Consider a system at equilibrium with *S = S(E, X)*

- with internal constraint bring reversibly to *S'(E, X)*
  requires work since *E = const* $\Rightarrow$ *heat flow*
- now adiabatically isolate the system
- turn off int. constraint
  system relaxes to *S(E, X)*

$$\Delta S = S - S' > 0$$ according to 2nd law,

equilibrium state is that for which *S* = global max

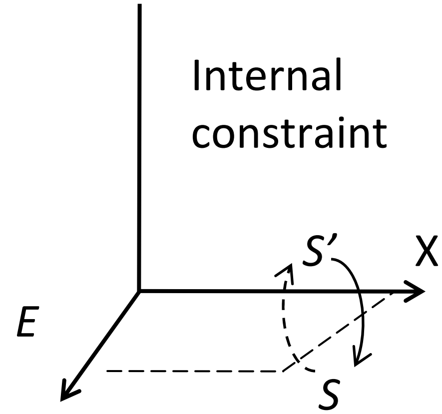
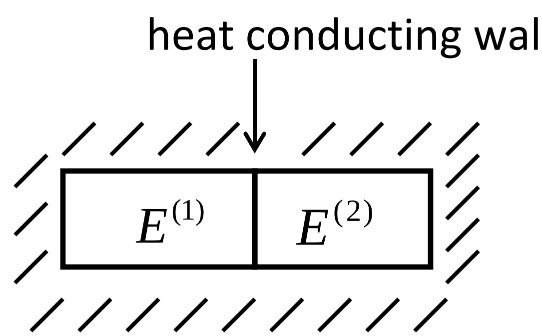


Fig. 4.1

Consider the system in adjacent figure
What are the final values of $E^{(1)}, E^{(2)}$

The final values of $E^{(1)}$ and $E^{(2)}$ *are those* maximize *S*, subject to $E = E^{(1)} + E^{(2)}$

Now show there is an energy minimum principle



assume we start at equilibrium and move energy between the subsystems

$$S\left(E^{(1)} - \Delta E, X^{(1)}\right) + S\left(E^{(2)} + \Delta E, X^{(2)}\right) < S\left(E^{(1)} + E^{(2)}, X^{(1)} + X^{(2)}\right)$$

S is a monotonically > function of *E*

Thus, there is an $E < E^{(1)} + E^{(2)}$ s.t

$$S\left(E^{(1)} - \Delta E, X^{(1)}\right) + S\left(E^{(2)} + \Delta E, X^{(2)}\right) = S\left(E, X^{(1)} + X^{(2)}\right)$$

E is a global minimum of *E(S, X,* int. constr.)

$$\Delta E = E(S, X, \delta Y) - E(S, X, 0)$$
$$= (\delta E)_{S,X} + \left(\delta^2 E)\right)_{S,X} + \ldots$$
$\left(\delta E\right)_{S,X} \geq 0$ for a small variation with $\delta Y = 0$

δY = variation of internal extensive variables due to constraint

$\left(\Delta E\right)_{S,X} > 0, \quad \left(\Delta S\right)_{E,X} < 0$ for small variations away from an equilibrium state

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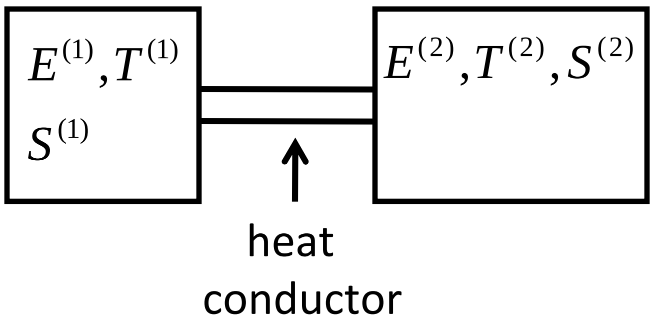

How are $T^{(1)}$, $T^{(2)}$ related at equilibrium?

$$\left(\delta S\right)_{E,X} \leq 0$$
$$E = E^{(1)} + E^{(2)} = const.$$
$$\delta E^{(1)} = -\delta E^{(2)}$$
$$S = S^{(1)} + S^{(2)}$$

consider a small displacement from equilibrium due to a constraint

$$\delta S = \delta S^{(1)} + \delta S^{(2)} = \left(\frac{\partial S^{(1)}}{\partial E^{(1)}}\right)_X dE^{(1)} + \left(\frac{\partial S^{(2)}}{\partial E^{(2)}}\right)\delta E^{(2)}$$
$$= \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right]\delta E^{(1)} \leq 0$$

Since this must hold for <u>any</u> variation $\delta E^{(1)}$

$\Rightarrow T^{(1)} = T^{(2)}$ at equilibrium evolve

Suppose $T^{(1)} \neq T^{(2)} \xrightarrow{\text{evolve}}$ to equilibrium

(not at equilibrium)

$$\Delta S^{(1)} + \Delta S^{(2)} = \Delta S > 0 \qquad \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right]\Delta E^{(1)} > 0$$

assuming *X* is fixed

if $T^{(1)} > T^{(2)} \Rightarrow \Delta E^{(1)} < 0$

energy flows from hot body to cold body!

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for a quasistatic process

$$C = \frac{dQ}{dT} = T\frac{dQ/T}{dT} = T\frac{dS}{dT}$$

$$C_f = T\left(\frac{\partial S}{\partial T}\right)_f, \quad C_X = T\left(\frac{\partial S}{\partial T}\right)_X$$

heat capacity

$C_f,\ C_X$ are extensive

Legendre transforms

$$f \cdot dX = -pdV + \Sigma \mu_i dn_i$$

rev. work

p = syst. pressure

μ_i = chem. pot.

n_i = # moles.

$$dE = TdS - pdV + \sum_{i=1}^{r} \mu_i dn_i$$

Suppose $f = f(x_1, \ldots, x_n)$

$$df = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i} \right)_{x_j} dx_i = \sum_{i=1}^{n} \mu_i dx_i$$

Let $g = f - \sum_{i=r+1}^{n} \mu_i x_i$

$$dg = df - \sum_{i=r+1}^{n} \left[\mu_i dx_i + x_i d\mu_i \right]$$

$$dg = \sum_{i=1}^{r} \mu_i dx_i - \sum_{i=r+1}^{n} x_i d\mu_i \longleftarrow$$ Legendre transform of *f*

construct a natural function of *T, V, n*

$$A = E - TS = A(T, V, n)$$

Helmholtz free energy

Alternate way to define Legendre Transformations

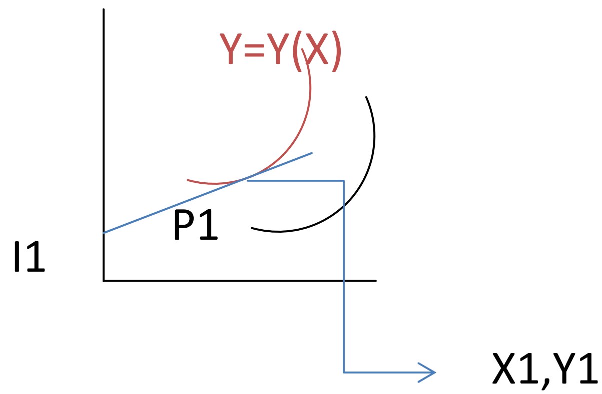
Energy $E(S,X)$ and Entropy $S(E,X)$ representations : extensive parameters are the independent variables.

One typically measures intensive parameters like T not S. How can one recast the problem so that T and P are the independent variables?

Answer: Legendre Transforms

Suppose $Y=Y(X)$

Slope $P=dY/dX$ Infinite number of curves have the same slope. However if you specify the slope and Y- intercept (let us call this I) then one can specify the curve in terms of P and I



$X1,Y1 \rightarrow P1,I1$

$$P = \frac{Y - I}{X - 0}$$

$$\boxed{I = Y - PX}$$

$$Example$$

$$Y = \frac{1}{4} X^2$$

$$P = dY / dX = X / 2 \Rightarrow X = 2P$$

$$I = Y - PX = \frac{1}{4} X^2 - PX = \frac{1}{4} 4P^2 - 2P^2 = -P^2$$

$$Therefore$$

$$I = -P^2$$

I is referred to as the Legendre transform of Y. i.e., **I=Y[P]**

The inverse problem is getting the relation Y=Y(X) from I=I(P)

$$I = Y - PX\,, dY = PdX$$

$$dI = dY - PdX - XdP = -XdP$$

$$-X = dI\,/\,dP$$

Y=Y(X)	I=I(P)
P=dY/dX	-X=dI/dP
I=-PX+Y	Y=XP+I

$$E(S, V, N_1, N_2, \ldots.)$$

$$T = \frac{\partial E}{\partial S}\bigg|_{V, N_1 \ldots.}$$

$$A = E[T] = E - TS$$

$$I = Y - PX$$

$$I = E - \left(\frac{\partial E}{\partial S}\right)_V S$$

$$A = E - TS$$

$$dE = TdS - pdV + \Sigma \mu_i dn_i$$

$$A = E - TS$$

$$dA = dE - TdS - SdT$$

$$\boxed{dA = -SdT - pdV + \sum_{i=1}^{r} \mu_i dn_i}$$

A is called the Helmholtz free energy

$$p = -\frac{\partial E}{\partial V}\bigg|_{S,N_1\ldots}$$

$$G = E[T, p]$$

$$G = E - TS + pV$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

$$H = E[p]$$

$$H = E + pV$$

$$dH = TdS + Vdp + \sum_i \mu_i dn_i$$

G is the Gibbs free energy

H is the enthalpy

μ_i refers to the chemical potential of the i^{th} component.

$$\mu_1 = \frac{\partial E}{\partial N_1}\bigg|_{S,V,N_2\ldots}$$

$$\left.\begin{array}{l}(S,V,n)\\(T,V,n)\\(S,p,n)\\(T,p,n)\end{array}\right\}$$ all adequate to specify an equilibrium system

$E(S,V,n)$
$A(T,V,n)$
$H(S,p,n)$
$G(T,p,n)$

(*T, S*) and *(p, V)* are conjugate variables

$$dG = -SdT + Vdp + \Sigma\mu_i dn_i$$

$$dH = TdS + Vdp + \Sigma\mu_i dn_i$$

$$dE = TdS - pdV + \Sigma\mu_i dn_i$$

$$dA = -SdT - pdV + \Sigma\mu_i dn_i$$

Maxwell relations

If $df = adx + bdy$

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y$$

example:

$$f = x^2 y$$

$$df = 2xydx + x^2 dy$$

$$\frac{\partial}{\partial y}(2xy) = 2x$$

$$\frac{\partial}{\partial x}(x^2) = 2x$$

Suppose we were interested in

$$\left(\frac{\partial S}{\partial V}\right)_{T,n}$$

consider

$$dA = -SdT - PdV + \Sigma\mu_i dn_i$$

natural function of *T, V, n*

$$\left(\frac{\partial S}{\partial V}\right)_{T.n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$$

example of a Maxwell relation

We already saw that

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,n}$$

Suppose we want to know how C_V changes with volume:

$$\left(\frac{\partial}{\partial V}C_V\right)_{T,n} = T\left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_{V,n}\right]_{T,n} = T\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_{T,n}\right]_{V,n}$$

$$= T\left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial T}\right)_{V,n}\right]_{V,n} = T\left[\frac{\partial^2 p}{\partial T^2}\right]_{V,n}$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{p,n}$$

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

$$(dS)_n = \left(\frac{\partial S}{\partial T}\right)_{V,n}(dT)_n + \left(\frac{\partial S}{\partial V}\right)_{T,n}(dV)_n$$

$$\left(\frac{\partial S}{\partial T}\right)_{p,n} = \left(\frac{\partial S}{\partial T}\right)_{V,n} + \left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{p,n}$$

$$C_p = T\left[\left(\frac{\partial S}{\partial T}\right)_{V,n} + \left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{p,n}\right]$$

$$C_p = C_V + T\left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{p,n}$$

$$= C_V + T\left(\frac{\partial p}{\partial T}\right)_{V,n}\left(\frac{\partial V}{\partial T}\right)_{p,n}$$

$$= C_V T + \left(\frac{\partial P}{\partial V}\right)_{T,n}\left[\left(\frac{\partial V}{\partial T}\right)_{p,n}\right]^2$$

coefficient of
thermal
compressibility

coefficient of
thermal exp

$$\left(\frac{\partial X}{\partial Y}\right)_Z = -\left(\frac{\partial X}{\partial Z}\right)_Y\left(\frac{\partial Z}{\partial Y}\right)_X$$

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