

Chapter 13 Natural Constraints

There are 3 types of constraints on the equations we have met:

- 2nd Law ($\Delta S \geq 0$)
- 3rd Law ($S \Rightarrow$ finite value as $T \rightarrow 0$)
- # independent variables = 3
 \therefore there must be interrelations between ^{the many} variables

These arise from the formulation, as opposed to the physical relations we saw in chapter 12

A. Second Law Constraints

We saw in Chapter 11 that $\Delta S \geq 0$ implies:

- heat flows from hot to cold
- volume is gained by the system having the greater pressure
- Particles flow toward the system with lower chemical potential.

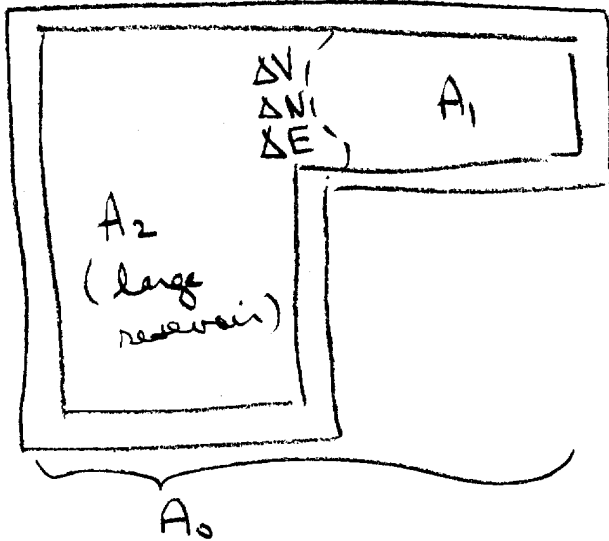
Let's recap & extend what we did in chapter 11

We had the 1st Law:

$$\Delta E = T \Delta S - P \Delta V + \mu \Delta N$$

$$\Rightarrow \Delta S = \frac{1}{T} \Delta E + \frac{P}{T} \Delta V - \frac{\mu}{T} \Delta N$$

For the system:



Closed System

$$\Delta E_2 = -\Delta E_1$$

$$\Delta V_2 = -\Delta V_1$$

$$\Delta N_2 = -\Delta N_1$$

$$\therefore \Delta S_0 = \Delta S_1 + \Delta S_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Delta E_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \Delta N_1$$

$= 0$ at equilibrium

$$\Rightarrow \left. \begin{array}{l} T_1 = T_2 \\ P_1 = P_2 \\ \mu_1 = \mu_2 \end{array} \right\} \text{at equilibrium}$$

> 0 in approach
to $\equiv 0$

We also saw $\Delta S_0 > 0$ as we approached Ξ^m

Using $\Delta E_1 = \Delta Q_1 - P_1 \Delta V_1 + \mu_1 \Delta N_1$,

and substit into ①:

$$\Delta S_0 = \underbrace{\left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Delta Q_1}_{> 0} + \underbrace{\frac{1}{T_2} (P_1 - P_2) \Delta V_1}_{\substack{\text{if } \Delta V_1 > 0 \\ \text{then } P_1 > P_2, \\ \text{ie expansion}}} - \underbrace{\frac{1}{T_2} (\mu_1 - \mu_2) \Delta N_1}_{\substack{\text{if } \Delta N_1 > 0 \\ \text{then } \mu_2 > \mu_1, \\ \text{ie things} \\ \text{go downhill}}}$$

if $\Delta Q_1 < 0$ then $T_1 > T_2$, ie hot \rightarrow cold.

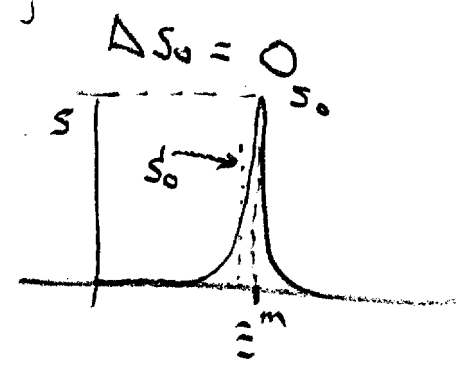
What else can we deduce?

Consider: if system is at Ξ^m , S_0 is a maximum

So if we perturb the system away from Ξ^m , $S_0 \downarrow$

ie $S'_0 - S_0 < 0$
 ↑ perturbed state ↙ Ξ^m state

or $\Delta S_0 < 0$



- If the reservoir, A_2 , is very large, then its $P, \mu + T$ won't change when we perturb the system.

- A_1 , however, is small & will change

$$\begin{aligned} T_1 &\rightarrow T_1 + \Delta T_1 & \bar{T}_1 &= T_1 + \frac{1}{2} \Delta T_1 \\ P_1 &\rightarrow P_1 + \Delta P_1 & \bar{P}_1 &= P_1 + \frac{1}{2} \Delta P_1 \\ \mu_1 &\rightarrow \mu_1 + \Delta \mu_1 & \bar{\mu}_1 &= \mu_1 + \frac{1}{2} \Delta \mu_1 \end{aligned} \Rightarrow$$

↑
average values during the perturbation

So the ΔS_0 for the perturbation away from \equiv^m

is

$$\Delta S_0 = \Delta S_1 + \Delta S_2 < 0$$

$$= \frac{1}{\bar{T}_1} (\Delta E_1 + \bar{P}_1 \Delta V_1 - \bar{\mu}_1 \Delta N_1) + \frac{1}{T_2} (\Delta E_2 + P_2 \Delta V_2 - \mu_2 \Delta N_2)$$

$\frac{1}{T_1(1 + \frac{\Delta T_1}{2T_1})} \approx \frac{1}{T_1} (1 - \frac{\Delta T_1}{2T_1})$
↑ $-\Delta E_1$
↑ $-\Delta V_1$
↑ $-\Delta N_1$

$$\begin{aligned} &= \frac{1}{T_1} \left[\Delta E_1 + (P_1 + \frac{\Delta P_1}{2}) \Delta V_1 - (\mu_1 + \frac{\Delta \mu_1}{2}) \Delta N_1 \right] \\ &\quad - \frac{\Delta T_1}{2T_1^2} \left[\Delta E_1 + (P_1 + \frac{\Delta P_1}{2}) \Delta V_1 - (\mu_1 + \frac{\Delta \mu_1}{2}) \Delta N_1 \right] \\ &\quad + \frac{1}{T_2} \left[-\Delta E_1 - P_2 \Delta V_1 + \mu_2 \Delta N_1 \right] \end{aligned}$$

Ignoring 3rd order terms

$$\therefore \Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Delta E_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) \Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) \Delta N_1$$

← this row = 0 from the \equiv^m condition

$$\begin{aligned}
 & - \frac{\Delta T_1 \Delta E_1}{T_1^2} + \underbrace{\frac{\Delta P_1 \Delta V_1}{T_1} - \frac{P \Delta T_1 \Delta V_1}{T_1^2}}_{\Delta\left(\frac{P}{T}\right) \Delta V_1} + \underbrace{\frac{\mu_1 \Delta T_1 \Delta N_1}{T_1^2} - \frac{\Delta \mu_1 \Delta N_1}{T_1^2}}_{-\Delta\left(\frac{\mu_1}{T_1}\right) \Delta N_1} \\
 & < 0
 \end{aligned}$$

\therefore We have 3 new constraints:

$$\Delta\left(\frac{P_1}{T_1}\right) \Delta V_1 \Big|_{E_1, N_1} < 0 \Rightarrow \text{if } V \uparrow, \frac{P}{T} \downarrow$$

$$\Delta T_1 \Delta E_1 \Big|_{V_1, N_1} > 0 \Rightarrow \text{if } E \uparrow, T \uparrow$$

$$\Delta\left(\frac{\mu_1}{T_1}\right) \Delta N_1 \Big|_{E_1, V_1} > 0 \Rightarrow \text{if } N \uparrow, \frac{\mu}{T} \downarrow$$

B. Maxwell's Relations

It is custom to define some new variables:

$$G = \text{Gibbs free energy} \equiv E - TS + pV \quad (= \mu N)$$

aka. thermodynamical potential

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

$$H = \text{Enthalpy} \equiv E + pV \quad \leftarrow \text{heat function}$$

Since $dE = Tds - pdv + \mu dN$

$$\begin{aligned} dG &= dE - Tds - sdT + pdv + vdp \\ &= \cancel{Tds} - \cancel{pdv} + \mu dN - \cancel{Tds} - sdT + \cancel{pdv} + vdp \\ &= -sdT + vdp + \mu dN \end{aligned}$$

$$\sim dF = -sdT - pdv + \mu dN$$

$$dH = Tds + vdp + \mu dN$$

Do h! Now we have $E, T, S, P, V, \mu, N, G, H, F$
10 in all. 3 independent at most.

These are all state variables,

ie $dE, dT, dS \dots$ etc are exact differentials

Recall: $dF = g dx + h dy$ is exact if

$$\frac{\partial g}{\partial y} = \frac{\partial h}{\partial x} \quad \text{where } g = \frac{\partial F}{\partial x}, \quad h = \frac{\partial F}{\partial y}$$

$$\text{ie } \frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x}$$

We'll use this to manipulate $dE = \dots$

$$dG = \dots$$

$$dH = \dots$$

$$dF = \dots$$

④

We can write $dE = T ds - p dV + \mu dN$ in 3 other ways:

$$ds = \frac{1}{T} dE + \frac{p}{T} dV + \frac{\mu}{T} dN \quad \text{①}$$

$$dV = -\frac{1}{p} dE + \frac{T}{p} ds + \frac{\mu}{p} dN$$

$$dN = \frac{1}{\mu} dE - \frac{T}{\mu} ds + \frac{p}{\mu} dV$$

We could do the same for $dG, dH + dF$.

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

$$\text{So } \frac{\partial}{\partial S} \left(\frac{\partial E}{\partial V} \right) = - \frac{\partial P}{\partial S} \Big|_{V,N} = \frac{\partial^2 E}{\partial S \partial V}$$

$$\& \frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S} \right) = \frac{\partial T}{\partial V} \Big|_{S,N} = \frac{\partial^2 E}{\partial V \partial S} \quad \text{equal}$$

$$\therefore - \frac{\partial P}{\partial S} \Big|_{V,N} = \frac{\partial T}{\partial V} \Big|_{S,N}$$

$$\text{also } \frac{\partial \mu}{\partial S} \Big|_{V,N} = \frac{\partial T}{\partial N} \Big|_{S,V} + \frac{\partial \mu}{\partial V} \Big|_{S,N} = - \frac{\partial P}{\partial N} \Big|_{S,V} \quad (\text{make transparency})$$

This enables us to move around & change the independent variables

48 relations in all.

See pg 217

x 3

= 16 x 3 = 48

Experimental verification:

- So what can we measure?
- We have instruments to measure

$$\left. \frac{\partial E}{\partial S} \right|_{V, N} = T \quad (\text{and } \Delta T)$$

$$-\left. \frac{\partial E}{\partial V} \right|_{S, N} = P \quad (\text{and } \Delta P)$$

Note, these derivatives may be formal and esoteric but they are often common variables we can relate to.

$$\text{also } C_V = \left. \frac{\partial Q}{\partial T} \right|_V = T \left. \frac{\partial S}{\partial T} \right|_V$$

$$C_P = \left. \frac{\partial Q}{\partial T} \right|_P = T \left. \frac{\partial S}{\partial T} \right|_P$$

$$\beta = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P \quad (\text{coeff. of vol. expansion})$$

$$\chi = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T \quad (\text{isothermal compressibility})$$

ΔV

ΔN (from mass)

$$\Delta Q \rightarrow \Delta S = \frac{\Delta Q}{T}$$

- μ is the most elusive. One way to get it is

$$\text{to look at } \Delta E = \frac{3}{2} k N \Delta T + N \Delta \mu$$

and experimentally check $\Delta \mu = \frac{\Delta E}{N} - \frac{3}{2} k \Delta T$ when a ΔE & ΔT is measured.

- In chemical reactions we can get $\Delta \mu$ from electron affinities (beyond scope of this course)

C. Sample Applications - Nondiffusive Applications

$$dN = 0$$

Example: We have $\Delta E = T \Delta S - p \Delta V + \mu \Delta N$
 so we have $\Delta E = \Delta E(S, V)$. ①

Suppose we want $\Delta E(T, P)$. How do we get that?

Sol'n

$$\Delta S(T, P) = \left. \frac{\partial S}{\partial T} \right|_P \Delta T + \left. \frac{\partial S}{\partial P} \right|_T \Delta P$$

$$\Delta V(T, P) = \left. \frac{\partial V}{\partial T} \right|_P \Delta T + \left. \frac{\partial V}{\partial P} \right|_T \Delta P$$

$$\begin{aligned} \therefore \textcircled{1} \Rightarrow \Delta E &= T \underbrace{\left. \frac{\partial S}{\partial T} \right|_P}_{c_p} \Delta T + T \underbrace{\left. \frac{\partial S}{\partial P} \right|_T}_{\substack{\text{maxwell's} \\ \text{relations}}} \Delta P - P \underbrace{\left. \frac{\partial V}{\partial T} \right|_P}_{V\beta} \Delta T - P \underbrace{\left. \frac{\partial V}{\partial P} \right|_T}_{-V\kappa} \Delta P \\ &= - \left. \frac{\partial V}{\partial T} \right|_P = -V\beta \end{aligned}$$

$$= c_p \Delta T - T V \beta \Delta P - P V \beta \Delta T + P V \kappa \Delta P$$

$$\therefore \Delta E = (c_p - P V \beta) \Delta T - (T \beta - P \kappa) V \Delta P$$

Neat huh!

Example Variations in Heat Capacity

How can we estimate C_v at volume 2 given C_v at Vol. 1?
 Could make another measurement.

Or: use
$$C_{v2} = C_{v1} + \int_{V_1}^{V_2} \underbrace{\left(\frac{\partial C_v}{\partial V}\right)_T}_{dC_v} dV$$

But
$$\begin{aligned} \left(\frac{\partial C_v}{\partial V}\right)_T &= \frac{\partial}{\partial V} \left(\frac{\partial Q}{\partial T}\right)_V = T \frac{\partial^2 S}{\partial V \partial T} = T \frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T \\ &= T \frac{\partial^2 P}{\partial T^2} \Big|_V \end{aligned}$$
 $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\therefore C_{v2} = C_{v1} + \int_{V_1}^{V_2} T \frac{\partial^2 P}{\partial T^2} \Big|_V dV$$

Can calculate if we know the equation of state for the substance, giving:

$$\sim C_{p2} = C_{p1} - \int_{P_1}^{P_2} \left(T \frac{\partial^2 V}{\partial T^2}\right)_P dP$$

Example: $\Delta S(p, v)$

Suppose we have a process in which $p \neq v$ change.

We want ΔS :

$$\Delta S(p, v) = \left. \frac{\partial S}{\partial p} \right|_v \Delta p + \left. \frac{\partial S}{\partial v} \right|_p \Delta v$$

$\uparrow \left(\frac{1}{T} \frac{\partial Q}{\partial p} \right)_v$
 $\quad \quad \quad \uparrow \left(\frac{1}{T} \frac{\partial Q}{\partial v} \right)_p \Leftarrow \text{could measure.}$

If we couldn't measure ΔQ what could we do?

Maxwell's relations give: $\left. \frac{\partial S}{\partial p} \right|_v = - \left. \frac{\partial v}{\partial T} \right|_s$

$$\left. \frac{\partial S}{\partial v} \right|_p = \left. \frac{\partial p}{\partial T} \right|_s$$

could measure these if we insulate ($\Delta S=0$)
 + compress it, measure $\Delta p \neq \Delta T$.

? But $v \neq \text{const}$?

$dS = T dQ$ if $v, N \text{ const.}$
 \therefore if $dQ=0$ (insulated)
 then $dS=0$

D. Third Law Constraints

Recall 3rd Law: $S \rightarrow 0$ as $T \rightarrow 0$
 \uparrow $k \ln \Omega + \Omega \rightarrow 1$ as $S \rightarrow 0$

$$\therefore \left. \frac{\partial S}{\partial V} \right|_{T=0} = 0, \quad \left. \frac{\partial S}{\partial P} \right|_{T=0} = 0 \quad (S \text{ not dependent on anything})$$

\therefore Maxwell's relations give:

$$\left. \frac{\partial P}{\partial T} \right|_V = 0, \quad \left. \frac{\partial V}{\partial T} \right|_P = 0$$

Also since $S = \text{finite}$ at $T = \text{finite}$ + $S = 0$ at $T = 0$,
 then $\left. \frac{\partial S}{\partial T} \right|_{T \rightarrow 0} = \text{finite}$

$$\therefore C = \frac{\partial Q}{\partial T} = T \frac{\partial S}{\partial T} = T \cdot (\text{finite})$$

$$\therefore C \rightarrow 0 \text{ at } T \rightarrow 0$$

Note: a small C means little capacity to absorb energy without raising T .

\therefore Low T experimentation is difficult,
 small outside influences cause big T fluctuations.

? ($\nu \rightarrow 0$?)