The idea that physical systems act to increase their entropy can be used to extract work from them

Theorem [Callen]: For all processes leading from the specified initial state to the specified final state of the primary system, the delivery of work is maximum (and the delivery of heat is minimum) for a reversible process

Maximum work theorem

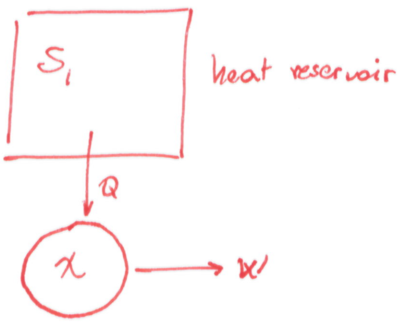
Definition: heat reservoir

A reservoir (system) that is large enough that, upon contact with another system, there is no change in its temperature even though there is heat flow.

We also consider that S is so large that Q is infinitesimal compared to the total energy of the system

$$\Rightarrow \Delta S_{S_1} = -\frac{Q}{T}$$ (heat flow out of the reservoir)

$Q > 0$



From the 1^{st} law applied to system x

$W = -\Delta E + Q$

$W > 0$ (the minus sign was already introduced as work will be done by the system)

From PII

$$0 \leq \Delta S_{tot} = \Delta S_x + \Delta S_{S_1}$$

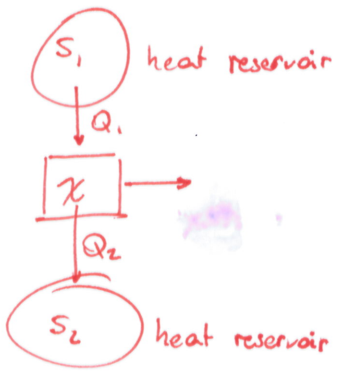
$$\boxed{\Rightarrow \Delta S_x - \frac{Q}{T} \geq 0}$$

$$\Rightarrow \boxed{W \leq T\Delta S_x - \Delta E}$$

The values of ΔS_x and ΔE are associated with system x and are thus specified for a set of given initial and final states

$\Rightarrow$ the delivery of work is maximum when we have the equality

i.e. $\Delta S_{tot} = 0 \rightarrow$ reversible process



cycle $\rightarrow$ x goes back to its initial state after 1 cycle

$\Delta S_x = 0$

$\Delta S_{S_1} = -\dfrac{Q_1}{T_1}$

$\Delta S_{S_2} = +\dfrac{Q_2}{T_2}$

$$\Rightarrow \Delta S_{tot} = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

For 1 cycle

$\Delta S_x = 0$

$\Delta E_x = 0$

$$\Rightarrow W = Q_1 - Q_2 = Q_1 - Q_1 \frac{T_2}{T_1} = Q_1 \underbrace{\left(1 - \frac{T_2}{T_1}\right)}_{\eta = \text{efficiency}} \qquad T_1 > T_2$$

Important: We have come up with a procedure that unambiguously provides a way to determine the ratios between two temperatures. This means temperature has a well-defined zero (we cannot apply an arbitrary constant shift to it). We can, however, multiply by a constant (rescale), since

$$\lambda S(U, V, N^{(i)}) = S(\lambda U, \lambda V, \lambda N^{(i)})$$

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Let's now go back to the concavity of the entropy and generalize it for more variables

Let's assume a homogeneous system with a fixed number of particles

$$S(2E, 2V) = 2S(E,V)$$

Let's now separate the system into two subsystems with energies $E \pm \Delta E$ and volume $V \pm \Delta V$

$$\Rightarrow \quad S(E+\Delta E, V+\Delta V) + S(E-\Delta E, V-\Delta V) > 2S(E,V) = S(2E, 2V)$$

assuming ~~concavity~~ convexity

This can only be true if we impose a constraint that makes the system inhomogeneous.

Thus, unless the system is heterogeneous, S must be concave

in other words, for fixe E and V, internal constraints will lead to

$$(\Delta S)_{(E,V)} \leq 0$$

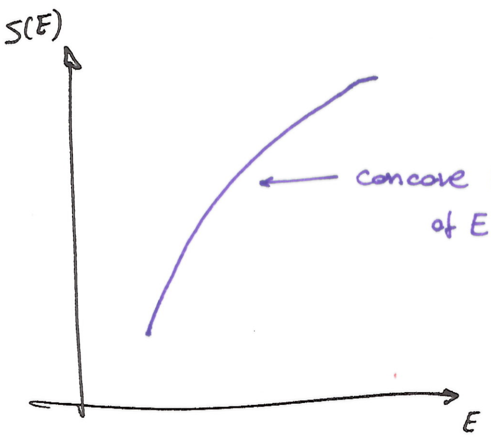
Taylor exponsion of $S(E \pm \Delta E, V \pm \Delta V)$ around $S(E,V)$ up to second order

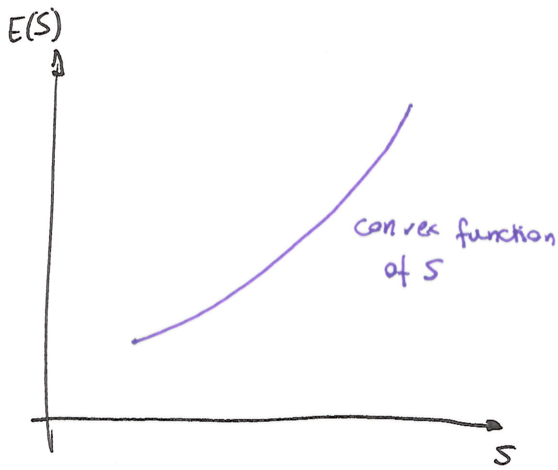
$$S(E \pm \Delta E, V \pm \Delta V) = S(E,V) \pm \Delta E \frac{\partial S}{\partial E} \pm \Delta V \frac{\partial S}{\partial V} + \frac{1}{2}(\Delta E)^2 \frac{\partial^2 S}{\partial E^2} + \frac{1}{2}(\Delta V)^2 \frac{\partial^2 S}{\partial V^2} + \Delta E \Delta V \frac{\partial^2 S}{\partial E \partial V} \quad (1)$$

$$S(E+\Delta E, V+\Delta V) + S(E-\Delta E, V-\Delta V) = \cancel{S(E,V)} + \cancel{\Delta E \frac{\partial S}{\partial E}} + \cancel{\Delta V \frac{\partial S}{\partial V}} + \frac{1}{2}(\Delta E)^2 \frac{\partial^2 S}{\partial E^2} + \frac{1}{2}(\Delta V)^2 \frac{\partial^2 S}{\partial V^2}$$
$$+ \Delta E \Delta V \frac{\partial^2 S}{\partial E \partial V} + \cancel{S(E,V)} - \cancel{\Delta E \frac{\partial V}{\partial E}} - \cancel{\Delta V \frac{\partial S}{\partial V}} + \frac{1}{2}(\Delta E)^2 \frac{\partial^2 S}{\partial E^2}$$
$$+ \frac{1}{2}(\Delta V)^2 \frac{\partial^2 S}{\partial V^2} + \Delta E \Delta V \frac{\partial^2 S}{\partial E \partial V}$$

$$= (\Delta E)^2 \frac{\partial^2 S}{\partial E^2} + (\Delta V)^2 \frac{\partial S^2}{\partial V^2} + \Delta E \Delta V \frac{\partial S}{\partial E \partial V} \nleq 0$$

From a graphical perpective





separate the system into two subsystems

$E = E_1 + E_2 \qquad V = V_1 + V_2$

introducing an internal constraint

$E_1 \to E_1 + \Delta E \qquad E_2 \to E_2 - \Delta E$

$V_1 \to V_1 + \Delta V \qquad V_2 \to V_2 - \Delta V$

$$\underbrace{S(E_1+\Delta E, V_1+\Delta V)}_{\text{increasing function of energy}} + S(E_2-\Delta E, V_2-\Delta V) \leq S(E,V)$$

$\Rightarrow$ There exists $\tilde{E} \geq E$ that gives

$$S(E_1+\Delta E, V_1+\Delta V) + S(E_2-\Delta E, V_2-\Delta V) = S(\tilde{E}, V)$$

this would be the energy of the system at constant S if the two systems were isolated

Thus, introducing a constraint can only increase the energy

$(\Delta E)_{(S,V)} \geq 0$ the energy is a convex function of S and V

$$\Rightarrow \quad E(S+\Delta S, V+\Delta V) + E(S-\Delta S, V-\Delta V) \geq 2E(S,V)$$

Taylor expanding

$$(\Delta S)^2 \frac{\partial^2 E}{\partial S^2} + (\Delta V)^2 \frac{\partial^2 E}{\partial V^2} + 2\Delta S \Delta V \frac{\partial^2 E}{\partial S \partial V} \geq 0 \qquad (2)$$

Let $f(x)$ be a convex function

$\Rightarrow \quad f''(x) \geq 0$

$\Rightarrow$ we define $f'(x) = u$

and we notice that, if $f(x)$ is convex u defines uniquely the value of x, i.e. $x = x(u)$

We then define the Legendre transform

$$g(u) = \mathrm{Max}\Big|_x F(u,x) = \mathrm{Max}\Big|_x -(ux - f(x))$$

where $\quad F(x,u) = f(x) - ux$

and $\quad \left.\dfrac{\partial F(x,u)}{\partial x}\right|_u = f'(x) - u = 0 \Leftarrow$ maximum

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Another way of defining a Legendre transform

Let's say we have a function $f(x,y)$ of two independent variables

$$\Rightarrow \quad df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = u\,dx + w\,dy$$

$$\left(\frac{\partial f}{\partial x}\right)_y = u \qquad \left(\frac{\partial f}{\partial y}\right) = w \qquad (3)$$

$\left.\begin{matrix}\{x, u\} \\ \{y, w\}\end{matrix}\right\}$ conjugate pairs

Now I propose a function $g(x,w) = f - wy$

$$\Rightarrow dg = \left(\frac{\partial g}{\partial x}\right)_w dx + \left(\frac{\partial g}{\partial w}\right)_x dw = df - d(wy) = (u\,dx + \cancel{w\,dy}) - (\cancel{w\,dy} + y\,dw)$$

$$= u\,dx - y\,dw$$

We notice that by defining $g(x; w)$ in this way we obtain

$$\left(\frac{\partial g}{\partial w}\right)_x = -y \qquad \text{conjugate pair}$$

Thus we can say that the Legendre transform takes us from a function of a set of variables to another function o the conjugate set of variables

A few properties of g

$$\left(\frac{\partial^2 g}{\partial w^2}\right)_x = -\left(\frac{\partial y}{\partial w}\right)_x = -\frac{1}{(\partial w/\partial y)_x} = -\frac{1}{(\partial^2 f/\partial y^2)_x} \qquad \frac{\partial^2 g}{\partial w^2}\frac{\partial^2 f}{\partial y^2} = -1$$

$\Rightarrow$ if $f \to$ convex $\Rightarrow g \to$ concave

$f \to$ concave $\Rightarrow g \to$ convex

If I want to change both variables I'll introduce

$$g(u,w) = f - wy - ux$$

$$\Rightarrow dg(u,w) = df - d(wy) - d(ux) = df - (w\,dy + y\,dw) - (u\,dx + x\,du)$$

$$= -x\,du - y\,dw$$

$$\left(\frac{\partial g}{\partial u}\right)_w = -x \qquad \left(\frac{\partial g}{\partial w}\right)_u = -y \qquad (4)$$

From (3)

$$\frac{\partial f}{\partial x} = u \qquad \frac{\partial f}{\partial y} = w \rightarrow \frac{\partial^2 f}{\partial x \partial x} = \frac{\partial u}{\partial x} \qquad \frac{\partial^2 f}{\partial y^2} = \frac{\partial w}{\partial y}$$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial w}{\partial x} \qquad \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial u}{\partial y}$$

$$\frac{\partial g}{\partial u} = -x \qquad \frac{\partial g}{\partial w} = -y \rightarrow \frac{\partial^2 g}{\partial u^2} = -\frac{\partial x}{\partial u} \qquad \frac{\partial^2 g}{\partial w^2} = -\frac{\partial y}{\partial w}$$

$$\frac{\partial^2 g}{\partial w \partial u} = -\frac{\partial x}{\partial w} \qquad \frac{\partial^2 g}{\partial u \partial w} = -\frac{\partial y}{\partial u}$$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \rightarrow \frac{\partial w}{\partial x} = \frac{\partial u}{\partial y}$$

$$\frac{\partial^2 g}{\partial u \partial w} = \frac{\partial^2 g}{\partial w \partial u} \rightarrow \frac{\partial x}{\partial w} = \frac{\partial y}{\partial u}$$

To make things clearer we'll use

$$x \to x_1 \qquad u \to u_1$$
$$y \to x_2 \qquad w \to u_2$$

$$\frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{\partial u_i}{\partial x_j} \qquad \frac{\partial^2 g}{\partial u_j \partial u_k} = -\frac{\partial x_j}{\partial u_k}$$

we notice that $\sum_j \frac{\partial u_i}{\partial x_j}\frac{\partial x_j}{\partial u_k} = \frac{\partial u_i}{\partial u_k} = \delta_{ik}$

independent variables for $i \neq k$

because $du_i = \sum_j \frac{\partial u_i}{\partial x_j} dx_j$

$$\sum_j \underbrace{\frac{\partial^2 f}{\partial x_i \partial x_j}}_{D_{ij}} \underbrace{\frac{\partial^2 g}{\partial u_j \partial u_k}}_{C_{jk}} = -\delta_{ik} \qquad (8)$$

$$\Rightarrow \quad -D_{ij} = [C]^{-1}_{ij} \qquad (9)$$

If $f(x_i)$ is convex $\forall x_i$ then

$$\frac{\partial^2 f}{\partial x_i \partial x_j} \geqslant 0 \qquad \forall i, j$$

Now let's go back to our variables and try to write them in terms of other variables, for example

1 $E(S,V,N)$ keeping N fixed

$$\left.\frac{\partial E}{\partial S}\right|_V = T$$ thus S and T are conjugate variables

$\Rightarrow$ using $F(T,V) = g(\omega,x) = f(x,y) - \omega y$

We let $S = y$

$$f(x,y) = E(S,V)$$

$$\left.\frac{\partial E}{\partial S}\right|_V = T = \omega$$

$$\boxed{F(T,V) = E - TS} \quad (5) \quad \Rightarrow \left.\frac{\partial F}{\partial T}\right|_V = -S \qquad \underbrace{\left.\frac{\partial F}{\partial V}\right|_T = -P}$$

Free energy

We did not change the variable V so it still has the same derivative as E

2 As a function of S and P

$E(S,V)$ and $\left.\frac{\partial E}{\partial V}\right|_S = -P$

$$\bar{H}(S,P) = g(x,\omega) = f(x,y) - \omega y$$

$x \equiv S$ $\qquad f(x,y) = E(S,V)$

$y \equiv V$ $\qquad \left.\frac{\partial E}{\partial V}\right|_S = -P \equiv \omega$

$$\boxed{\bar{H}(S,P) = E + PV} \qquad \underbrace{\left.\frac{\partial \bar{H}}{\partial S}\right|_P = T} \qquad \left.\frac{\partial \bar{H}}{\partial P}\right|_T = V \quad (6)$$

Enthalpy

the same relation with $E(S,V)$

3 as function of T and P

$$G(T,P) = g(u,\omega) = f - \omega y - u x$$

$f(x,y) \equiv E(S,V)$

$x \equiv S$

$y \equiv V$

$$\left.\frac{\partial E}{\partial S}\right|_V = T \equiv u$$

$$\left.\frac{\partial E}{\partial V}\right|_S = -P \equiv \omega$$

$$\boxed{G(T,P) = E(S,V) + PV - TS}$$

Gibbs Potential

7

$$\left.\frac{\partial G}{\partial T}\right|_P = -S \qquad \left.\frac{\partial G}{\partial P}\right|_T = V$$

Using the relations in 5

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

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

From

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \Rightarrow \left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V$$

Using the relations in 7

$$\left.\frac{\partial G}{\partial T}\right|_P = -S \qquad \left.\frac{\partial G}{\partial P}\right|_T = V$$

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right) = -\left.\frac{\partial S}{\partial P}\right|_T \qquad \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \left.\frac{\partial V}{\partial T}\right|_P$$

$$\Rightarrow \quad \left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P$$

This is part of a class of relations known as Maxwell's relations.

What if instead of taking the Legendre transform of the energy we took the transform of the entropy?

$$S = S(E,V,N) \qquad \text{keeping } N \text{ fixed}$$

$$\left.\frac{\partial S}{\partial E}\right|_V = \frac{1}{T}$$

$$\Phi_1\left(\frac{1}{T}, V\right) = g(u,y) = f(x,y) - xu = S - \frac{E}{T} = -\frac{F}{T}$$

$$f(x,y) \equiv S(E,V) \qquad x \equiv E$$

$$\left.\frac{\partial f}{\partial x}\right|_y = u \equiv \frac{1}{T}$$

$$\left.\frac{\partial \Phi_1}{\partial (1/T)}\right|_V = -E \qquad \underbrace{\left.\frac{\partial \Phi_1}{\partial V}\right|_{1/T} = \frac{P}{T}}_{\text{keeps the same relation as } S \text{ for } V}$$

Let's now suppose a quasi-static process which receives an ammount of heat $đQ$ keeping one or more thermodynamic variables fixed. Provided dT is the increase in temperature

quasi-static

$$C_y = \left.\frac{đQ}{dT}\right|_y = \left.T\frac{dS}{dT}\right|_y$$

heat capacity

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$$C_V = \left.\frac{đQ}{dT}\right|_V = \left.T\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial E}{\partial T}\right|_V$$

heat capacity at constant volume

$$C_P = \left.\frac{đQ}{dT}\right|_P = \left.T\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial \bar{H}}{\partial S}\right|_P \left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial \bar{H}}{\partial T}\right|_P$$

heat capacity at constant pressure.

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Let's now define three new intensive variables

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P$$

Expansion coefficient at constant pressure

$$K_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$$

Coefficient of isothermal compressibility

$$K_S = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_S$$

coefficient of adiabatic compressibility

With that in mind we consider

$$z(x,y)$$

$$dz = \frac{\partial z}{\partial x}\bigg|_y dx + \frac{\partial z}{\partial y}\bigg|_x dy$$

if we choose $z(x,y) = \text{constant}$ (surface)

$$\frac{\partial z}{\partial x}\bigg|_y dx = -\frac{\partial z}{\partial y}\bigg|_x dy$$

$$\Rightarrow \frac{\partial z}{\partial x}\bigg|_y \frac{\partial x}{\partial y}\bigg|_z = -\frac{\partial z}{\partial y}\bigg|_x$$

$$\boxed{\frac{\partial x}{\partial y}\bigg|_z \frac{\partial y}{\partial z}\bigg|_x \frac{\partial z}{\partial x}\bigg|_y = -1}$$

For the case of (T, P, V)

$$\boxed{\frac{\partial T}{\partial P}\bigg|_V \frac{\partial P}{\partial V}\bigg|_T \frac{\partial V}{\partial T}\bigg|_P = -1}$$

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For $S(T,P)$

$$TdS = T\left(\frac{\partial S}{\partial T}\bigg|_P dT + \frac{\partial S}{\partial P}\bigg|_T dP\right) = \underbrace{T\frac{\partial S}{\partial T}\bigg|_P}_{C_P} dT + \underbrace{T\frac{\partial S}{\partial P}\bigg|_T}_{-\frac{\partial V}{\partial T}\big|_P} dP$$

From Maxwell's relation

$$= C_P dT - TV\underbrace{\left(\frac{1}{V}\frac{\partial V}{\partial T}\bigg|_P\right)}_{\alpha} dP = C_P dT - TV\alpha dP$$

keeping V constant

$$T\frac{\partial S}{\partial T}\bigg|_V = C_p - TV\alpha\frac{\partial P}{\partial T}\bigg|_V = C_p - \frac{TV\alpha^2}{k_T}$$

$$\boxed{C_p - C_v = \frac{TV\alpha^2}{k_T}}$$

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Now we consider

$$TdS = \underbrace{T\frac{\partial S}{\partial T}\bigg|_V}_{C_V} dT + T\underbrace{\frac{\partial S}{\partial V}\bigg|_T} dV$$

$$\frac{\partial P}{\partial T}\bigg|_V = -\underbrace{\frac{\partial P}{\partial V}\bigg|_T}_{\frac{1}{k_T V}} \underbrace{\frac{\partial V}{\partial T}\bigg|_P}_{\alpha V} = \frac{\alpha}{k_T}$$

Maxwell relation

$$= c_v dT + \frac{T\alpha}{k_T} dV$$

For constant $S \rightarrow dS = 0$

$$C_V \underbrace{\frac{\partial T}{\partial P}\bigg|_S} + \frac{T\alpha}{k_T}\underbrace{\frac{\partial V}{\partial P}\bigg|_S}_{-k_S V} = 0$$

$$\frac{\partial T}{\partial P}\bigg|_S = -\underbrace{\frac{\partial S}{\partial P}\bigg|_T}_{\frac{\partial V}{\partial T}\big|_P} \underbrace{\frac{\partial T}{\partial S}\bigg|_P}_{\frac{T}{C_p}}$$

$$\alpha V = \frac{\partial V}{\partial T}\bigg|_P$$

$$C_V\frac{\alpha \cancel{V}\cancel{T}}{C_p} - \frac{\cancel{T}\cancel{\alpha}\cancel{V} k_S}{k_T} = 0$$

$$\boxed{\frac{C_p}{C_V} = \frac{k_T}{k_S}}$$

Let's now rescale all of our extensive quantities by λ

$$E \rightarrow \lambda E$$
$$V \rightarrow \lambda V$$
$$N \rightarrow \lambda N$$

$$\lambda S(E, V, N) = S(\lambda E, \lambda V, \lambda N)$$

differentiating with respect to λ

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

$$S(E, V, N) = \frac{dS(E', V', N')}{dE'}\Bigg|_{\substack{E' = \lambda E \\ V' = \lambda V \\ N' = \lambda N}} E + \frac{dS}{dV'} V + \frac{dS}{dN'} N$$

taking $\lambda = 1$

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

$$G \equiv \mu N = E - TS + P$$

$$dG = \frac{\partial G}{\partial T}\bigg|_{P,N} dT + \frac{\partial G}{\partial P}\bigg|_{T,N} dP + \frac{\partial G}{\partial N}\bigg|_{P,T} dN = -SdT + VdP + \mu dN$$

or using

$$G = \mu N \Rightarrow dG = \mu dN + N d\mu$$

$$-SdT + VdP + \cancel{\mu dN} = \cancel{\mu dN} + N d\mu$$

$$N d\mu + SdT - VdP = 0$$

Gibbs-Duhem relation