transition (coexistence line:)

$s_2 - s_1 = \frac{Q_{latent}}{NT} = \frac{q_{latent}}{T}$

e.g. $v_2 - v_1 = v_{gas} - v_{fluid} \approx v_{gas}$ $\quad$ e.g. in vapor phase $\quad PV \approx NkT \quad P v_{gas} = kT$

$v_{gas} \approx \frac{kT}{P_{gas}}$

$\frac{dP}{dT} \approx \frac{q_{latent}}{T \frac{kT}{P}} \Rightarrow \frac{dP}{P} = \frac{q_{latent}}{k} \frac{dT}{T^2} \Rightarrow \ln P = -\frac{q_l}{kT} + \text{co}$

$\boxed{P(T) = C e^{-\frac{q_l}{kT}}}$