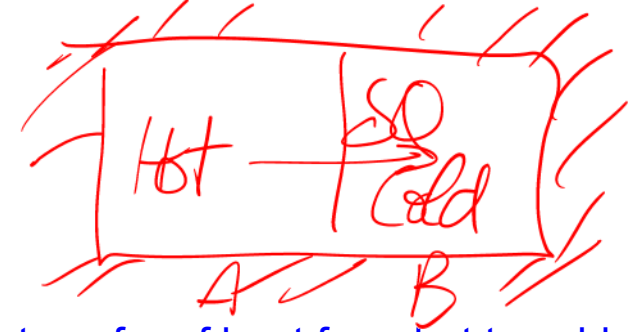


Chapter 1.2: Thermodynamic Potentials



Observation: Systems strive to reach equilibrium by spontaneous transfer of heat from hot to cold.

Therefore $dS = \delta Q(1/T_{\text{cold}} - 1/T_{\text{hot}}) \geq 0$ if $dE = 0$ and $dV = 0$.

The entropy strives to become as large as possible in equilibrium for a given E and V .

Maximization principle

If volume and energy changes are allowed, we have instead

for reversible processes $dE = \delta Q + \delta W = T dS - p dV$ and therefore $dS = dE/T + p dV/T$

$E(S, V)$

$S(E, V)$

for general processes $dS \geq dE/T + p dV/T$

and therefore $dE \leq T dS - p dV$

S increases until equilibrium

then $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$ $\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_E$

E is minimum in equilibrium

then for S, V $T = \left(\frac{\partial E}{\partial S}\right)_V$ $-p = \left(\frac{\partial E}{\partial V}\right)_S$

1.2-2 Potentials

For reversible processes

$$dE = T dS - p dV$$

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

$$dS = dE/T + p dV/T$$

Question: what "potentials" can be used to calculate S, V, \dots at given T, p, \dots

Other variables and potentials

here: interesting for A as a thermodynamic potential

Def. 1.5:

From a given function $A(x,y)$ with exact differential $dA = a(x,y) dx + b(x,y) dy$ a Legendre transformation can be applied to define a new function

$$A = \int dA$$

$$B = A - a x$$

$$\left(\frac{\partial A}{\partial x}\right)_y = a$$

$$\left(\frac{\partial A}{\partial y}\right)_x = b$$

extreme at given a, b

The transformed function $B(a,y)$ has an exact differential $\underline{dB = dA - da x - x da = -x da + b dy}$

$$B(a,y) = \int dB$$

$$\left(\frac{\partial B}{\partial a}\right) = -x$$

$$\left(\frac{\partial B}{\partial y}\right) = b$$

new thermodynamic potential which is extremum at given

Reminder: in classical mechanics Lagrangian $L(q, \dot{q}, t)$ a and y

Hamiltonian $H(p,q) = qp - L(q, \dot{q})$

$$\dot{p} = -\frac{\partial H}{\partial q} \quad \dot{q} = \frac{\partial H}{\partial p}$$

1.2-4 Potentials

Example: Legendre transformation of $E(S, V)$ with $dE = T dS - p dV$

Gives free energy $F = E - TS$ where $dF = -S dT - p dV$

$$F(T, V)$$

$$dF = dE - d(TS) = dE - SdT - TdS = -SdT - p dV$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_V \quad -p = \left(\frac{\partial F}{\partial V}\right)_T \quad (*)$$

$E(S, V)$ is min

so for non equilibrium $dE < TdS - pdV$

$$dF = dE - SdT - TdS < \overbrace{TdS - pdV} - SdT - TdS$$

$dF < -SdT - pdV$ striving to equilibrium

in equilibrium

$F(T, V)$ is min. and (*)

1.2-5 Potentials

Def. 1.6:
Thermodynamic potentials

in equilibrium

- a.) Entropie $S(E, V)$ with $dS = dE/T + p dV/T$ ✓ *max*
- b.) Energy $E(S, V)$ with $dE = T dS - p dV$ ✓ *min*
- c.) Free energy $F(T, V) = E - TS$ with $dF = -S dT - p dV$ *min*
- d.) Enthalpy $H(S, p) = E + pV$ with $dH = T dS + V dp$ *min*
- e.) Gibbs free energy $G(T, p) = E - TS + pV$ with $dG = -S dT + V dp$ *min*

$$\rightarrow -S = \left(\frac{\partial G}{\partial T} \right)_p$$

$$V = \left(\frac{\partial G}{\partial p} \right)_T$$

*What about other variables B (fields)
N*

Other thermodynamic variables

In general the energy of a system may depend on a much larger set of parameters α

$$E(S, V, N, B, \alpha, \dots)$$

$$dE = TdS - pdV - F_2 d\alpha + \mu dN$$

Def. 1.7:

If the energy depends on a parameter α , the corresponding derivative is called a generalized force

$$F_\alpha = - \left(\frac{\partial E}{\partial \alpha} \right)_{S, rest}$$

e.g. $M = - \left(\frac{\partial E}{\partial B} \right)_{S, V}$
total Magnetization

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S, rest}$$

The derivative in respect to particle number is called chemical potential

$$dF = dE - TdS - SdT = -SdT - pdV - F_2 d\alpha + \mu dN \dots$$

$$-p = \left(\frac{\partial F}{\partial V} \right)_{T, \alpha, N}$$

$$F_2 = - \left(\frac{\partial F}{\partial \alpha} \right)_{T, V, N}$$

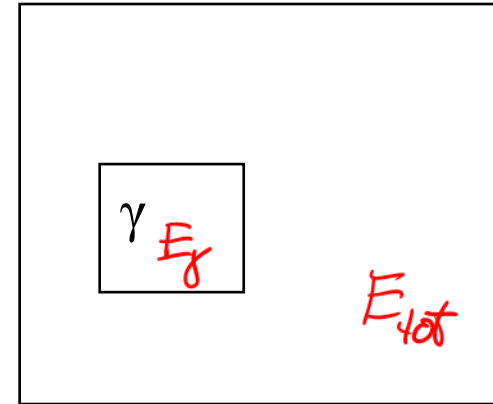
Special case: homogeneous Systems

Extensive variables are proportional to the system size:

$$E, V, S, F, G, H, \dots$$

Intensive variables are independent of the system size:

$$p, T, \dots$$



Consider a fraction γ of a homogeneous system in equilibrium

$$E_\gamma = \gamma E_{tot} \quad V_\gamma = \gamma V_{tot} \quad S_\gamma = \gamma S_{tot}$$

$S_{tot} = S(\underline{E}_{tot}, \underline{V}_{tot}, \underline{N}_{tot})$ is a well defined function

$$S_\gamma = \gamma S_{tot} = S(E_\gamma, V_\gamma, N_\gamma) \stackrel{\text{homogeneous}}{=} S(\gamma E_{tot}, \gamma V_{tot}, \gamma N_{tot}) \quad \left. \frac{\partial}{\partial \gamma} \right|_{\gamma=1}$$

$$\begin{aligned} \left. \frac{\partial S_{tot}}{\partial E_{tot}} \right|_{\gamma=1} &= \frac{E_{tot}}{T} \\ S_{tot} &= \left(\frac{\partial S}{\partial E_{tot}} \right) E_{tot} + \left(\frac{\partial S}{\partial V_{tot}} \right) V_{tot} + \left(\frac{\partial S}{\partial N_{tot}} \right) N_{tot} \\ &= \frac{E_{tot}}{T} + \frac{p}{T} V_{tot} - \frac{\mu}{T} N_{tot} \end{aligned}$$

$$S = \frac{E}{T} + \frac{p}{T} V - \frac{\mu}{T} N$$

Def. 1.8:

For homogeneous systems the Gibbs Duhem relation states that

$$\underline{E = TS - pV + \mu N}$$

$$F = E - TS = -pV + \mu N$$

$$G = E - TS + pV = \mu N \quad \rightarrow \quad \mu = \frac{G}{N}$$

in differential form

$$dE = TdS + \underline{SdT} - pdV - \underline{Vdp} + \mu dN + \underline{Nd\mu}$$

$$\stackrel{!}{=} TdS - pdV + \mu dN$$

$$\Rightarrow 0 = SdT - Vdp + Nd\mu$$