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Lecture Notes - General Thermodynamics

Prof. Yarger's Hand Written Lecture Notes

These set of notes started as student lecture notes from a class by Prof. George Wolf. They were further developed over several years of teaching Thermodynamics at the University of Wyoming and Arizona State University. This is a subset of lecture notes on the fundamentals of thermochemistry. The notes have been compiled as a foundation for teaching 'thermodynamics with a biological focus'

ASU BCH 341 - 'Physical Chemistry With A Biological Focus' - i.e. BioPhysical Chemistry
BioPchem: Thermo

<u>Lecture Notes - Set 2 - Topics:</u>

Entropy & 2nd Law (44-53), Fundamental Equation for dS (54-57), Temperature Dependence of Entropy (58), dS/ΔS Phase Transformations (59-60), V & P Dependence of Entropy (61-64), Irreversible Processes (65-67), Extremum Principle (68-70), Entropy & Disorder (71-73), Entropy of Ideal Gas (74-77), Entropy of Mixing (78-82), 3rd Law (83-87), Phase Transitions (88-89), Absolute Entropy (90-91), Fundamental Equations for a Closed System (92-97), Legendre Transforms (98-103), Maximum Work (104-106), Maxwell Relations (107-109), Massieu Functions (110-111), Why are Thermodynamic Potentials Useful? (112), Other Types of Work (113), Extremum Principle - Revisited (114-115), Constrained Equilibrium (116-117), Energy Minimum Principle - Revisited (118-122), Isothermal/Isochoric Processes (123-124), Isothermal/Isobaric Processes (125), Summary (126-127).

Entropy & The 2nd Law of Thermodynamics

Recall, The 1st-law restricts allowed processes to those that satisfy the Energy conservation principle:

$$dU = -dU^*$$

system ↵ ↳ Surroundings

or $$dU = đq + đw$$

The Second Law Embodies the inherent irreversibility of Nature, i.e., directionality of Spontaneous processes, & the pervasive "degradation of Energy" in the universe. The Essence of the 2nd-law can be reduced to 2 observations (actually They are equivalent) of inherent irreversibility of Nature:

① heat flows spontaneously from hot to Cold.

hot ⟶ Cold (with ⟵ crossed out)

↳ never the reverse unless work is done to accomplish this transfer.

② Work can be converted Entirely to heat. However, There are restrictions on the Efficiency by which heat can be converted to work.

work ⟶ Heat

⟵ (restrictions)

⇒ Pervasive degradation of the quality of Energy in the universe.

Classical Statements of the 2nd law

Clausius Statement: It is impossible to devise an engine which, working in a cycle, shall produce no other effect than the transfer of heat from a colder body to a hotter body.

Alternative statement: "no process is possible whose sole result is the transfer of heat from a colder body to a hotter body."

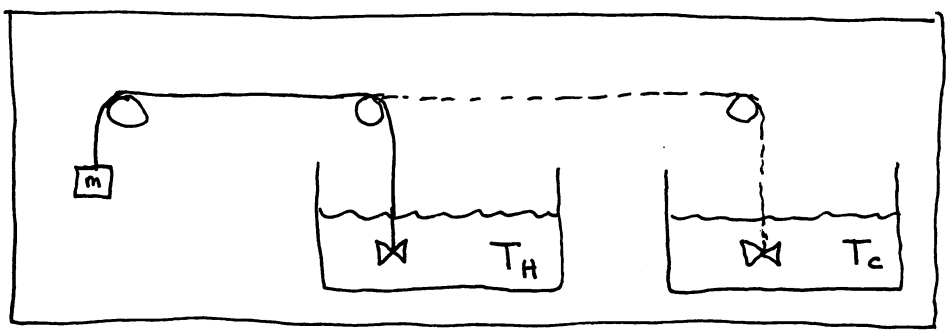
Kelvin Statement: It is impossible to devise an engine which, working in a cycle, shall produce no other effect than the extraction of heat from a thermal reservoir and the performance of an Equal amount of work.

In the following pages we will quantitatively develop This observation of irreversibility and discover a new state function called the <u>Entropy</u>, S.

We will see that S is a quantitative scale of irreversibility. In an <u>isolated system</u>, spontaneous processes <u>always</u> lead to an increase in the entropy of the system. Thus, even though the <u>energy</u> of an isolated system cannot change ($\Delta U = 0$), processes can occur within the system & will ultimately lead to a degradation of the "quality" of the energy of the system, i.e., loss of "available work".

Consider an isolated system comprised of a suspended mass (potential energy) & two thermal reservoirs at T_H & T_c ($T_H > T_c$).

Isolated System ($\Delta U = 0$)



Obviously, there are many ways to <u>distribute</u> the internal energy, U, of the system without violating the 1st-law. We could change the relative amounts of energy in each part of the system.

For Example, we could <u>dissipate</u> the mechanical work entirely into heat in either the T_H or T_c reservoir.

① $W \longrightarrow Q$ @ T_H {less degraded energy}

or

② $W \longrightarrow Q$ @ T_C {more degraded energy}

in both ① & ② the same amount of Q is Transferred. However, in process ② the energy is more degraded since heat in T_H can spontaneously flow from $T_H \rightarrow T_C$ but not in reverse.

The <u>simplest</u> quantitative expression we could come up with to rank the degree of degradation (or the degree of irreversibility) in these processes in that:

$$\Delta S_1 = \frac{Q}{T_H}$$

$$\Delta S_2 = \frac{Q}{T_C}$$

Note $\Delta S_2 > \Delta S_1$ ∴

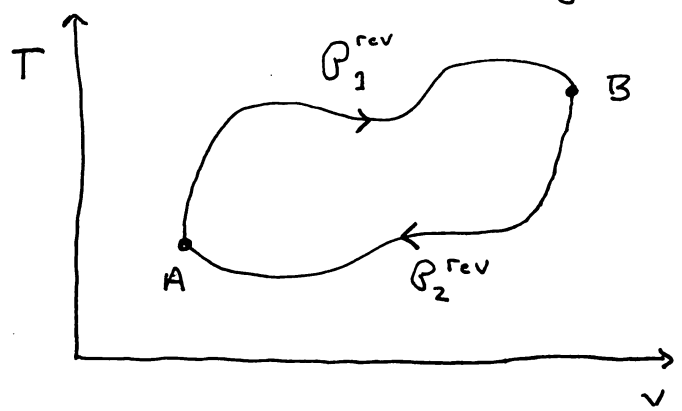
$$S_2 - S_1 = Q\left(\frac{1}{T_C} - \frac{1}{T_H}\right)$$

ΔS is a measure of the degree of irreversibility or the degree of degradation of energy.

S, Entropy as a State Function

Since $\oint dq_{rev}/T = 0$, this suggests that dq_{rev}/T is a total differential of a state function & That $\int_A^B dq_{rev}/T$ is independent of path.

To prove the path independence, consider two different reversible paths connecting A & B.



Together, the two paths form a complete cycle:

$$\oint \frac{dq_{rev}}{T} = \int_{A,P_1}^{B} \frac{dq_{rev}}{T} + \int_{B,P_2}^{A} \frac{dq_{rev}}{T} = 0$$

$$\Rightarrow \int_{A,P_1}^{B} \frac{dq_{rev}}{T} = -\int_{B,P_2}^{A} \frac{dq_{rev}}{T} = \int_{A,P_2}^{B} \frac{dq_{rev}}{T}$$

since P_2 is reversible

Thus, we can define a <u>New state function</u>, the <u>Entropy</u>, S, by the Equation:

$$\Delta S = S_B - S_A = \int_{A,P_{rev}}^{B} \frac{dq_{rev}}{T}$$

The Entropy is a state function, like H, U, P, etc. whereby S has a precise value for every equilibrium state of the system. ΔS between any two Equilibrium states is calculated by choosing any convenient reversible path connecting the two states, Then computing the above integral. Like the internal Energy, only changes in the Entropy can be determined from The above equation. However, we will see later That The 3rd law of Thermodynamics gives us a precise value of S @ T = 0K for all substances at Equilibrium. Therefore, an <u>Absolute</u> value S can be obtained for every Equilibrium state of The system.

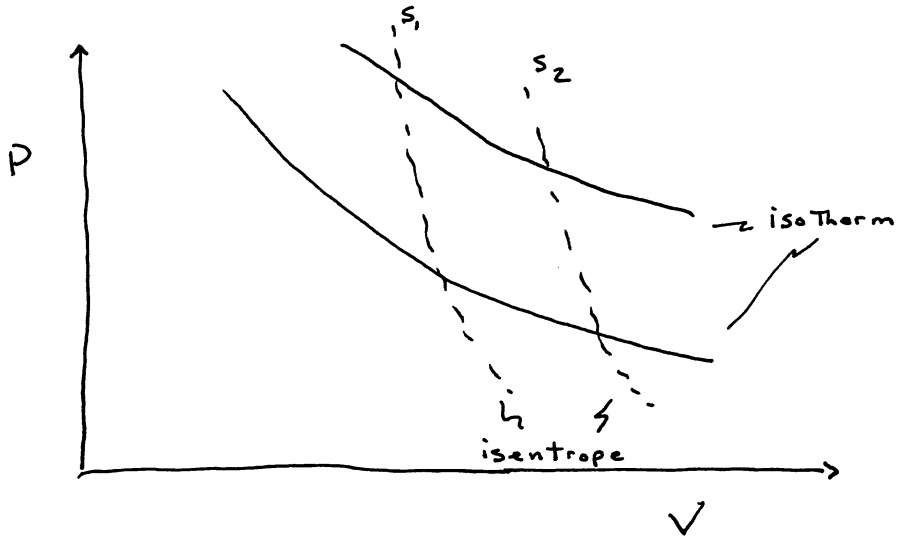
Isentropic Surfaces (constant S Surface)

recall, $dS = \frac{đq_{rev}}{T}$

Thus, along any reversible adiabat of the system,

$dS = 0$ reversible Adiabats "Isentrope"

Ideal Gas:



In this example, $S_2 > S_1$, since we have to Add heat to the system to go from $S_1 \rightarrow S_2$ surfaces.

ΔS along an isotherm:

$$đq_{rev} = dU - đw_{rev}$$

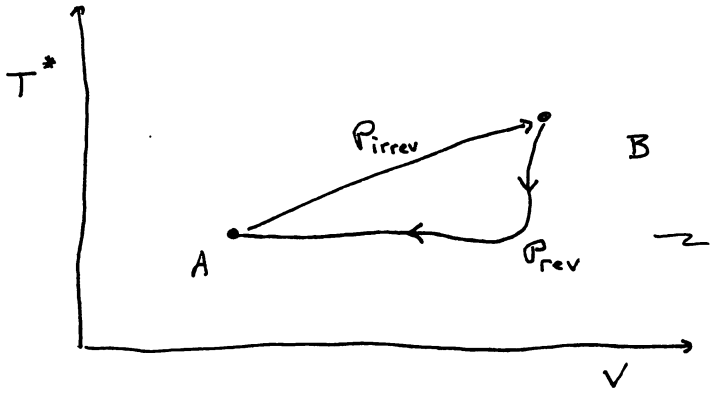
for an ideal gas, $đq_{rev} = C_v dT + \frac{NRT}{V} dV$

$$\Rightarrow dS = \frac{đq_{rev}}{T} = \frac{NR}{V} dV$$

$$\Delta S = NR \ln\left(\frac{V_2}{V_1}\right)$$

Relation between ΔS & Q for Irreversible Processes

Consider some irreversible process which brings the system from state A $\longrightarrow$ state B.



These two states can Always be connected by some reversible process.

From the Clausius Inequality, $\oint_{\text{cycle}} \frac{dq}{T^*} \leq 0$

$$\int_{A\ P_{irrev.}}^{B} \frac{dq}{T^*} + \int_{B\ P_{rev}}^{A} \frac{dq_{rev}}{T} \leq 0$$

$$\Rightarrow \int_A^B \frac{dq}{T^*} < -\int_B^A \frac{dq_{rev}}{T} = \int_A^B \frac{dq_{rev}}{T} \equiv \Delta S$$

So,

$$\boxed{\Delta S = S_B - S_A \geq \int_A^B \frac{dq}{T^*}}$$

also, for differential processes: $\underline{dS \geq dq/T^*}$

The entropy change of the system for irreversible processes is always greater than that determined from the heat flow alone.

Note, for any adiabatic process, $dq = 0$

$$\Delta S \geq \int \frac{dq}{T} \quad (dq = 0)$$

$$\Rightarrow \boxed{\Delta S \geq 0 \quad \text{for any Adiabatic process}}$$

This is a profound statement. It says that for any adiabatic process, the Entropy of the system cannot decrease. Only if the process is reversible will there be NO Entropy production within the system. For adiabatic irreversible processes there will always be Entropy Production within the system. This Entropy production results from the internal dissipation of available mechanical work which always accompanies an irreversible process.

Arrow of Time: Philosophically, we can generalize this statement to that of the universe. Since the universe is closed (we think), All processes that take place within the universe are adiabatic (consider the universe to be a closed system)

$$\Delta S_{\text{universe}} \geq 0 \quad \text{for all processes}$$

Entropy of the universe must always increase. Thus, The 2nd law imposes a directionality to time.

Entropy Exchange & Entropy Production

We have seen that we can change the entropy of a system by exchanging heat with the surroundings. We have also seen that we can produce entropy within the system for irreversible processes even if the process is adiabatic. These can be thought of as 2 distinct ways of changing the entropy of a system. We can thus write:

$$dS = d_e S + d_i S$$

$d_e S$ → Entropy Exchange with Surroundings

$d_i S$ → internal Entropy production

by definition, the Entropy Exchange term is given by:

$$\boxed{d_e S \equiv \frac{dQ}{T^*}}$$ Entropy Exchange

which can be positive or negative depending on the sign of dQ

Recall, from the 2nd law,

$$dS = d_e S + d_i S \geq \frac{dQ}{T^*}$$ for any process

$$\Rightarrow \boxed{d_i S \geq 0 \quad \text{for any process}}$$

Therefore, in general, in any irreversible process, there is always some internal Entropy production in the system (even in an adiabatic process).

This entropy production, d_iS, can be related to the work that could have been extracted from the system if the process was carried out reversibly. Instead, this available work energy is dissipated or degraded within the system resulting in entropy production.

Example of reversible isothermal expansion versus free Adiabatic Expansion of an Ideal Gas.

ΔS is the same in both cases. However, in the reversible case entropy increases arises from exchange with the surroundings and in the irreversible free expansion case, entropy arises from internal dissipation.

In reversible processes there is no internal entropy production $d_iS = 0$. Entropy changes within the system result from exchange of entropy between system and surroundings. In reversible processes, there are no dissipative processes acting. All available work is extracted from the system.

For a specified process we can break up dS into its exchange & internal parts:

Note, $$dS = \frac{\delta q_{rev}}{T} = \frac{dU - \delta w_{rev}}{T}$$

for a specified process, $$dU = \underbrace{\delta q + \delta w}_{\text{Actual quantities during process}}$$

$$\Rightarrow dS = \frac{\delta q}{T} + \frac{(\delta w - \delta w_{rev})}{T}$$

$$= \frac{\delta q}{T^*} + \frac{\delta q}{T} - \frac{\delta q}{T^*} + \frac{(\delta w - \delta w_{rev})}{T}$$

$$= \underbrace{\frac{\delta q}{T^*}}_{d_eS} + \underbrace{\delta q\left(\frac{1}{T} - \frac{1}{T^*}\right) + \frac{\delta w - \delta w_{rev}}{T}}_{d_iS}$$

$$dS = d_eS + d_iS$$

Note That both terms in d_iS are positive definite, so $d_iS \geq 0$

① $\delta q \left(\frac{1}{T} - \frac{1}{T^*} \right) \geq 0$

if $T^* > T$ Then $\delta q > 0$ as expected.

We saw before that this quantity is related to the work that could be extracted from the heat transfer if the process were carried out reversibly.

② $\frac{\delta w - \delta w_{rev}}{T} \geq 0$

Note: $-\delta w_{rev} > -\delta w$ always

$\Rightarrow \quad -\delta w_{rev} - (-\delta w) \geq 0$

This term represents the additional work that could have been extracted if the process were carried out reversibly.

In irreversible processes this work is instead dissipated within the system resulting in Entropy production.

Fundamental Equation for dS → Combined 1st & 2nd laws

Because S is a state Function we can calculate ΔS between any two Equilibrium states by connecting the two states with any reversible path,

$$\Delta S = S_B - S_A = \int_{P_{rev}}^{B}{}_{A} \frac{đq_{rev}}{T}$$

From the 1st law:

$$đq_{rev} = dU - đw_{rev}$$

↳ all reversible work terms

$$dS = \frac{1}{T} dU - \frac{1}{T} đw_{rev}$$

For Compression / Expansion work only,

Fundamental Eqn for dS

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

closed system w/ only PV work

or Since $dU = dH - d(PV) = dH - PdV - VdP$

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

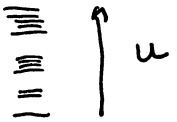
closed system w/ only PV work

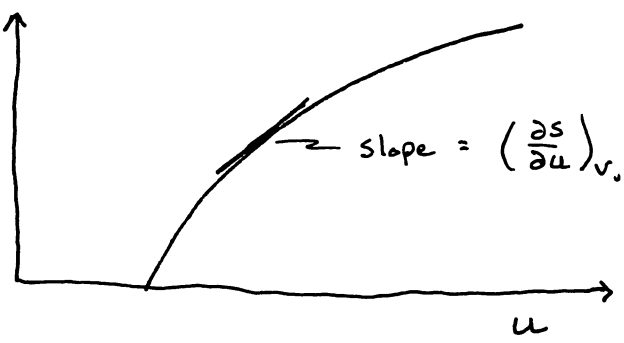
$$\Rightarrow \quad \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \left(\frac{\partial S}{\partial H}\right)_{P,N}$$

This Equality gives a formal thermodynamic definition of temperature.

Temperature is defined by the relationship between Entropy changes & Internal Energy changes

Available states increases with U





at low T's a small change in U results in a very large change in Entropy (low Quality)

Calculating ΔS — 2 Examples

I. Isochoric Heating ($\Delta V = 0$)

$$\boxed{dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV}$$ fundamental Eqn.

$$= \frac{C_V}{T}\,dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \cancel{dV}_{\to 0}$$

$$\boxed{dS = \frac{C_V}{T}\,dT \qquad \text{fixed } V, N}$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{C_V}{T}}$$ Thermodynamic Identity

Thus, $$S_2(T_2, V) - S_1(T, V) = \int_{T_1}^{T_2} \frac{C_V}{T'}\,dT' = C_V \ln\left(T_2/T_1\right)$$

* If C_V is not a function of temperature.

II. Isobaric Heating

$$dS = \frac{1}{T}\,dH - \frac{V}{T}\,dP$$

$$= \frac{C_P}{T}\,dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_V - V\right] \cancel{dP}_{=0}$$

$$\boxed{dS = \frac{C_P}{T}\,dT \qquad @ \text{ fixed } P, N}$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial T}\right)_{P,N} = \frac{C_P}{T}}$$ Thermodynamic Identity

Thus, $$S_2(T_2, P) - S_1(T_1, P) = \int_{T_1}^{T_2} \frac{C_P}{T'}\,dT' = C_P \ln\left(T_2/T_1\right)$$

* If C_P is not a function of Temperature.

III Isothermal Expansion $\{ V_1 \to V_2 \quad w/ \quad \Delta T = 0 \}$

$$\boxed{dS = \frac{1}{T} dU + \frac{P}{T} dV}$$ fundamental Eqn.

Now expanding dU in terms of T & V

$$dS = \frac{1}{T} \left\{ C_V \, dT + \left(\frac{\partial U}{\partial V} \right)_T dV \right\} + \frac{P}{T} dV$$

$$= \frac{C_V}{T} dT + \left[\frac{1}{T} \left(\frac{\partial U}{\partial V} \right)_T + \frac{P}{T} \right] dV$$

recall, $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$

$$\boxed{dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV}$$ Expansion of S in Terms of T & V

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V}$$ Thermodynamic Identity (Maxwell Relation)

for isothermal Expansion,

$$\Delta S = S(V_2, T) - S(V_1, T) = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T} \right)_V dV$$ fixed T

for ideal gas, $\left(\frac{\partial P}{\partial T} \right)_V = \frac{NR}{V}$

$$\Rightarrow \Delta S = NR \int_{V_1}^{V_2} \frac{dV}{V} = NR \ln \left(\frac{V_2}{V_1} \right)$$ ideal gas

for VDW, $\left(\frac{\partial P}{\partial T} \right)_V = \frac{NR}{V - Nb}$

$$\Rightarrow \Delta S = NR \ln \left(\frac{V_2 - Nb}{V_1 - Nb} \right)$$ VDW gas

IV Isothermal Expansion $\{P_1 \to P_2$ at $\Delta T = 0\}$

$$\boxed{dS = \frac{1}{T}\,dH - \frac{V}{T}\,dP}$$ fundamental Eqn.

Now expand dH in terms of T & P

$$dS = \frac{1}{T}\left[C_P\,dT + \left(\frac{\partial H}{\partial P}\right)_T dP\right] - \frac{V}{T}\,dP$$

$$= \frac{1}{T}\,C_P\,dT + \left[\frac{1}{T}\left(\frac{\partial H}{\partial P}\right)_T - \frac{V}{T}\right] dP$$

recall, $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$

$$\Rightarrow \boxed{dS = \frac{C_P}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP}$$ Expansion of S in terms of T & P

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$ Thermodynamic Identity (Maxwell Reln)

for isothermal Expansion,

$$\Delta S \equiv S(P_2, T) - S(P_1, T) = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP$$ fixed T

for Ideal gas $\left(\frac{\partial V}{\partial T}\right)_P = \frac{NR}{P}$

$$\Delta S = -\int_{P_1}^{P_2} \frac{NR}{P}\,dP = -NR\ln\left(P_2/P_1\right)$$ for ideal gas.

T Dependence of S & Heat Capacities

For the fundamental equation for dS we have:

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV \qquad \text{fixed } N \text{ (closed)}$$

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{C_V}{T}$$

Also,

$$dS = \frac{1}{T}\,dH - \frac{V}{T}\,dP \qquad \text{fixed } N \text{ (closed)}$$

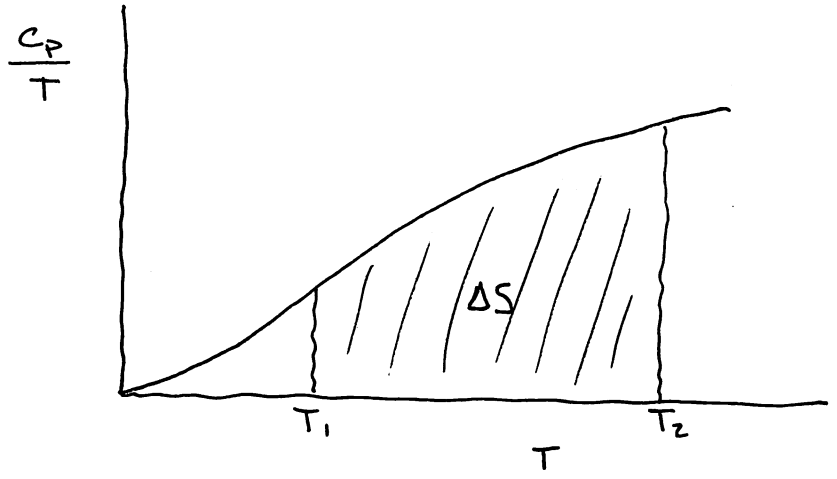
$$\left(\frac{\partial S}{\partial T}\right)_{P,N} = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{P,N} = \frac{C_P}{T}$$

isochoric Heating:

$$S_2(T_2, V) - S_1(T_1, V) = \int_{T_1}^{T_2} \frac{C_V}{T'}\,dT'$$

isobaric Heating:

$$S_2(T_2, P) - S_1(T_1, P) = \int_{T_1}^{T_2} \frac{C_P}{T'}\,dT'$$

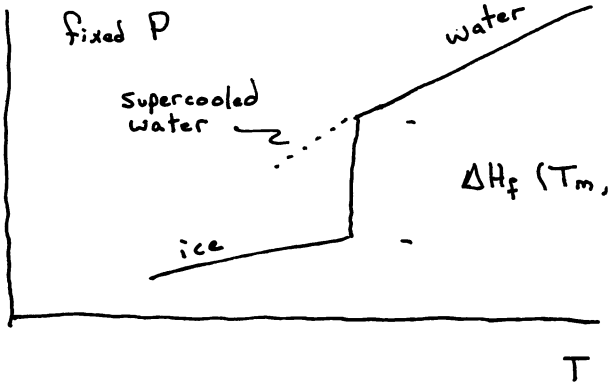


ΔS of phase transformations

recall, $dS = \frac{dq_{rev}}{T}$

Thus, to calculate $\Delta S_{\alpha \to \beta} = S_\beta(T,P) - S_\alpha(T,P)$ between the two phases α & β, we must connect the two phases via a <u>reversible thermodynamic path</u>.

For Example, consider the melting of ice. Only at the melting point, T_m, is the transformation between ice and water reversible.



$\Delta H_f(T_m,P) \equiv$ Heat of fusion at the melting pt.

$$\boxed{\Delta S_f(T_m,P) = \frac{\Delta H_f(T_m,P)}{T_m}} = \frac{Q_{rev}}{T_m}$$

Entropy change of melting (fusion) at the melting pt.

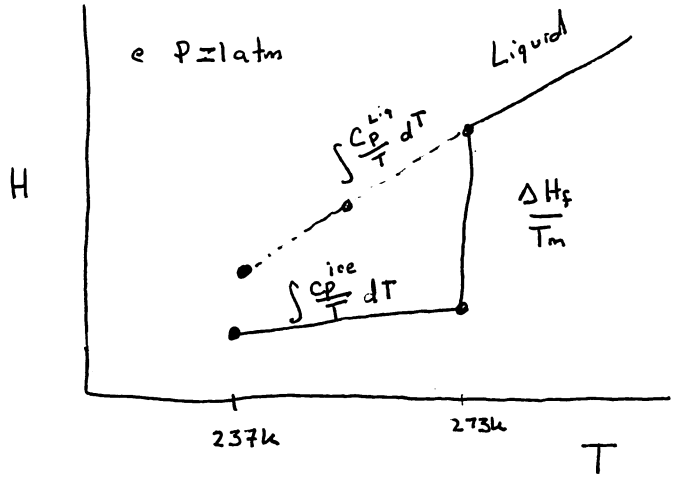
$$\boxed{\Delta S_{vap}(T_b,P) = \frac{\Delta H_{vap}(T_b,P)}{T_b}}$$

Entropy change of vaporization at the boiling point, T_b.

It is important to point out that we can only use this formula <u>at the Equilibrium melting or boiling point</u>.

If we need $\Delta S_{\alpha \to \beta}$ at any other temperature, we must connect the states via a reversible path.

Typically, we use C_p data to connect the entropy of the phase to the phase equilibrium temperature, i.e.,



$$S^{water}(237k, 1atm) - S^{ice}(237k, 1atm) =$$

$$\int_{237}^{273} \frac{C_p^{ice}}{T'} dT' + \frac{\Delta H_f}{273k} + \int_{273}^{237} \frac{C_p^{water}}{T'} dT' \left(\neq \frac{\Delta H_f(237k)}{237k} \right)$$

In general, for phase transformations between any 2 phases:

$$\Delta S_{\alpha \to \beta} \equiv \frac{\Delta H_{\alpha-\beta}(T_{\alpha-\beta})}{T_{\alpha-\beta}}$$

where $T_{\alpha-\beta} \equiv$ Equilibrium transition temp.

Volume dependence of S

Recall the fundamental Equation,

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

isothermal reversible expansion of an ideal gas

for an ideal gas, $dU = 0$ (if the path is isothermal)

$$dS = \frac{P}{T} dV \qquad \text{"isoergic" path}$$

$$\Delta S = \int_{V_1}^{V_2} \frac{P}{T} dV = \int_{V_1}^{V_2} \frac{NR}{V} dV = NR \ln V_2/V_1$$

this eqn. is only valid for an ideal Gas.

What about a non-ideal gas? Here, isothermal does NOT imply isoergic. In general, we will have

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

if there is no phase change, we can expand dU in Terms of T & V

$$dS = \frac{1}{T}\left[C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \right] + \frac{P}{T} dV$$

or

$$dS = \frac{C_V}{T} dT + \left[\frac{P}{T} + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T \right] dV$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Thus, we need to know $\left(\partial U/\partial V\right)_T$ if we are to proceed!

We will see later that the volume derivative of the Entropy is related to the temperature derivative of the pressure through a <u>Maxwell Relation</u>.

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

Thermodynamic Identity
Maxwell Relation

$$\Longrightarrow \quad dS = \frac{C_V}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

<u>*</u> Isothermal expansion of an ideal gas:

$$dS = \frac{C_V}{T}\,\cancel{dT}^{\,=0} + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$P = \frac{NRT}{V} \quad \Rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{NR}{V}$$

$$dS = \frac{NR}{V}\,dV \qquad \text{ideal gas, isothermal}$$

$$\boxed{\Delta S = NR \ln\left(\frac{V_2}{V_1}\right)} \qquad \text{ideal gas only}$$

Pressure Dependence of S

$$dS = \frac{1}{T}\,dH - \frac{V}{T}\,dP$$

Fundamental Equation (closed system)

Expanding H in T & P

$$dS = \frac{C_P}{T}\,dT + \left[\frac{1}{T}\left(\frac{\partial H}{\partial P}\right)_T - \frac{V}{T}\right] dP$$

$$\downarrow$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Thus, to proceed we need $\left(\frac{\partial H}{\partial P}\right)_T$

we shall show later that the pressure derivative of S is related to the T derivative of V through an addition Maxwell Relation.

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

thermodynamic Identity Maxwell Relation

$$\Rightarrow dS = \frac{C_P}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

Example, isothermal Expansion of an ideal gas (repeat of p. 72)

$$\Rightarrow dS = \frac{C_P}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dS = -\left(\frac{\partial V}{\partial T}\right)_P dP \qquad V = \frac{NRT}{P}$$

$$= -\frac{NR}{P}\,dP$$

$$\Delta S = -NR \ln P_2/P_1$$

We can obtain the relation between T & V along the isoergic path by the following :

$$dT = \left(\frac{\partial T}{\partial V}\right)_{u,N} dV$$

we have expanded T in Terms of V & u and then recognize. That u is fixed along the path.

$$dT = -\left(\frac{\partial T}{\partial u}\right)_{V,N} \left(\frac{\partial u}{\partial V}\right)_{T,N} dV$$

recall, $\left(\frac{\partial T}{\partial u}\right)_{V,N} = \frac{1}{C_V}$

&

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\Rightarrow dT = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

for van der Waals, $P = \frac{NRT}{V-Nb} - a\frac{N^2}{V^2}$

$$\Rightarrow dT = -\frac{aN^2}{C_V V^2} dV$$

integrating along the path & assuming C_V is a constant,

$$T(V) = T_1 + \frac{aN^2}{C_V}\left[\frac{1}{V} - \frac{1}{V_1}\right]$$

Entropy Calculation : Irreversible Processes

Because S is a state function, as long as we know the initial & final states we can calculate ΔS regardless of whether the process was reversible or irreversible. We need only connect the two states via a reversible path and then compute ΔS along the reversible path from:

$$\Delta S = \int_{P_{rev}} \frac{dq_{rev}}{T}$$

Example: Consider the free adiabatic expansion of a real gas.

This is a highly irreversible process where,

$$V_1 \longrightarrow V_2$$

If the gas is NON-Ideal there will also be a temperature change $T_1 \longrightarrow T_2$

For any gas, real or ideal, the Energy does not change in a free adiabatic expansion.

$$\Delta U = 0 \qquad U_1 \rightarrow U_1 \qquad \text{"isoergic"}$$

There are several different ways that we can go about solving this problem. In A first step, since we know ΔV & ΔU we can expand $S(U,V)$:

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV$$

} also a fundamental Eqn.

Since $\Delta U = 0$ (free adiabatic Expansion)

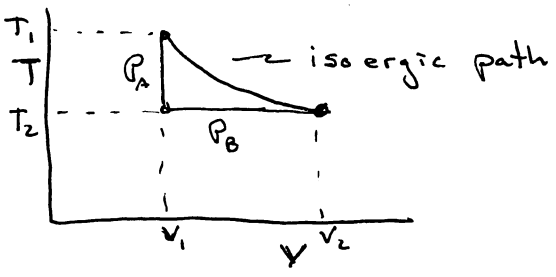
$$\int dS = \int_{V_1}^{V_2} \frac{P}{T}\, dV \qquad \text{isoergic path}$$

van der Waals :

$$P = \frac{NRT}{V-Nb} - a\frac{N^2}{V^2}$$

$$\Delta S = \int_{V_1}^{V_2} \frac{NR}{V-Nb} - a\frac{N^2}{TV^2}\, dV$$

The difficulty here is that T is NOT constant along the isoergic path. Thus, to carry out the integral we would need to know $T(V)$ along the isoergic path.



As long as the initial & final states are the same it doesn't matter the path. Therefore, one way to approach This is along the constant T & V paths :

P_A

$$\Delta S_A = \int_{T_1}^{T_2} \frac{C_V}{T}\, dT = C_V \ln T_2/T_1$$

where $T_2 = T_1 + a\frac{N^2}{C_V}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$

P_B

$$\Delta S_B = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV = \int_{V_1}^{V_2} \frac{NR}{V-Nb}\, dV$$

$$= NR \ln\left(\frac{V_2 - Nb}{V_1 - Nb}\right)$$

$$\Delta S_{Total} = \Delta S_A + \Delta S_B$$

Now we can go back to our integral Equation for ΔS:

$$\Delta S = \int_{V_1}^{V_2} \frac{NR}{V-Nb} - a\frac{N^2}{TV^2}\, dV$$

$$\hookrightarrow T(V) = T_1 + a\frac{N^2}{C_v}\left(\frac{1}{V} - \frac{1}{V_1}\right)$$

Plugging in for $T(V)$ we have:

$$\Delta S = NR \ln\left(\frac{V_2 - Nb}{V_1 - Nb}\right) - aN^2 \int_{V_1}^{V_2} \frac{1}{V^2\left[T_1 + a\frac{N^2}{C_v}\left(\frac{1}{V} - \frac{1}{V_1}\right)\right]}\, dV$$

$$= NR \ln\left(\frac{V_2 - Nb}{V_1 - Nb}\right) - aN^2 \int_{V_1}^{V_2} \frac{1}{T_1V^2 + a\frac{N^2}{C_v}V - a\frac{N^2}{C_v}\frac{V^2}{V_1}}\, dV$$

The final integral is messy!

- but would be no problem for numerical integrators.

Extremum Principle

Recall from the 2nd law, $dS \geq \frac{dq}{T^*}$

> Thus, for any adiabatic process, ($dq = 0$)
>
> $\Rightarrow dS \geq 0$ Entropy of the system must increase in any adiabatic process

This equation holds regardless if any mechanical work is performed on or by the system.

It is convenient to express the 2nd law in terms of system thermodynamic variables. Using the 1st law we can write, $dq = dU - dw$

$$\Rightarrow dS \geq \frac{dq}{T^*} = \frac{1}{T^*} dU + \frac{P^*}{T^*} dV$$

{ compression/Expansion work in a closed system

From this Eqn. we can note that if both U & V of the system are fixed ($dU = 0$ & $dV = 0$), we call this an "isolated system", then

> $dS \geq 0$ for any processes in an isolated system ($dU = 0$, $dV = 0$, $dN = 0$)

In an isolated system there is no energy exchange with the surroundings ($dq = 0$ & $dw = 0$). An equivalent way to state this is that $dU = 0$ & $dV = 0$. In an isolated system, the entropy of the system must increase for any spontaneous process.

Thus, in an isolated system, the entropy must always increase, i.e., any process that occurs results in an increase in entropy of the system.

At some point, an isolated system will reach thermodynamic Equilibrium & will cease to change. This final Equilibrium state represents that state with the <u>maximum possible Entropy</u>. Any hypothetical process originating from the Equilibrium state results in a decrease in the Entropy of the system.

The above development allows us to establish an <u>Extremum Principle</u> for determining the final Equilibrium state of an isolated system:

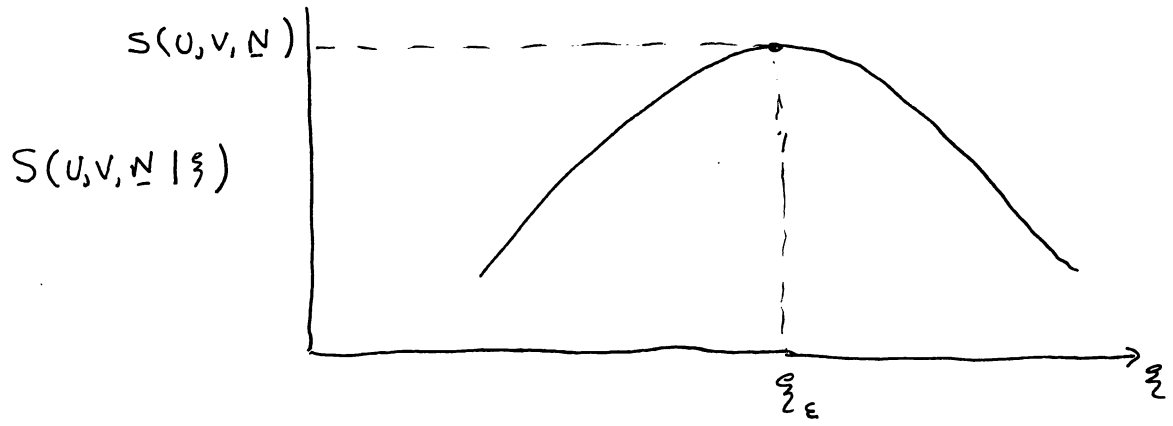
> In an <u>isolated system</u>, (U, V & N fixed) The final Equilibrium state is that state which maximizes the System's Entropy

Callen Postulate II

Mathematically, we can write this:

$$S(U,V,N) = \max_{\xi} \{ S(U,V,N \mid \xi) \}$$

where ξ represents any "internal" constraint on the Energy or mass distribution within the system. In principle, we could calculate $S(U,V,N \mid \xi)$ for any "constrained" state. If we removed the constraint, the final Equilibrium state would be identical to that constrained state which maximizes the Entropy of the system.



$\xi_\varepsilon \equiv$ Equilibrium mass or Energy distribution.

Formally, we can write:

$$\left(\frac{\partial S}{\partial \xi}\right)_{U,V,\underline{N}} = 0 \qquad \text{at Equilibrium}$$

Much of thermodynamics involves calculation to determine or predict the final Equilibrium state, i.e., the extent of a chemical Reaction or the Equilibrium phase assemblage of a system. In an <u>isolated</u> system we would calculate the Entropy, S, of the system as a function of the Extent of a reaction, ξ. The final state will be that where $S(\xi)$ at fixed $U, V, \underline{N}$ is a <u>maximum</u>.

<u>Callens Postulate III</u>

Entropy of a composite system is additive over the constituent subsystems (i.e. Extensive Property). S is continuous & differentiable & is a monotonically increasing function of the Energy.

Entropy & Disorder

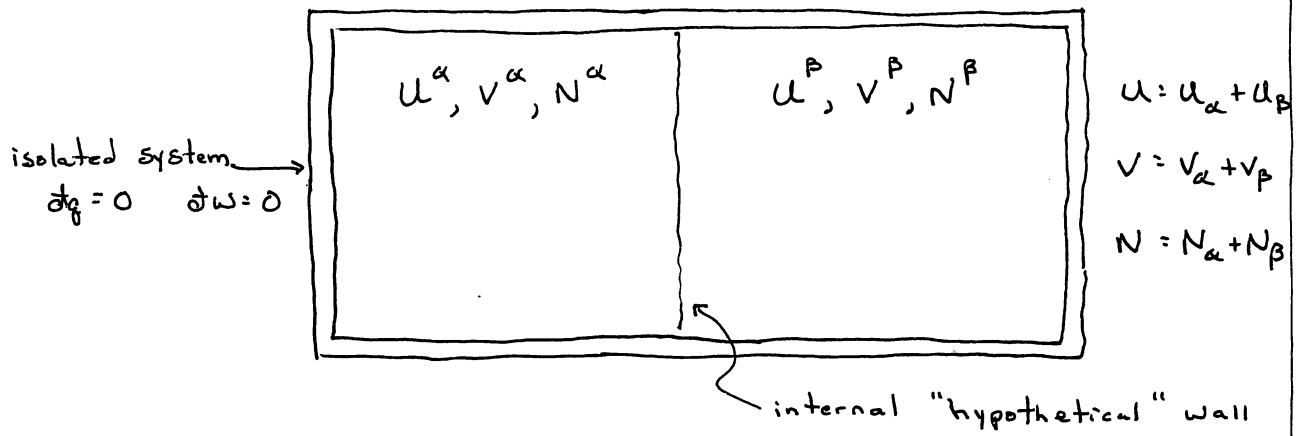
We have seen from the 2nd law, that the final Equilibrium state of an isolated system (U, V, N fixed) is that state which maximizes the entropy.

An alternative approach to determining this final state would be to apply statistical probability theory at the microscopic level. In this approach we would state that the Equilibrium state of an isolated system is that state which has the greatest probability.

Thus we see that there must be a relationship between Entropy & microscopic probability.

This is the subject of a discipline known as Statistical Mechanics — which makes possible the link between the microscopic & macroscopic. We will not have the time to discuss this discipline in much detail now. We will only try to motivate one of its most important concepts → The relationship between Entropy & the State of disorder. This relationship will help to provide a better intuition of Entropy & will help us understand the macroscopic thermodynamics behavior of a system in terms of behavior at the microscopic level.

Consider, for example, an isolated system in thermodynamic equilibrium. Lets hypothetically break this system up into 2 parts ($\alpha + \beta$):



Suppose $\Omega(U,V,N)$ is the number of distinguishable microscopic configurations ("microstates") available to a system at fixed U, V, N. By the laws of statistical Probability theory we can also write:

$$\Omega(U,V,N) = \Omega^\alpha(U^\alpha, V^\alpha, N^\alpha) \cdot \Omega^\beta(U^\beta, V^\beta, N^\beta)$$

From thermodynamics we know that the Entropy is an Extensive state function. Hence,

$$S(U,V,N) = S^\alpha(U^\alpha, V^\alpha, N^\alpha) + S^\beta(U^\beta, V^\beta, N^\beta)$$

The only mathematical relationship between S & Ω that is consistent with the above 2 equations is that

$$\boxed{S(U,V,N) = k_B \ln \Omega(U,V,N)}$$

Boltzmann Equation

where k_B is a proportionality constant, "Boltzmann Constant"

$$k_B = 1.3806 \times 10^{-23} \ J/K \cdot \text{molecule}$$

Example: |↑↓↑| |↑↓↑| 3 $I = 1/2$ spins on each side

Thermal vs Configurational Entropy

It is often the case that we can conceptually separate the entropy of a system into two parts → a structural configurational part and a dynamical (or thermal) part. This separation is best viewed in the classical mechanical picture where the microstate of the system is specified when we specify both the position, $\underline{x}$, and momentum, $\underline{p}$, of all of the particles in the system.

$$\{ \underset{\sim}{x}_1, \underset{\sim}{x}_2, \cdots \underset{\sim}{x}_n ; \underset{\sim}{p}_1, \underset{\sim}{p}_2, \cdots \underset{\sim}{p}_n \}$$ single microstate of n-particle system

In the classical picture we can express Ω, the total # of microstates available to the system, as the product:

$$\boxed{\Omega = \Omega^{dyn.} \Omega^{config.}}$$ for a given u, V, N

where $\Omega^{conf.}$ represents the # of distinguishable ways the particles can be distributed over the space available and $\Omega^{dyn.}$ represents the number of ways in which the kinetic energy of the particles can be distributed.

$$\boxed{S = S^{dyn.} + S^{config.}}$$

I. Example : Entropy of Ideal Gas

We can change the entropy of a gas by changing either its volume or its energy. Volume changes of an ideal gas lead to changes in the <u>configurational</u> contribution to the entropy while temperature changes result in changing the <u>dynamic</u> contribution.

<u>Isothermal Expansion</u> : $V_1 \rightarrow V_2$ $\quad \Delta T = 0$

Since the particles of an ideal gas are independent, the total # of distinguishable microstates available to the gas is proportional to V^n :

$$\Omega^{\text{config.}} = \frac{V^n}{n!} \qquad n = \text{total \# molecules}$$

we divide by $n!$ since the gas molecules are indistinguishable (assuming a pure gas)

Note:
$\log_a(x^n) = n \log_a(x)$
$\log_a(xy) = \log_a x + \log_a y$

$$\Rightarrow \quad S^{\text{config}}(V) = k_B \ln \Omega^{\text{config.}}$$

$$\Delta S = S_2(V_2) - S_1(V_1) = k_B \ln\left(\frac{\Omega_2}{\Omega_1}\right)$$

$$= k_B \ln\left(\frac{V_2}{V_1}\right)^n = n k_B \ln\left(\frac{V_2}{V_1}\right)$$

$$= n\,(R/N_0) \ln\left(\frac{V_2}{V_1}\right)$$

$$\boxed{\Delta S = NR \ln\left(\frac{V_2}{V_1}\right)}$$

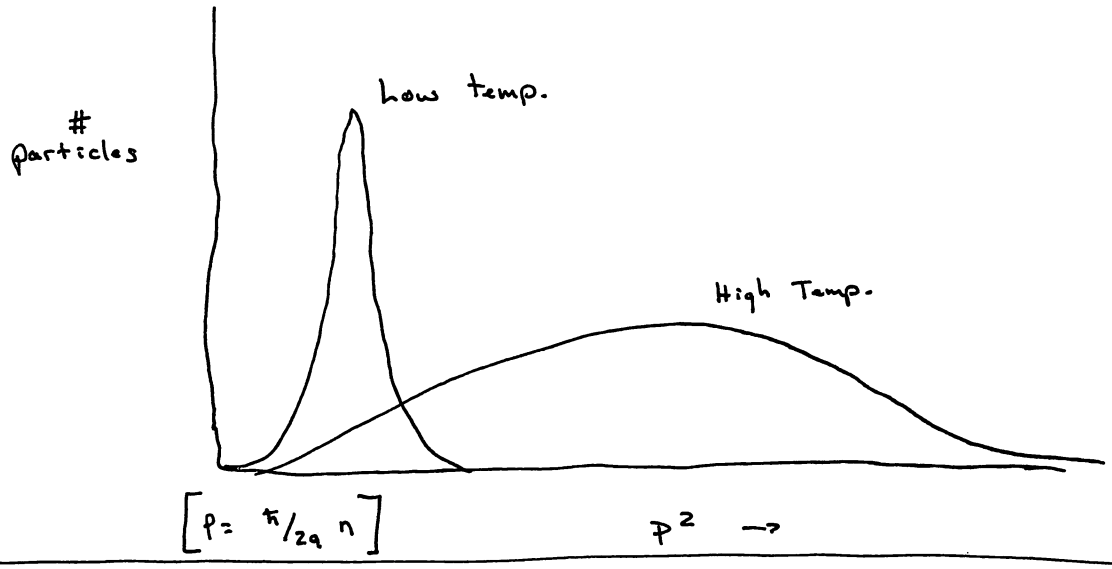
$R \equiv N_0 k_B$

$N_0 \equiv$ Avogadro's #

$N \equiv$ # moles

Isocheric Heating $T_1 \rightarrow T_2$ $\Delta V = 0$

On heating a gas at constant volume, the average kinetic energy of the gas increases. As we increase this energy there is a larger & larger number of momentum states the particles can exist in. From the kinetic theory of gases we know that the distribution of momentum states depends on the temperature of the gas:



Note: $\mathcal{E}_i = \frac{k^2}{2ma^2}(n_{xi}^2 + n_{yi}^2 + n_{zi}^2)$

$\Phi(E) = \frac{1}{8}\left(\frac{4\pi R^3}{3}\right)$

$R^2 = \frac{2ma^2 E}{\hbar^2}$

$\Phi(E) \propto E^{3/2} V$ for 1 particle

$\Phi(E) = E^{3/2\, n} V^n$ for n particles

$\Omega(E) = \partial\Phi/\partial E$

$\approx 3/2\, n\, E^{3/2 n - 1} V^n$

$\sim 3/2\, n\, E^{3/2 n} V^n \quad n \gg 1$

The average momentum & the width of the momentum distribution both increase w/ Temp. It can be shown that:

$\Omega^{\text{Trans}} \propto T^{3/2\, n}$ Translational momentum states

$\Rightarrow \Delta S = S_2(T_2) - S_1(T_1) = \underbrace{\frac{3}{2} NR}_{C_V} \ln\left(\frac{T_2}{T_1}\right)$

which is the same result we obtained previously for a monatomic gas!

II. Example : Vaporization

The entropy change associated with vaporization primarily arises from a change in the configurational entropy :

For a liquid : $\Omega^{conf.} = \frac{V_{liq}^n}{n!}$

For a gas : $\Omega^{conf.} = \frac{V_{gas}^n}{n!}$

$$\Delta S_{vap} = k_B \ln \left(\frac{V_{gas}}{V_{liq}} \right)^n$$

So for water $V_{liq} = 1 cm^3$
$V_{gas} = 22 \times 10^3 cm^3$

$\sim NR \ln \frac{22 \times 10^3}{1} = 83 J/mol \cdot K$

$$\boxed{\Delta S_{vap} = NR \ln \left(\frac{V_{gas}}{V_{liq}} \right)}$$

III. Example : melting

The entropy change associated with melting also primarily arises from a change in the configurational entropy. The only difference from the above example of vaporization is that the molecules in a crystal <u>are</u> distinguishable. They reside on specified lattice points. In a crystal the atoms are confined to a small <u>cell volume</u> $\sim V/N$. Whereas, in a liquid each molecule can diffuse over the entire volume of the system.

$$\Omega_{solid}^{conf} = \left(\frac{V_{solid}}{n} \right)^n$$

$$\Omega_{liq.}^{conf} = \left(\frac{V_{liquid}}{n!} \right)^n$$

$$\Delta S_{melting} = k_B \ln\left(\frac{V_{Liquid}^{n}}{n!}\right) - k_B \ln\left(\frac{V_{solid}}{n}\right)^{n}$$

$$= n k_B \ln V_{Liq.} - k_B \ln n! - n k_B \ln V_{solid} + n k_B \ln n$$

Stirling's formula : $\boxed{\ln n! \sim n \ln n - n \quad \text{valid for large } n}$

$$\Rightarrow \quad \Delta S_{melting} = n k_B \ln\left(\frac{V_{liq}}{V_{sol}}\right) - n k_B \ln n + n k_B + n k_B \ln n$$

$$\boxed{\Delta S_{melt} = NR \ln\left(\frac{V_{liq}}{V_{sol}}\right) + NR}$$

if $V_{Liq} \sim V_{sol}$ $\quad \boxed{\Delta S_{melt} \sim NR}$

This rule is qualitatively observed for a number of simple liquids.

IV Example: Entropy of Mixing (on a lattice)

Consider the entropy of mixing two different atom types A & B on a crystal lattice

$n_A \equiv$ # A type atoms

$n_B \equiv$ # B type atoms

if these atoms are mixed randomly on a lattice of $n_A + n_B$ sites, the number of distinguishable configurations, Ω_{mix}, is given by:

$$\Omega_{mix} = \frac{(n_A+n_B)!}{n_A! + n_B!}$$

this can be compared to a completely ordered lattice where,

$$\Omega_{ordered} = 1$$

$$\Rightarrow \quad \Delta S_{mix} = k_B \ln\left(\frac{\Omega_{mix}}{\Omega_{ordered}}\right)$$

$$= k_B \ln (n_A+n_B)! - k_B \ln n_A! - k_B \ln n_B!$$

Applying Stirling's formula:

$$\frac{\Delta S_{mix}}{k_B} = (n_A+n_B)\ln(n_A+n_B) - (n_A+n_B) - n_A \ln n_A + n_A - n_B \ln n_B + n_B$$

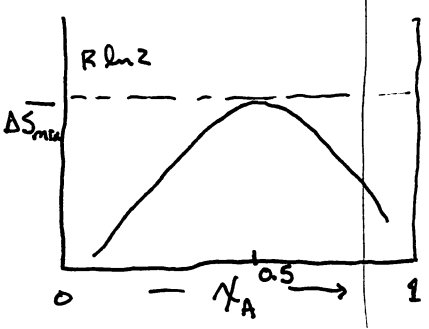
$$= -n_A \ln\left(\frac{n_A}{n_A+n_B}\right) - n_B \ln\left(\frac{n_B}{n_A+n_B}\right)$$

$$\Rightarrow \Delta S_{mix} = -N_A R \ln \chi_A - N_B R \ln \chi_B$$

$(n_A = N_A N_0, \; n_B = N_B N_0)$ where, $\chi_A \equiv N_A/(N_A+N_B)$ (mole fraction) $\quad \chi_B \equiv N_B/(N_A+N_B)$

Molar Entropy of mixing:

$$\Delta\bar{S}_{mix} \equiv \frac{\Delta S_{mix}}{N_A+N_B} = -R\chi_A \ln \chi_A - R\chi_B \ln \chi_B$$



or in general for S species $\quad \Delta S_{mix} = -R \sum_i^S \chi_i \ln \chi_i$

IV Example: Entropy of mixing (Liquid or gas)

Consider the entropy change associated with mixing two different molecular species, A & B, in a liquid or gas.

$$\Omega_{pure} = \frac{V_A^{n_A}}{n_A!} \cdot \frac{V_B^{n_B}}{n_B!}$$

n_A	n_B
V_A	V_B

$$\Omega_{mix} = \frac{(V_A + V_B)^{n_A + n_B}}{n_A!\, n_B!}$$

assuming that there is no volume change on mixing.

$$\Delta S_{mix} = k_B \ln \left\{ \frac{(V_A + V_B)^{n_A + n_B}}{V_A^{n_A} V_B^{n_B}} \right\}$$

$$= k_B (n_A + n_B) \ln (V_A + V_B) - k_B n_A \ln V_A - k_B n_B \ln V_B$$

$$= k_B n_A \ln \left(\frac{V_A + V_B}{V_A} \right) + k_B n_B \ln \left(\frac{V_A + V_B}{V_B} \right)$$

$$\boxed{\Delta S_{mix} = N_A R \ln \left(\frac{V_A + V_B}{V_A} \right) + N_B R \ln \left(\frac{V_A + V_B}{V_B} \right)}$$

if the gases are ideal & were initially at the same pressure, P, then

$$V_A = \frac{N_A RT}{P} \quad \& \quad V_B = \frac{N_B RT}{P}$$

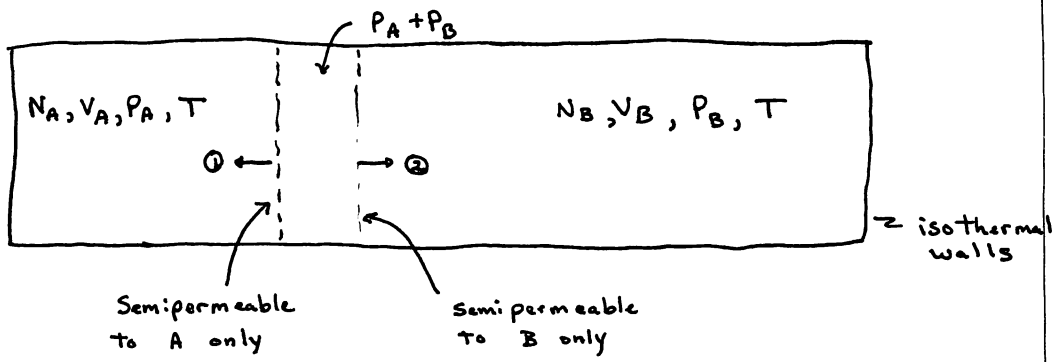
$$\Rightarrow \Delta S_{mix} = N_A R \ln \left(\frac{N_A + N_B}{N_A} \right) + N_B R \ln \left(\frac{N_A + N_B}{N_B} \right)$$

$$\boxed{\Delta S_{mix} = -N_A R \ln \chi_A - N_B R \ln \chi_B}$$ ideal gas

Example V – from a different perspective

Entropy of mixing of Ideal Gases – from the 2nd law:

2 pure gases initially separated & unmixed.



(Note: Since we can separate the gases via a semipermeable membrane, then the gases must be distinguishable.)

Now we reversibly move each partition to each wall under isothermal conditions. The entropy change can be viewed as a sum of two reversible expansions:

$$\Delta S_{①} = \int \frac{dq_{rev}}{T} = \int_{V_B}^{V_B+V_A} \frac{P_B}{T}\,dV = \int_{V_B}^{V_B+V_A} \frac{N_B R}{V}\,dV = N_B R \ln\left(\frac{V_A+V_B}{V_B}\right)$$

$$\Delta S_{②} = \int \frac{dq_{rev}}{T} = \int_{V_A}^{V_A+V_B} \frac{P_A}{T}\,dV = \int_{V_A}^{V_A+V_B} \frac{N_A R}{V}\,dV = N_A R \ln\left(\frac{V_A+V_B}{V_A}\right)$$

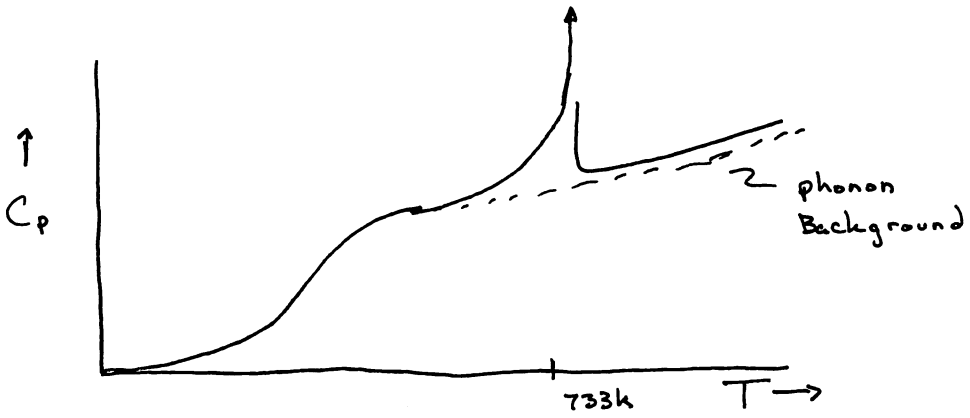
$$\Delta S_{mix} = \Delta S_{①} + \Delta S_{②} = N_A R \ln\left(\frac{V_A+V_B}{V_A}\right) + N_B R \ln\left(\frac{V_A+V_B}{V_B}\right)$$

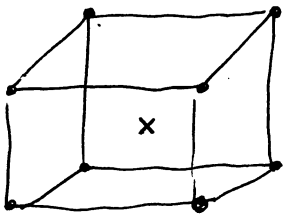
which is the same result as we obtained before.

VI Example: Heat Capacity Anomalies → Configurational Entropy

We would normally Expect the thermal motion of the atoms of a material to increase Smoothly as the temperature rises. In some materials it is found that Superimposed on the Smoothly varying vibrational heat capacity, There is an extra contribution which appears as a relatively sharp peak – heat capacity anomaly. The rapid rise in the heat capacity associated with the anomaly indicates a rapid change in order in the substance. At temperatures below the anomaly, Some aspect of the system is relatively ordered & above the anomaly this aspect is completely disordered. This is called an order-disorder transition.

Example → Specific heat of β-brass (50:50 Cu-Zn Alloy)





• Cu
x Zn

bcc lattice

well below 733k Cu & Zn are nearly perfectly ordered on a bcc lattice. Near 733k the atoms become randomly disordered on the lattice.

The molar Entropy:

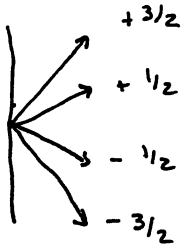
$$\Delta \bar{S}_{mix} = -R\ \tfrac{1}{2} \ln \tfrac{1}{2} - R\ \tfrac{1}{2} \ln \tfrac{1}{2} = \underline{R \ln 2}$$

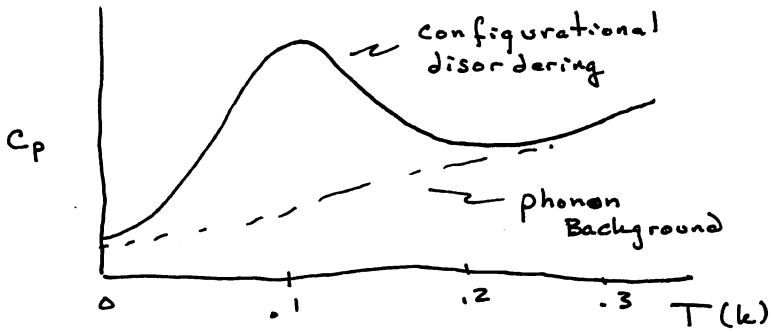
VII Example - Curie Point → magnetic ordering in a paramagnetic salt.

In paramagnetic salts, the heat capacity anomaly is typically within a few degrees of 0 K. This anomaly results from a change in the magnetic order, another example of an order-disorder transition involving one aspect of the Entropy.

Consider chromium potassium alum salt:

Cr^{+3} is a spin 3/2 ions. ∴ there are four possible orientations for the spin dipole.





At low temperatures ferromagnetic domains form where all the spins are alligned in the same direction. Near the heat capacity anomaly the spin orientations become disordered ∴ uncorrelated.

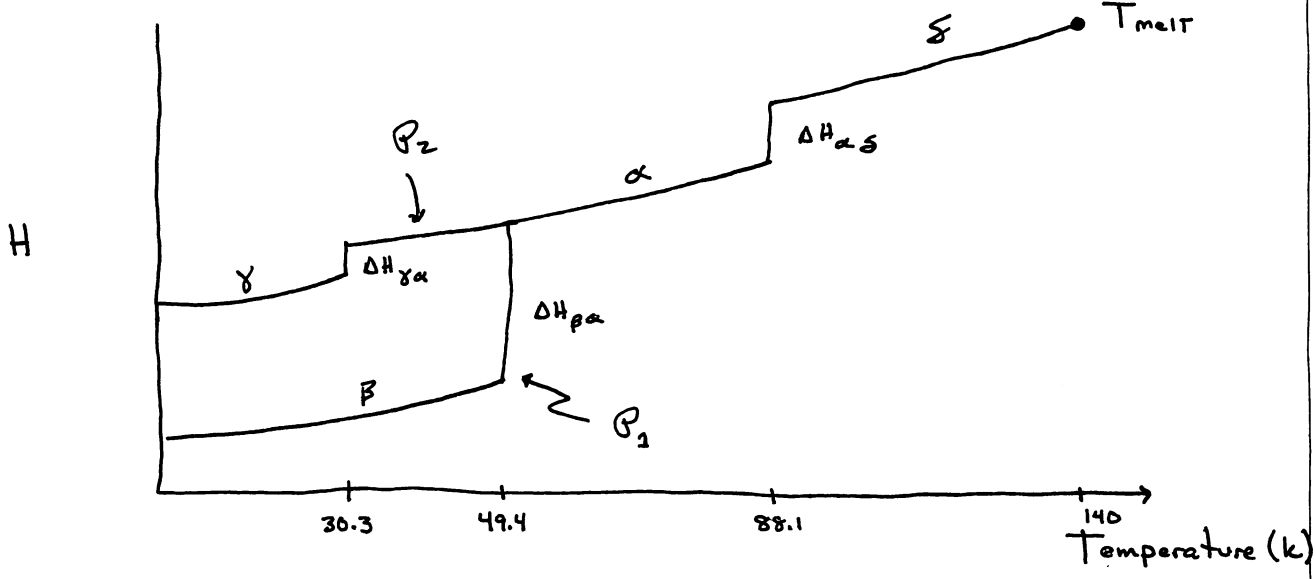
$$\Delta S = k_B \ln \frac{\Omega_{disordered}}{\Omega_{ordered}} = k_B \ln \frac{4^n}{1^n}$$

where n is the # of Cr atoms

$$\Delta S = NR \ln 4$$

Third Law of Thermodynamics

The 3rd law of thermodynamics is concerned with the limiting behavior of materials as the temperature approaches absolute zero. Consider the following calorimetric data on the cooling of phosphine (PH_3), which is known to have 4 allotropic crystalline forms at ambient pressure.



- At 88.1 K the δ phase transforms to the α phase. This transition is rapid & cannot be supercooled.
- At 49.4 K the α phase transforms to β if the cooling is slow (hrs). The β phase can then be cooled to near 0 K without any further phase change.
- If cooling is more rapid (minutes), the α phase can be supercooled to 30.3 K where it transforms reversibly to the γ phase. The γ phase can then be cooled to near 0 K without further phase changes.

Starting from the α phase @ 49.4 K we can calculate the ΔS to 0 K along the two routes (P_1 & P_2):

		ΔS (J/K mol)
P_1	α → β	-15.730
	49.4K → 0K	-18.335
	ΔS_{tot} =	-34.07 J/K.mol
P_2	49.4 → 30.3	-20.095
	α → γ	-2.710
	30.3 → 0	-11.220
	ΔS_{tot} =	-34.03 J/K.mol

within the Experimental Error, the β & γ crystal phases have the same entropy at Zero K !!

This was a remarkable — and unanticipated - discovery at the time. The β & γ phases have completely different structures - yet they have the same entropy. Observations like these on a number of other compounds that display allotropic behavior at low T led to the statement of the 3rd law:

Simon Statement of the 3rd law

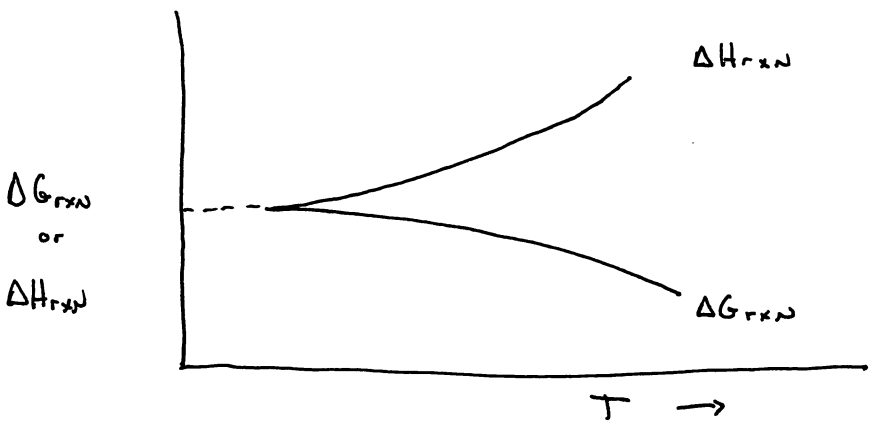
The contribution to the Entropy of a system by Each aspect which is in internal thermodynamic Equilibrium tends to zero as the temperature Tends to Zero

By "Aspect" is meant a part of the system that has only a weak dynamic coupling with the rest of the system & therefore makes an essentially independent contribution to the entropy of the total system. One example of this separation is the vibrational and magnetic aspects of a paramagnetic salt or the structural & vibrational aspects of a disordered solid. According to the 3rd law, the entropy of each of these aspects will separately tend to zero as the temperature approaches zero K, Provided that they are in thermal Equilibrium.

i.e. vibrational, structural, magnetic, electronic,

→

It was also found that the entropy change of any rxn, ΔS_{rxn}, also tended to zero as $T \to 0K$.



Since, $G \equiv H - TS$, $\Delta G = \Delta H - T\Delta S$

Note That $\Delta G \to \Delta H$ asymptotically as $T \to 0k$

$\Rightarrow$ $\Delta S_{rxn} \to 0$ as $T \to 0K$.

Statements of the 3rd Law

Nernst Statement (1906)

For any isothermal process.

$$\lim_{T \to 0} \Delta S_T = 0$$

Planck Statement (1912)

The Entropy of a chemically homogeneous substance has the value of Zero at absolute zero.

Lewis Statement (1923)

The Entropy of a perfect crystal becomes Zero at absolute zero.

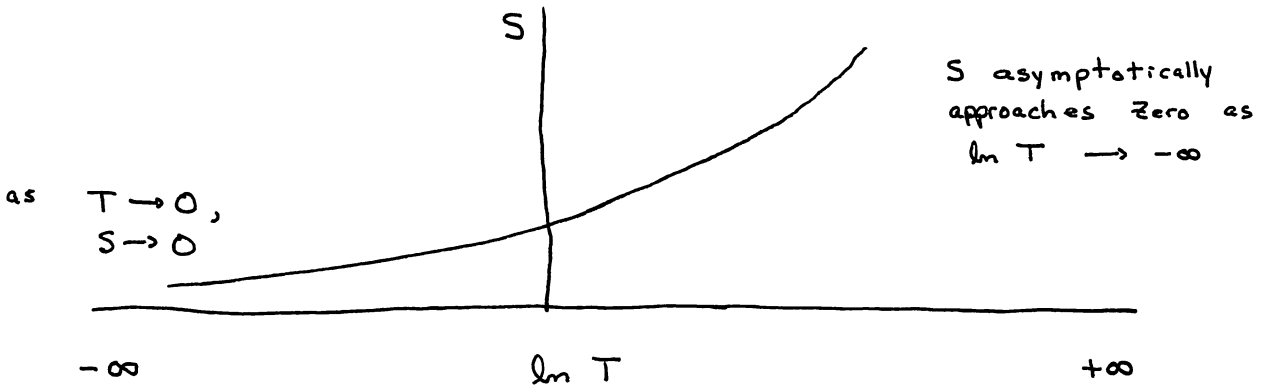
Simon Statement

The contribution to the entropy of a system by each "aspect" which is in internal thermodynamic Equilibrium tends to zero as the temperature tends to zero.

Physical Consequences of the 3rd law

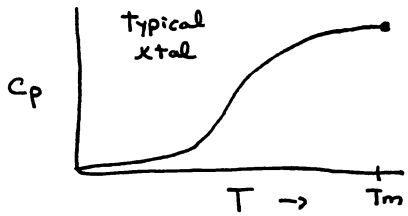
I Heat Capacities,

$$C_x \equiv T\left(\frac{\partial S}{\partial T}\right)_x = \left(\frac{\partial S}{\partial \ln T}\right)_x$$



Since $S \to 0$ as $\ln T \to -\infty$ $(T \to 0)$

$$\lim_{T\to 0} C_x \to 0$$



All heat capacities tend to zero as $T \to 0$

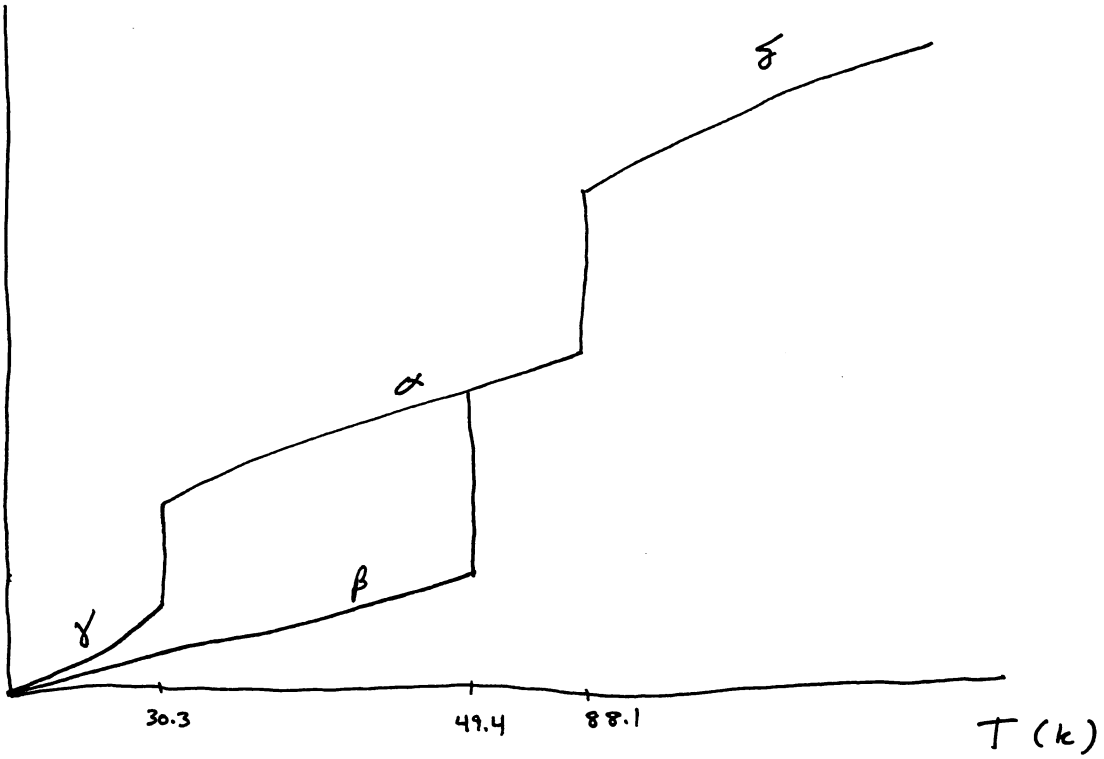
$C_p \to aT^3$	non-magnetic insulating crystals (3-dim) (vibrational contribution)
$C_p \to aT^2$	Layered crystals: graphite, BN, Surface heat capacity
$C_p \to \gamma T + aT^3$	metals
$C_p \to jT^{3/2} + aT^3$	ferromagnetic crystals below T_c
$C_p \to mT^3$	antiferromagnetic crystals below T_c.

V. Phase Transitions

Since the entropy of any phase under internal Equilibrium Tends to Zero as $T \to 0$ (Even for metastable phases):

$$\lim_{T \to 0} \quad \Delta S_{\alpha\beta} \longrightarrow 0$$

Recall Phosphine,



VI. Chemical Reactions

Again, since the entropy of all phases tend to Zero as $T \to 0$:

$$\lim_{T \to 0} \quad \Delta S_{rxn} \longrightarrow 0$$

Thus, the 3rd law allows us to obtain ΔS_{rxn} (at any T) <u>without</u> having to actually run a reversible reaction:

$$\Delta S_{rxn}(T,P) = \int_0^T \frac{\Delta C_{p,rxn}(T',P)}{T'}\, dT'$$

to obtain ΔH_{rxn}, the reaction must actually be run. However, this is much easier to obtain calorimetrically since we do <u>NOT</u> have to run the rxn reversibly to obtain ΔH_{rxn}.

recall $\Delta H_{rxn}(T,P) = Q$ if $T_i = T_f = T$

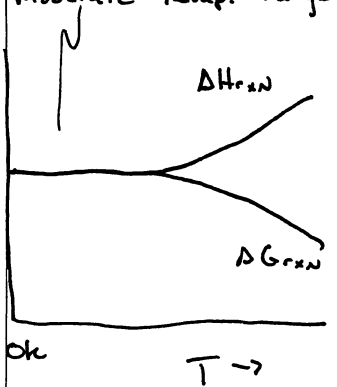
$P_i = P_f = P$

Thus, with $\Delta H_{rxn}(T,P)$ & $\Delta S_{rxn}(T,P)$ we can obtain $\Delta G_{rxn}(T,P)$ since,

$$\Delta G_{rxn}(T,P) = \Delta H_{rxn}(T,P) - T\Delta S_{rxn}(T,P)$$

$$\lim_{T\to 0} \Delta G_{rxn} \to \Delta H_{rxn}$$

$\Delta G_{rxn} \sim \Delta H_{rxn}$ over a moderate Temp. range!



also, since

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H_{rxn}}{\partial T}\right)_P - T\left(\frac{\partial \Delta S_{rxn}}{\partial T}\right)_P - \Delta S_{rxn}\left(\frac{\partial T}{\partial T}\right)_P$$

$$\lim_{T\to 0} \left(\frac{\partial \Delta G_{rxn}}{\partial T}\right)_P \to \left(\frac{\partial \Delta H_{rxn}}{\partial T}\right)_P$$

Absolute Entropies

Because of the 3rd law ($S \to 0$ as $T \to 0$) we can actually determine the absolute value of the entropy of any substance in internal equilibrium via calorimetric measurements. This is in contrast to the other "potential functions", U, H, A & G, where only differences can be determined.

$$S_\alpha(T,P) = \int_0^T \frac{C_{P,\alpha}(T',P)}{T'}\, dT' + \text{any contributions due to phase Transformations}$$

These absolute Entropies can be combined to yield ΔS values for chemical reactions:

$$\Delta S_{rxn}(T,P) = \sum_i \nu_i \bar{S}_i(T,P)$$

where $\bar{S}_i(T,P)$ is the absolute molar Entropy of Species i at T, P.

ν_i are the stoichiometric coefficients for the mass-balance chemical reaction.

ν_i	> 0	products
ν_i	< 0	reactants

For an Example, consider the following reaction:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

$$\Delta S_{rxn} = 2\,\bar{S}_{H_2O(g)} - 2\,\bar{S}_{H_2(g)} - \bar{S}_{O_2(g)} \qquad @\ 25^\circ C$$

$$\Delta S_{rxn} = 2(69.91) - 2(130.15) - 1(205.03)$$

$$= -325.51\ J/K$$

Thus, ΔS_{rxn} can be obtained without Even Carrying out the reaction!

In contrast, to obtain ΔH_{rxn}, the reaction must be carried out & the heat of the reaction measured.

ΔS_{rxn} & ΔH_{rxn} can then be combined to obtain ΔG_{rxn}.

$$\Delta G_{rxn}(T,P) = \Delta H_{rxn}(T,P) - T\,\Delta S_{rxn}(T,P)$$

Fundamental Eqns for a closed system

Recall, from the combined first & 2nd laws, we derived a "fundamental Equation" for dS (for a closed system)

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \qquad S(U,V)$$

$$dS = \frac{1}{T} dH - \frac{V}{T} dP \qquad S(H,P)$$

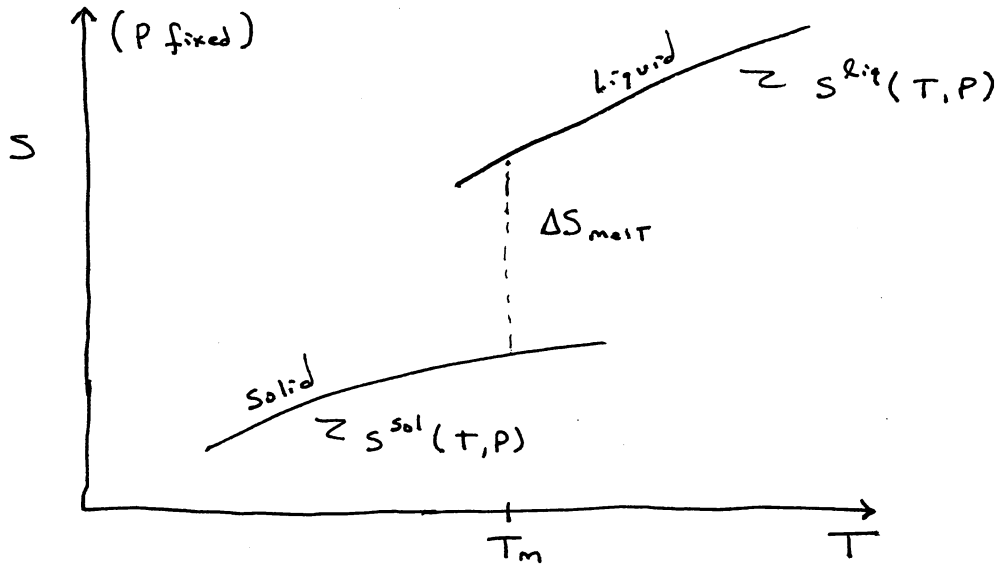
These Equations are called "fundamental" because they are derived directly from the thermodynamic laws. Numerous other Expressions of dS can be obtained by Expanding dS in terms of any complete set of independant thermodynamic variables, ie,

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad S(T,P)$$

$$= \frac{C_P}{T} dT - \alpha V dP$$

This Equation, however, is only a mathematical Expansion. These non-fundamental Expansions are only valid along a continuous thermodynamic surface, and hence, are only valid when we are interested in calculating changes in thermodynamic quantities of a single homogeneous phase. They are <u>NOT</u> valid across phase transitions.

For example, consider $S(T,P)$ across the solid-liquid phase change.



The solid & liquid phases have distinct $S(T,P)$ surfaces which are <u>discontinuous</u> at the equilibrium melting point, T_m. From the T, P expansion of dS we can calculate changes in S along each of the single phase surfaces:

$$dS^{liq} = \frac{C_p^{liq}}{T} dT - (\alpha V)^{liq} dP$$

&

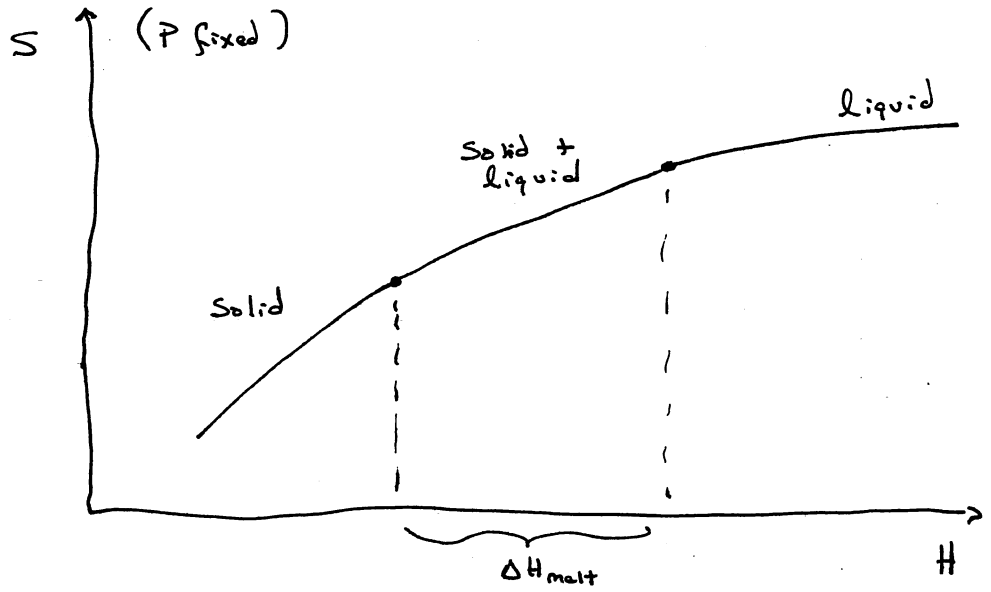
$$dS^{sol} = \frac{C_p^{sol}}{T} dT - (\alpha V)^{sol} dP$$

However, we <u>cannot</u> use these equations to calculate ΔS across the phase transition.

In contrast, the fundamental expressions for dS are valid across the <u>equilibrium phase transition boundary</u>!

Consider the expansion of S in terms of H & P

$$ds = \frac{1}{T}\,dH - \frac{v}{T}\,dP \qquad s(H,P)$$



This Equilibrium surface is continuous & is valid across the phase change:

$$\Delta S_{melt} = \int_{H^{sol}}^{H^{liq}} \frac{1}{T}\,dH = \frac{\Delta H_{melt}}{T_m}$$

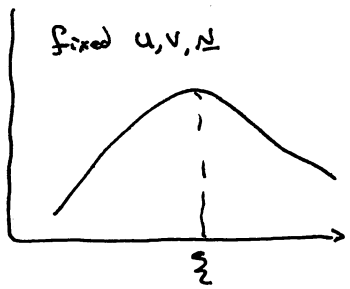
A second important feature of the fundamental equation is that the <u>Equilibrium state satisfies an Extremum principle</u>. Since our fundamental expression for ds was derived directly from the 1st & 2nd laws, we found that we could use an <u>Extremum</u> principle to determine the final Equilibrium state.

recall, $dS \geq 0$ for all spontaneous processes in a closed system at fixed U & V

Note that U & V are the expansion variables in the fundamental expression for dS ($dS = \frac{1}{T}dU + \frac{P}{T}dV$). Thus, the equilibrium state of a closed system at fixed U & V is that state with the maximum Entropy. At Equilibrium S is a maximum with respect to any internal constraint!

$$\left(\frac{\partial S}{\partial \xi}\right)_{U,V,\underline{N}} = 0$$

$$\& \quad \left(\frac{\partial^2 S}{\partial \xi^2}\right)_{U,V,\underline{N}} \leq 0$$



A similar Extremum principle can be derived for the fundamental Expression of dS in terms of H & P.

$$dS \geq \frac{dq}{T^*} = \frac{1}{T^*}dU + \frac{P^*}{T^*}dV$$

$$dU = dH - d(PV) = dH - PdV - VdP$$

$$dS \geq \frac{1}{T^*}dH - \frac{V}{T^*}dP + \frac{(P^*-P)}{T^*}dV$$

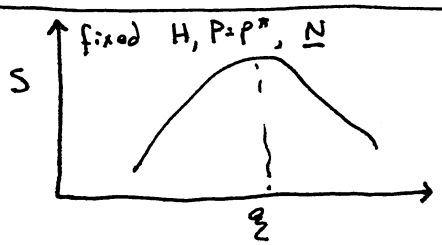
at fixed H & $P(=P^*)$, $dS \geq 0$

$dS \geq 0$ for all Spontaneous processes in a closed System at fixed H & $P=P^*$

Thus,

$$\left(\frac{\partial S}{\partial \xi}\right)_{H,P=P^*,\underline{N}} = 0$$

$$\left(\frac{\partial^2 S}{\partial \xi^2}\right)_{H,P=P^*,\underline{N}} \leq 0$$



By rearranging the fundamental Eqns for dS, we can obtain analogous fundamental equations for dU & dH.

$$dU = TdS - PdV$$

fundamental Eqn. for dU (closed system)

$$dH = TdS + VdP$$

fundamental Eqn. for dH (closed system)

These fundamental equations also satisfy an extremum condition.

$$dS \geq \frac{1}{T^*} dU + \frac{P^*}{T^*} dV$$

$$\Rightarrow dU \leq T^* dS - P^* dV$$

Thus, if S & V of the system are fixed,

$$dU \leq 0$$

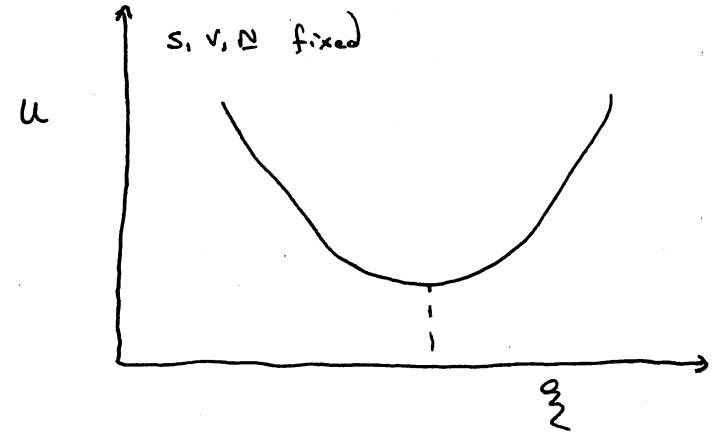
for all spontaneous processes in a system at fixed $S, V, \underline{N}$

In this case, U is a minimum for the Equilibrium state at fixed $S, V, \underline{N}$.

$$\left(\frac{\partial U}{\partial \xi}\right)_{S,V,\underline{N}} = 0$$

$$\left(\frac{\partial^2 U}{\partial \xi^2}\right)_{S,V,\underline{N}} \geq 0$$

} at Equilibrium



An analogous extremum condition for the enthalpy can be derived in a similar way:

$$dU \leq T^* dS - P^* dV$$

Substitute $dU = dH - d(PV)$ $\quad (U = H - PV)$

$$= dH - PdV - VdP$$

$$\Rightarrow \quad dH \leq T^* dS + VdP - (P^* - P)\, dV$$

Thus, if S is fixed & $P = P^*$

$$\Rightarrow \boxed{dH \leq 0}$$

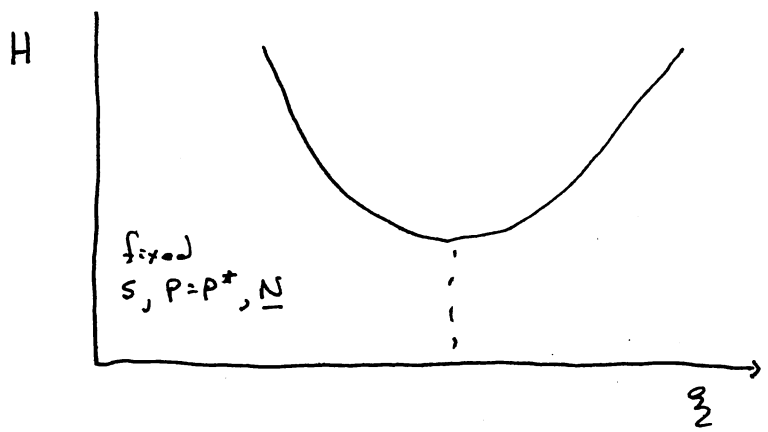
for all spontaneous processes in a system at fixed S, $P = P^*$, $\underline{N}$.

also, at equilibrium:

$$\left(\frac{\partial H}{\partial \xi_2}\right)_{S,\, P=P^*,\, \underline{N}} = 0$$

&

$$\left(\frac{\partial^2 H}{\partial \xi_2^2}\right)_{S,\, P=P^*,\, \underline{N}} \geq 0$$



Legendre Transforms - other thermodynamic Potential Functions

The fundamental Equation for dU is an Expansion of the differential in terms of S & V.

$$dU = TdS - PdV$$

Recall, how we created the Enthalpy function, H, from U:

$$H \equiv U + PV$$

As we found,

The total differential of H can also be expressed in a fundamental Equation by:

$$dH = dU + d(PV) = TdS + VdP$$

Note that the fundamental Equation for dH is an Expansion in S & P while the fundamental Equation for dU is an Expansion in (S & V).

As you might expect we can create new thermodynamic potentials & additional fundamental Equations which are Expansions in different Sets of Variables.

This procedure is known as a <u>Legendre Transform</u>.

As an Example, consider some function $F(y, z)$

$$dF = g\,dy + h\,dz \qquad \text{where} \begin{cases} g \equiv \left(\frac{\partial F}{\partial y}\right)_z \\ h \equiv \left(\frac{\partial F}{\partial z}\right)_y \end{cases}$$

Now <u>define</u> $G \equiv F - gy$

$$\Rightarrow dG = dF - d(gy) = dF - g\,dy - y\,dg$$

Substituting $dF = g\,dy + h\,dz$

$$\Rightarrow \boxed{dG = -y\,dg + h\,dz}$$

In this procedure we have created a new function G whose differential is naturally expressed as an expansion in q & z instead of y & z.

This is really what we were doing when we defined the Enthalpy, H.

Starting from the fundamental Equation,

$$dU = TdS - PdV$$

$H \equiv U + PV$ Legendre transform of U with respect to P-V conjugate pair

$$\Rightarrow \boxed{dH = TdS + VdP} \qquad H(S,P)$$

We can also perform a Legendre transform of U with respect to the T-S conjugate pair.

$$\boxed{A \equiv U - TS}$$ Helmholtz Free Energy

$$dA = dU - TdS - SdT$$

Substituting $dU = TdS - PdV$

$$\Rightarrow \boxed{dA = -SdT - PdV} \qquad A(T,V)$$

This Expansion of A in terms of T & V is also a fundamental Eqn.

Similarly, we can perform a Legendre transform of U with respect to <u>both</u> (T,S) & (P,V) conjugate pairs of variables

$$\boxed{G \equiv U + PV - TS}$$ Gibbs Free Energy

$$dG = dU + PdV + VdP - TdS - SdT$$

Substituting $dU = TdS - PdV$

$$\boxed{dG = -SdT + VdP} \qquad G(T,P)$$

This Expansion is also a fundamental Eqn but has T & P as the set of independent variables!

The beauty of the Legendre Transform is that it allows us to obtain alternate fundamental Equations which are Expressed in different Sets of independent variables. Sometimes one set of variables is preferred over another.

For Example, in chemistry, one typically can easily control T & P in an experiment. Thus, the Gibbs Free Energy is a more Natural choice to use for the funamental Equation.

i.e., $G = U - TS + PV$

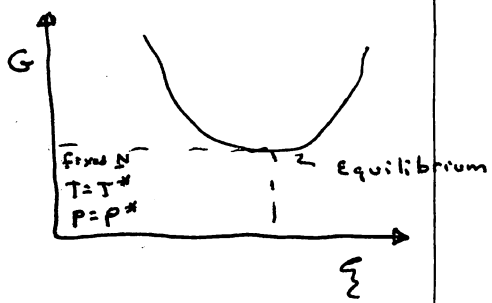
$\Updownarrow$

$dG = -SdT + VdP \qquad G(T,P)$

We will see below that G also satisfies an Extremum principle to determine the final Equilibrium state. In particular, if $T = T^*$ & $P = P^*$ The final Equilibrium state is that which minimizes the Gibbs Free Energy.

i.e. $\left(\frac{\partial G}{\partial \xi}\right)_{T=T^*,\, P=P^*,\, \underline{N}} = 0$

$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T=T^*,\, P=P^*,\, \underline{N}} \geq 0$



To show this consider:

$$dU \leq T^* dS - P^* dV$$

substituting:

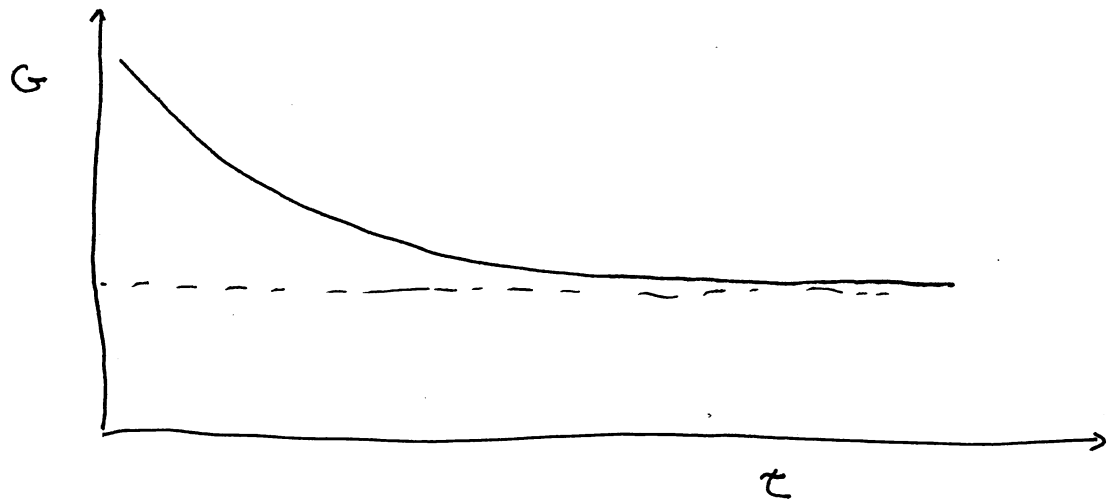
$$dU = dG + TdS + SdT - PdV - VdP \qquad (dG = dU - d(TS) + d(PV))$$

$$\Rightarrow \quad dG \leq -SdT + VdP + (T^* - T)dS - (P^* - P)dV$$

Thus, if $T = T^*$ & $P = P^*$

$$dG \leq 0$$

That is, all spontaneous processes in a closed system at fixed $T = T^*$ & $P = P^*$ will result in a decrease in the Gibbs Free Energy until the Equilibrium State is reached.



at Equilibrium,

$$\left(\frac{\partial G}{\partial \xi}\right)_{T=T^*,\, P=P^*,\, \underline{N}} = 0$$

&

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T=T^*,\, P=P^*,\, \underline{N}} \geq 0$$

any fluctuation increases G $\Rightarrow$ Stable system.

In physics, it is often more useful to work with T & V as independent variables. This is a more natural set to use when defining physical models of Nature. With this set of variables we would need to use the Helmholtz Free Energy Function, $A(T,V)$.

$$A \equiv U - TS$$

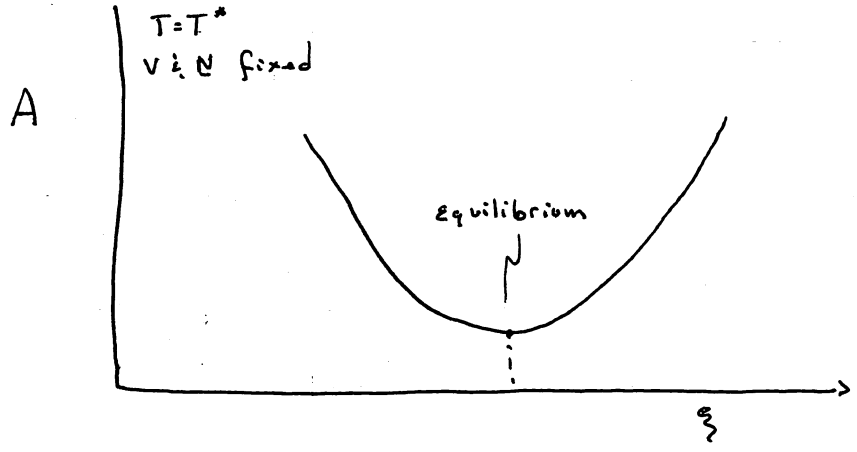
$$dA = -SdT - PdV \qquad A(T,V)$$

The Helmholtz free energy also satisfies an <u>Extremum principle</u>, which defines the final Equilibrium state of a system at fixed $T = T^*$ & V.

At Equilibrium:

$$\left(\frac{\partial A}{\partial \xi}\right)_{T=T^*,V,N} = 0$$

$$\left(\frac{\partial^2 A}{\partial \xi^2}\right)_{T=T^*,V,N} \geq 0$$



To show this consider:

$$dU \leq T^* dS - P^* dV$$

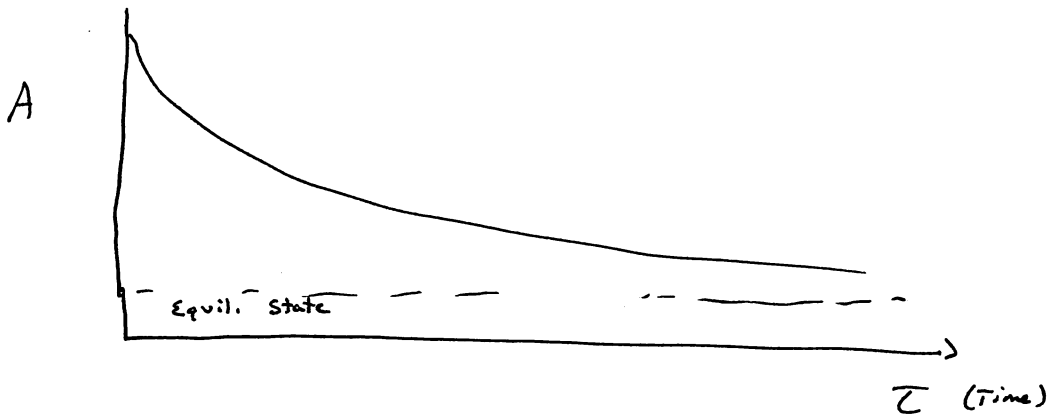
substitute: $dU = dA + T dS + S dT$ $\quad (dA = dU - d(TS))$

$$\Rightarrow dA \leq -S dT - P^* dV + (T^* - T)\, dS$$

Thus, if $T = T^*$ & V is fixed,

$$dA \leq 0$$

That is, all spontaneous processes in a <u>closed</u> system at fixed $T = T^*$ & fixed V, will result in a decrease in the Helmholtz Free Energy until the Equilibrium state is reached.



at Equilibrium,

$$\left(\frac{\partial A}{\partial \xi}\right)_{T=T^*, V, \underline{N}} = 0$$

$$\left(\frac{\partial^2 A}{\partial \xi^2}\right)_{T=T^*, V, \underline{N}} \geq 0$$

any fluctuation increases A.

Relation of A & G to Maximum Work

Maximum Total Work

Consider a change of state of a system in a fixed T^* environment:

From the 1st-law,

$$w' = Q - \Delta U$$

From the 2nd-law,

$$\Delta S \geq Q/T^*$$

$$w' \leq -\Delta U + T^* \Delta S$$

Maximum total work that can be extracted from a change in state of a system in a fixed T^* environment

Special Case: $T_1 = T_2 = T^*$

in an isothermal case,

$$w' \leq -\Delta U + T\Delta S = -\Delta A \quad (T = T^*)$$

$$\Rightarrow \quad w'_{max} = -\Delta A \quad (T = T^*)$$

isothermal case

An important application of these results is determining w'_{max} that can be extracted from a chemical rxn.

Maximum "Available" Work

Consider a change of state of a system in a fixed T^*, P^* Environment.

$$\Delta U = Q - P^* \Delta V + W_e \qquad 1^{st}\text{-law}$$

(W_e: Extra work)

$$W_e' = -\Delta U + Q - P^* \Delta V$$

$$\Delta S \geq Q/T^* \qquad 2^{nd}\text{-law}$$

$$\boxed{W_e' \leq -\Delta U + T^* \Delta S - P^* \Delta V}$$

Maximum available work that can be obtained from a change in state of a system in a fixed T^*, P^* Environment

Special Cases:

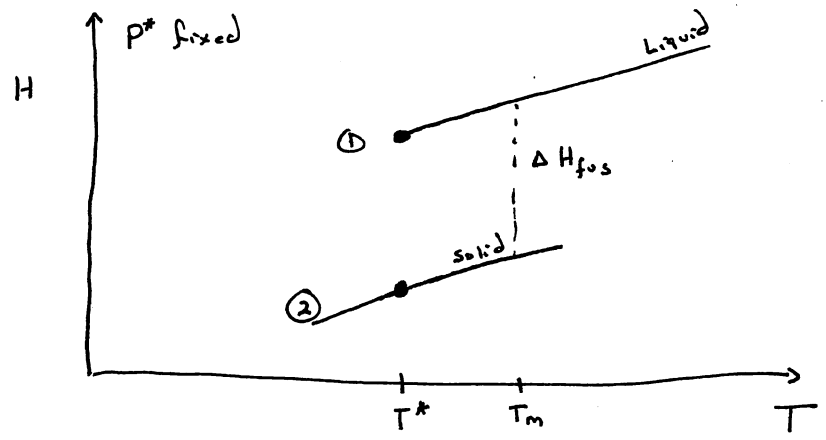
$$P_1 = P_2 = P^*$$

$$W_e' \leq -\Delta H\,(P=P^*) + T^* \Delta S\,(P=P^*)$$

$$P_1 = P_2 = P^* \quad \& \quad T_1 = T_2 = T^*$$

$$W_e' \leq -\Delta G\,(T=T^*, P=P^*)$$

Example - Recall your homework problem:



$$dw_e' = -dq\,(1 - T^*/T)$$

dq = heat adsorbed by reaction system.

@ constant $P = P^*$, $dq = dH$

$$\Delta H = \Delta U + P^*\Delta V = Q - P^*\Delta V + P^*\Delta V = Q$$

$$\Rightarrow dw_e' = -dW\left(1 - \frac{T^*}{T}\right)$$

$$= -\int_{T^*}^{T_m} C_p^{\,l}\left(1 - \frac{T^*}{T'}\right)dT' + \Delta H_{fus}\left(1 - \frac{T^*}{T_m}\right) - \int_{T_m}^{T^*} C_p^{\,s}\left(1 - \frac{T^*}{T'}\right)dT'$$

$$= -\int_{T^*}^{T_m} C_p^{\,l}\,dT' + T^*\int_{T^*}^{T_m} C_p^{\,l}\,\frac{dT'}{T'} + \Delta H_{fus} - \frac{T^*\Delta H_{fus}}{T_m} - \int_{T_m}^{T^*} C_p^{\,s}\,dT' + T^*\int_{T_m}^{T^*}\frac{C_p^{\,s}}{T'}\,dT'$$

$$= \underbrace{-\int_{T^*}^{T_m} C_p^{\,l}\,dT' + \Delta H_{fus} - \int_{T_m}^{T^*} C_p^{\,s}\,dT'}_{-\Delta H(T^*,P^*)} + \underbrace{T^*\left[\int_{T^*}^{T_m} C_p^{\,l}\,\frac{dT'}{T'} - \frac{\Delta H_{fus}}{T_m} + \int_{T_m}^{T^*} C_p^{\,s}\,\frac{dT'}{T'}\right]}_{T^*\Delta S(T^*,P^*)}$$

$$\Rightarrow w_{e\,max}' = -\Delta G(T^*, P^*)$$

Maxwell Relation's

Another Extremely useful application of the Fundamental Equations is that it provides us a set of partial derivative identities know as "Maxwell Relations". as well as a set of thermodynamic identies.

→ Consider $u(s,v)$ $\quad du = Tds - Pdv$

$$\left(\frac{\partial u}{\partial s}\right)_{v,N} \equiv T \quad \& \quad \left(\frac{\partial u}{\partial v}\right)_{s,N} \equiv -P \qquad \text{identies}$$

Since, $\frac{\partial^2 u}{\partial v \partial s} = \frac{\partial^2 u}{\partial s \partial v}$

Maxwell Relation (Since du is Exact differential)

$$\boxed{\left(\frac{\partial T}{\partial v}\right)_{s,N} = -\left(\frac{\partial P}{\partial s}\right)_{v,N}}$$

→ Consider $H(s,P)$ $\quad dH = Tds + vdP$

$$\left(\frac{\partial H}{\partial s}\right)_{P} \equiv T \qquad \left(\frac{\partial H}{\partial P}\right)_{s} \equiv v \qquad \text{identies}$$

Maxwell Relation

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_{s,N} = \left(\frac{\partial v}{\partial s}\right)_{P,N}}$$

→ Consider $A(T,v)$ $\quad dA = -sdT - Pdv$

$$\left(\frac{\partial A}{\partial T}\right)_{v,N} \equiv -s \quad \& \quad \left(\frac{\partial A}{\partial v}\right)_{T,N} \equiv -P$$

Maxwell Relation

$$\boxed{\left(\frac{\partial s}{\partial v}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{v,N}}$$

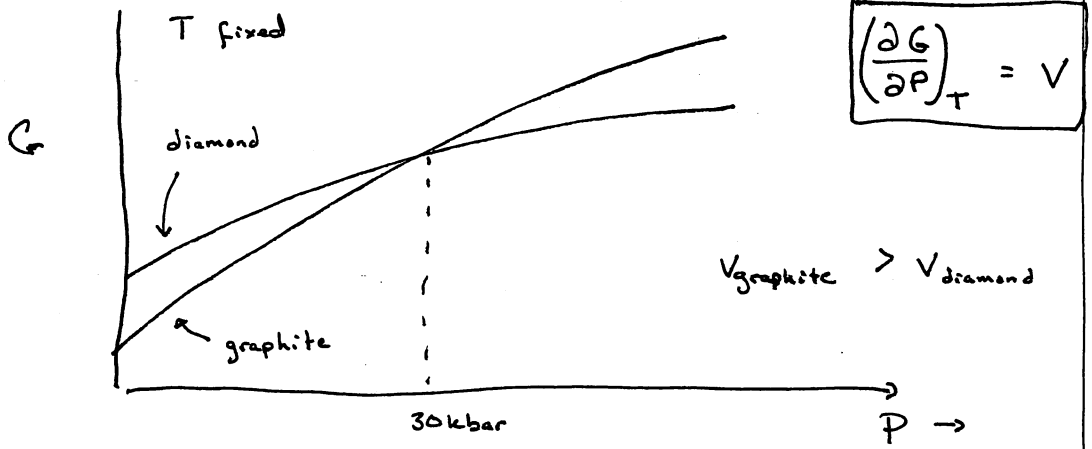
→ Consider $G(T,P)$ $\quad dG = -SdT + VdP$

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} \equiv V \quad \& \quad \left(\frac{\partial G}{\partial T}\right)_{P,N} \equiv -S$$

Maxwell Relation

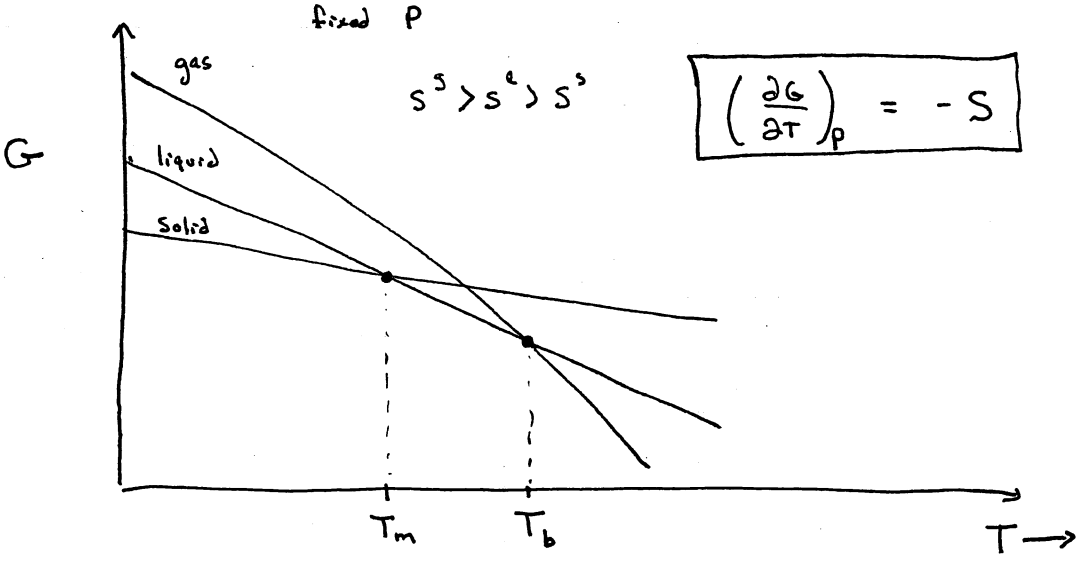
$$\boxed{\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}}$$

The Pressure & Temperature dependence of G is determined by V & -S



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

$V_{graphite} > V_{diamond}$



$S^s > S^\ell > S^g$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S}$$

Application of Maxwell Relations

I. $\left(\frac{\partial U}{\partial V}\right)_{T,N}$

$$dU = TdS - PdV$$

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

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

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_{T,N} = T\left(\frac{\partial P}{\partial T}\right) - P}$$

II. $\left(\frac{\partial H}{\partial P}\right)_{T,N}$

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_{T,N} = T\left(\frac{\partial S}{\partial P}\right)_{T,N} + V$$

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

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_{T,N} = -T\left(\frac{\partial V}{\partial T}\right)_{P,N} + V}$$

III Relation between C_p & C_v

(Hwk - 3 problem # 1a)

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

IV Relation between k_s & k_T

(Hwk - 3 problem # 1b,c)

$$\boxed{k_s + \frac{TV\alpha^2}{C_p} = k_T}$$

also,

$$\boxed{\frac{C_p}{C_v} = \frac{k_T}{k_s}}$$

V. The Maxwell Reln's involving $\left(\partial s/\partial p\right)_T$ & $\left(\partial s/\partial v\right)_T$ make it convenient to solve integral Equations along reversible adiabats $(ds = 0)$

- $T(v)$ along reversible adiabats :

$$dT = \left(\frac{\partial T}{\partial v}\right)_s dv + \left(\frac{\partial T}{\partial s}\right)_v \cancel{ds}^{\,0}$$

$$= -\left(\frac{\partial T}{\partial s}\right)_v \left(\frac{\partial s}{\partial v}\right)_T dv = -\frac{T}{C_v}\left(\frac{\partial p}{\partial T}\right)_v dv$$

$$\boxed{dT = -\frac{T\alpha}{C_v k_T}\, dv}$$

- $T(p)$ along reversible adiabats:

$$dT = \left(\frac{\partial T}{\partial p}\right)_s dp + \left(\frac{\partial T}{\partial s}\right)_p \cancel{ds}^{\,0}$$

$$dT = -\left(\frac{\partial T}{\partial s}\right)_p \left(\frac{\partial s}{\partial p}\right)_T dp = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$\boxed{dT = \frac{T v \alpha}{C_p}\, dp}$$

- $V(p)$ along reversible adiabat :

$$dv = \left(\frac{\partial v}{\partial p}\right)_s dp = -k_s v\, dp = -\left(\frac{C_v}{C_p}\right) v k_T\, dp$$

$$\Rightarrow \boxed{dv = -\frac{v k_T}{\gamma}\, dp \quad \text{where} \quad \gamma = \frac{C_p}{C_v}}$$

Massieu Functions

Before leaving our discussion of Legendre transforms & Fundamental Equations, it should be mentioned that there are a complementary set of Fundamental Equations which can be derived from Legendre transforms of the dS fundamental Equation. We'll mention a few of the more important ones below:

$$dS = \frac{1}{T}\,dH - \frac{V}{T}\,dP$$

$$S - \frac{H}{T} = -\frac{G}{T} \qquad \text{Legendre transform}$$

$$\Rightarrow \; d\left(-\frac{G}{T}\right) = -H\,d\frac{1}{T} - \frac{V}{T}\,dP$$

or

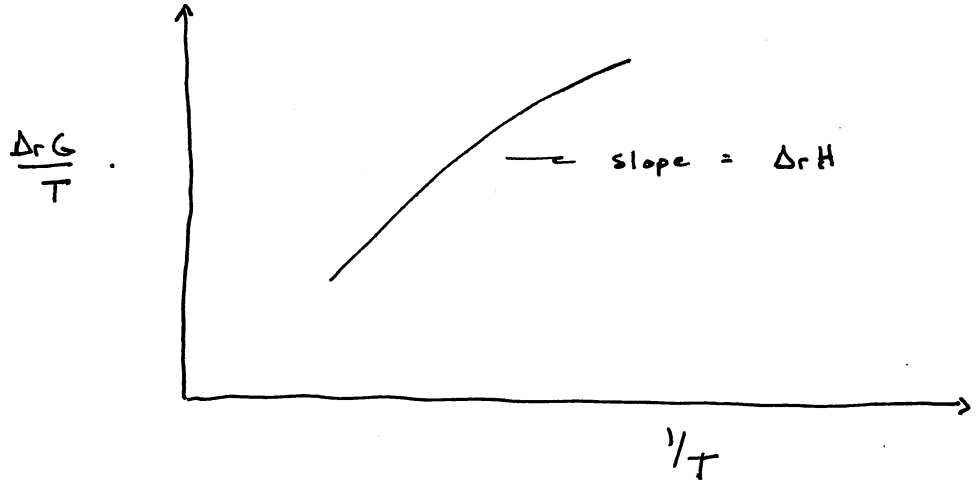
$$\boxed{d\frac{G}{T} = H\,d\frac{1}{T} + \frac{V}{T}\,dP}$$

$$\Rightarrow \boxed{\left(\frac{\partial G/T}{\partial 1/T}\right)_{P,N} = H}$$

Gibbs-Helmholtz Eqn:

$$\left(\frac{\partial \Delta_r G/T}{\partial 1/T}\right)_p = \Delta_r H$$

Thus, if we know $\Delta_f G$ at several temperatures we can obtain $\Delta_r H$.



Another useful Equation can be derived from a Legendre Transform of ,

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

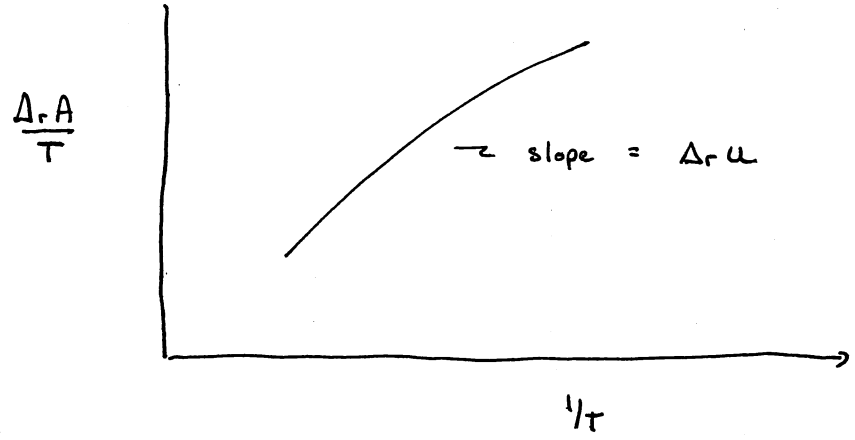
$$S - \frac{1}{T} U = - \frac{A}{T} \qquad \text{Legendre transform}$$

$$\Rightarrow \quad d - \frac{A}{T} = -U\, d\frac{1}{T} + \frac{P}{T} dV$$

or

$$d \frac{A}{T} = U\, d\frac{1}{T} - \frac{P}{T} dV$$

$$\Rightarrow \boxed{\left(\frac{\partial A/T}{\partial 1/T} \right)_{V,N} = U} \qquad \text{also,} \quad \left(\frac{\partial \Delta_r A/T}{\partial 1/T} \right)_{V} = \Delta_r U$$



Why are these thermodynamic Potentials Useful?

I. Each provides important thermodynamic definitions & useful Maxwell Relations.

II. Potential functions can sometimes be related to calorimetric heat measurements or to the maximum work that can be extracted from a system in a change of state under different External Conditions.

III. Each potential is a "Lyapounov Function". That is, each satisfies an Extremum Condition That can be Exploited to determine the final Equilibrium state of a system.

IV. The potentials provide thermodynamic criteria for the stability of a system with respect to its own fluctuations.

Extension to closed systems w/ other types of work.

Recall, $dU = TdS + \delta W_{rev}$

in general, $\delta W_{rev} = \sum_i F_i \, dX_i$

F_i: generalized field variable

X_i: Extensive mechanical variable conjugate to F_i

$$\boxed{dU = TdS + \sum_i F_i \, dX_i}$$

Fundamental Rel'n's General work Terms closed system

$$dS = \frac{1}{T} dU - \sum_i \frac{F_i}{T} dX_i$$

For other types of work we can define analogous functions to the Enthalpy, For Example.

Elastic Band: $dU = TdS + f\,dL$

$$H \equiv U - fL$$

$$\Rightarrow \quad dH = d(U - fL) = dU - f\,dL - L\,df$$

fundamental relation for rubber band.

$$\Rightarrow \boxed{dH = TdS - L\,df}$$

$$H(S,f) \equiv U - fL \equiv U[f]$$

$$dH = TdS - L\,df$$

$$A(T,L) \equiv U - TS \equiv U[T]$$

$$dA = -S\,dT + f\,dL$$

$$G(T,f) \equiv U - TS - fL \equiv U[T,f]$$

$$dG = -S\,dT - L\,df$$

Extremum Principle Revisited → Internal Constraints

We define $\{\xi_i\}$ to represent a set of internal constraints of the system (either actual or mental) which restrict the distribution of some thermodynamic quantity within the system:

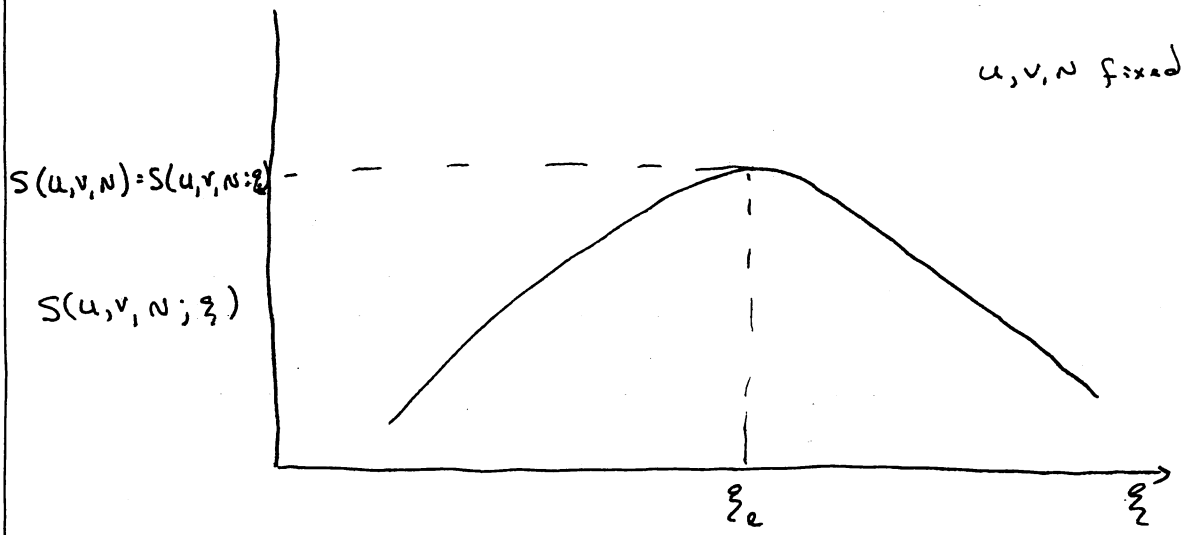
- distribution of Energy
- distribution of mass
  via: chemical species, phases, rxns, etc...
- Volume

These internal constraints on the system are in addition to the external constraints or "walls" which restrict the distribution of Energy, mass and volume between the system & its surroundings.

The Equilibrium state of the system under all of its constraints is specified when we specify the total U, V, N of the system plus all of the internal constraints.

i.e., $S(U, V, N ; \{\xi_i\})$
- U, V, N → External constraints
- $\{\xi_i\}$ → Internal Constraints

Thus, keeping U, V, N fixed, we change S of the system when we change the distribution of Energy & mass within the system. This can be represented graphically in the following way:



The maximum value of $S(U,V,N;\xi)$ occurs at some value ξ_ε. This is the state that the system will ultimately seek when all of the internal constraints are removed.

External Constraints

$$S(U,V,N) = S(U,V,N;\xi_\varepsilon)$$

Internally constrained state which maximizes The system Entropy

final Equilibrium state which would result when all of the internal constraints are lifted.

"Constrained" Equilibrium States & the Fundamental Equation

Recall, the fundamental equation for dS is given by,

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV \qquad \text{(fixed } N\text{, } PdV \text{ work only)}$$

This total differential tells us the mathematical relation between the different <u>Equilibrium states</u> of a system — assuming no internal constraints are acting on the system.

We can generalize this expression to include internally constrained states away from Equilibrium.

$$\boxed{dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV + a\,d\xi}$$

here, ξ is the parameter that describes the constrained distribution of some quantity away from Equilibrium, i.e., "Extent of rxn"; a is called the "affinity" and is formally given by,

$$\boxed{a \equiv \left(\frac{\partial S}{\partial \xi}\right)_{U,V,N}}$$

Note, for the true Equilibrium states (no internal constraints), $\left(\frac{\partial S}{\partial \xi}\right)_{U,V,N} = 0$ or $a = 0$. With changes in U & V the unconstrained Equilibrium state will track along that value of ξ_e that maximizes the Entropy. Thus, for the true Equilibrium states (unconstrained) we obtain the usual fundamental Eqn.,

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV$$

Note also, That from the Expanded Equation for dS for the constrained states, the thermodynamic definition for $1/T$ is given by,

$$\left(\frac{\partial S}{\partial U}\right)_{V,N,\xi} = \frac{1}{T}$$

How is this definition for T reconcited with our original thermodynamic identity,

$$\left(\frac{\partial S}{\partial U}\right)_{V,N}\Big|_{\xi_\varepsilon} = \frac{1}{T}$$

↳ in the unconstrained case, ξ_ε is allowed to change as U changes to maintain the Equilibrium condition.

From the Expanded Equation for dS for unconstrained states we have,

$$\left(\frac{\partial S}{\partial U}\right)_{V,N}\Big|_{\xi_\varepsilon} = \frac{1}{T} + a\left(\frac{\partial \xi}{\partial U}\right)_{V,N}\Big|_{\xi_\varepsilon}$$

↳ However, this quantity a is Equal to zero when Evaluated at Equilibrium.

Energy Minimum Principle - revisited

From the 2nd law we have shown that the unconstrained Equilibrium state of a system @ fixed $U, V, \underline{N}^{EXT}$ is that state which maximizes the Entropy of the system, S. It is also true that any Equilibrium state (for example, where $T, V, \underline{N}^{EXT}$ are fixed or where $T, P, \underline{N}^{EXT}$ are fixed, etc..) These Equilibrium states satisfy the condition that,

$$\left(\frac{\partial S}{\partial \xi}\right)_{U,V,\underline{N}^{EXT}}\Bigg|_{\xi_\varepsilon} = 0$$

$$\left(\frac{\partial^2 S}{\partial \xi^2}\right)_{U,V,\underline{N}^{EXT}}\Bigg|_{\xi_\varepsilon} \leq 0$$

} valid for any Equilibrium state.

As we will see below the unconstrained Equilibrium state is also an extremum state for the other thermodynamic potentials.

To motivate this, consider the 2nd-law:

$$dS \geq \frac{dq}{T^*} \qquad \text{closed system}$$

$$dS \geq \frac{1}{T^*}dU + \frac{P^*}{T^*}dV \qquad \text{closed system}$$

rearranging:

$$dU \leq T^* dS - P^* dV$$

or

$$dU \leq 0 \qquad \text{for system with } S, V, N \text{ fixed}$$

Thus, $dU \leq 0$ for all spontaneous processes at fixed $S, V, \underline{N}^{EXT}$

The final Equilibrium state is that where $dU = 0$ and U must be a minimum.

More formally, lets consider:

$$\left(\frac{\partial U}{\partial \xi}\right)_{S,V,N}\Big|_{\xi_\varepsilon} = -\left(\frac{\partial U}{\partial S}\right)_{V,N,\xi}\Big|_{\xi_\varepsilon}\left(\frac{\partial S}{\partial \xi}\right)_{U,V,N}\Big|_{\xi_\varepsilon}$$

↳ Evaluated at The Equilibrium Configuration.

$$\left(\frac{\partial U}{\partial \xi}\right)_{S,V,N}\Big|_{\xi_\varepsilon} = -T\left(\frac{\partial S}{\partial \xi}\right)_{U,V,N}\Big|_{\xi_\varepsilon}$$

Since $\left(\frac{\partial S}{\partial \xi}\right)_{U,V,N}\Big|_{\xi_\varepsilon} = 0$ at Equilibrium,

$$\boxed{\left(\frac{\partial U}{\partial \xi}\right)_{S,V,N}\Big|_{\xi_\varepsilon} = 0 \quad \text{at Equilibrium}}$$

Since $T > 0$

Thus, the unconstrained Equilibrium state is also an Extremum state of the Energy, U, with the respect to ξ at fixed S, V, N^{EXT}.

To determine whether this extremum is a maximum or minimum we will have to look at the second derivate – evaluated at ξ_e

$$\left(\frac{\partial^2 u}{\partial \xi^2}\right)_{s,v,\underline{N}} = \left(\frac{\partial}{\partial \xi}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{s,v,\underline{N}}$$

Expanding $\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}$ in terms of u, v, N & ξ

$$d\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}} = \left(\frac{\partial}{\partial u}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{v,N,\xi} du + \left(\frac{\partial}{\partial v}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{u,N,\xi} dv$$

$$+\left(\frac{\partial}{\partial N}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{u,v,\xi} dN + \left(\frac{\partial}{\partial \xi}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{u,v,\underline{N}} d\xi$$

$$\Rightarrow \left(\frac{\partial}{\partial \xi}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{s,v,\underline{N}} = \left(\frac{\partial}{\partial u}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{v,\underline{N},\xi}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}} + \left(\frac{\partial}{\partial \xi}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{u,v,\underline{N}}$$

The second term can be expanded giving:

$$\left(\frac{\partial}{\partial \xi}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{s,v,\underline{N}} = \left(\frac{\partial}{\partial u}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{v,\underline{N},\xi}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,N} - \left(\frac{\partial}{\partial \xi}\left(\frac{\partial u}{\partial s}\right)_{v,\underline{N},\xi}\left(\frac{\partial s}{\partial \xi}\right)_{u,v,\underline{N}}\right)_{u,v,\underline{N}}$$

Applying the chain rule to the second term:

$$\left(\frac{\partial^2 u}{\partial \xi^2}\right)_{s,v,\underline{N}} = \left(\frac{\partial}{\partial u}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\right)_{v,\underline{N},\xi}\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}} - \left(\frac{\partial u}{\partial s}\right)_{v,\underline{N},\xi}\left(\frac{\partial^2 s}{\partial \xi^2}\right)_{u,v,\underline{N}}$$

$$-\left(\frac{\partial s}{\partial \xi}\right)_{u,v,\underline{N}}\left(\frac{\partial}{\partial \xi}\left(\frac{\partial u}{\partial s}\right)_{v,\underline{N},\xi}\right)_{u,N,\underline{N}}$$

Evaluating this 2nd derivative @ equilibrium,

$$\left(\frac{\partial u}{\partial \xi}\right)_{s,v,\underline{N}}\Big|_{\xi_e} = 0 \quad ; \quad \left(\frac{\partial s}{\partial \xi}\right)_{u,v,\underline{N}}\Big|_{\xi_e} = 0 \quad ; \quad \left(\frac{\partial u}{\partial s}\right)_{v,\underline{N},\xi}\Big|_{\xi_e} = T$$

$$\left(\frac{\partial^2 u}{\partial \xi^2}\right)_{s,v,\underline{N}}\Big|_{\xi_e} = -T\left(\frac{\partial^2 s}{\partial \xi^2}\right)_{u,v,\underline{N}}\Big|_{\xi_e} \quad \text{and since,} \quad \left(\frac{\partial^2 s}{\partial \xi^2}\right)_{u,v,\underline{N}}\Big|_{\xi_e} \leq 0$$

so, $\boxed{\left(\frac{\partial^2 u}{\partial \xi^2}\right)_{s,v,N}\Big|_{\xi_e} \geq 0}$

General Form of S, U, & Surface (fixed V & N)

See figure 5.1 & 5.2 in H. Callen's Book.

For any unconstrained Equilibrium state, point A for example above, the Equilibrium state is simultaneously a Maximum on the constant U surface & a minumum on the constant S Surface. The Equilibrium state is an Extremum state in both U & S

Analogy:

- A circle is the geometric form that gives a maximum area for a given perimeter.
- A circle is the geometric form that gives a minumum perimeter for a given Area.

Extremum Principle for the Thermodynamic Potentials

One of the most useful applications of the thermodynamic potentials is that they can be exploited to predict the final Equilibrium state of a system under various External Conditions.

the general statement of the 2nd-law is,

$$dS \geq \frac{dq}{T^*} \quad \text{or} \quad dS - \frac{dq}{T^*} \geq 0$$

from the 1st-law, $dq = dU - dw$

$$\boxed{dS - \frac{1}{T^*} dU + \frac{1}{T^*} dw \geq 0}$$

General Extremum Principle

If the Surroundings is always in Equilibrium, the latter two terms is the Entropy change of the Surroundings!

$$\Rightarrow \boxed{dS_{system} + dS^*_{surroundings} \geq 0}$$

For the Surroundings,

$$dS^* = \frac{1}{T^*} dU^* - \frac{1}{T^*} \sum \vec{F}_i^* d\chi_i^*$$

but, $dU^* = -dU$ conservation of Energy

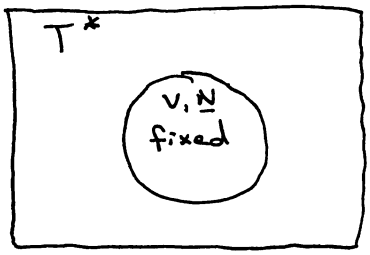
& $d\chi_i^* = -d\chi_i$ mechanical variables

$$dS^* = -\frac{1}{T^*} dU + \frac{1}{T^*} \sum F_i^* d\chi_i$$

$$\boxed{dS^* = -\frac{1}{T^*} dU + \frac{1}{T^*} dw}$$

Isothermal, Isochoric Processes

Consider a closed, isochoric system in thermal contact with a reservoir @ T^*.



From the general Extremum Principle

$$\underbrace{\Delta S}_{\Delta S} - \underbrace{\frac{1}{T^*}\Delta U - \frac{P^*}{T^*}\Delta V}_{\Delta S^*} \geq 0$$

$\Delta S + \Delta S^* \geq 0$ (Total Entropy must increase)

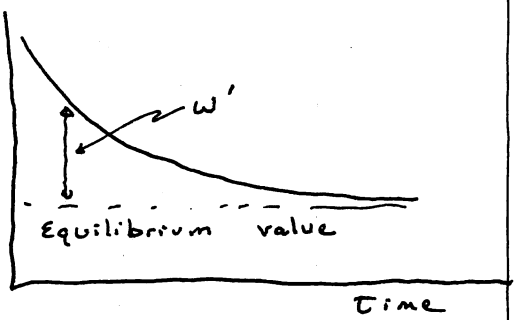
if $\Delta V = 0$ then $\Delta S - \frac{1}{T^*}\Delta U \geq 0$

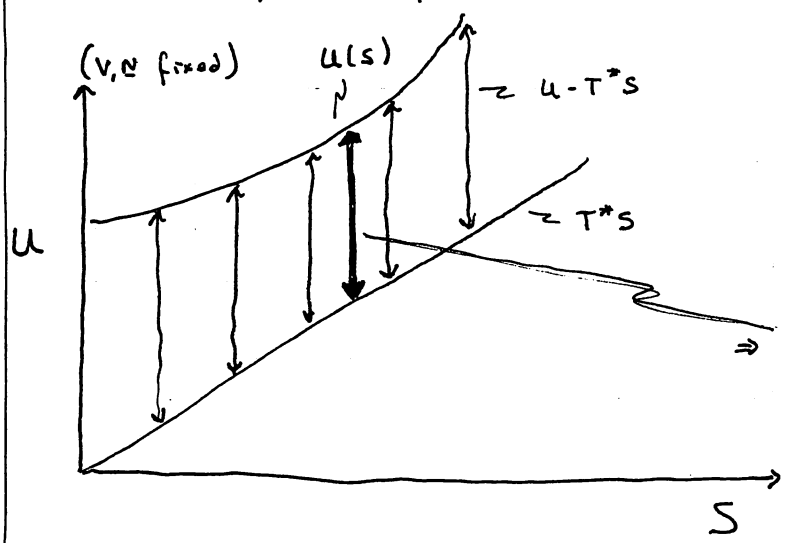
or $\boxed{\Delta U - T^*\Delta S \leq 0}$ → Maximum available work (at fixed V) must decrease for spontaneous processes.

if T^* is fixed, we can write: $U - T^*S$

$$\Delta(U - T^*S) \leq 0$$

⇒ $U - T^*S$ is a minimum at the final Equilibrium state.





minimum value of $U - T^*S$ ⇒ final Equilibrium state

At the final Equilibrium state, the system will thermally Equilibrate with the Surroundings so that $T = T^*$, The minimum value of $U - T^*S$ occurs where $\left(\frac{\partial U}{\partial S}\right)_{V,N} = T^*$ or $T = T^*$

For a differential change, recall

$$dU - T^* dS + P^* dV \leq 0$$ general Extremum condition

Substitute, $dA = dU - d(TS)$

$$= dU - TdS - SdT$$

or $$dU = dA + TdS + SdT$$

$$\Rightarrow \quad dA + TdS + SdT - T^* dS + P^* dV \leq 0$$

$$dA + (T + T^*)\, dS + SdT + P^* dV \leq 0$$

Thus, if $T = T^*$ & V is fixed,

$$\boxed{dA \leq 0}$$

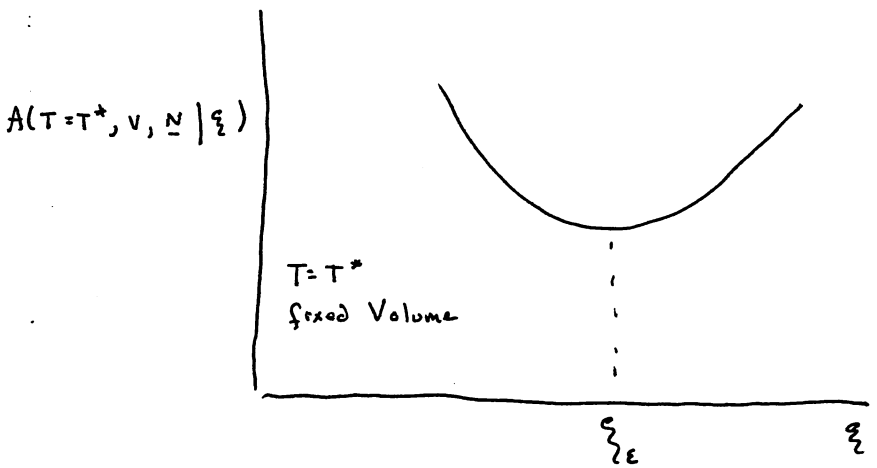
for all spontaneous processes in a closed system where $T = T^*$ & V is fixed

Extremum condition,

$$\left(\frac{\partial A}{\partial \xi} \right)_{T=T^*, V, \underline{N}} = 0$$

$$\left(\frac{\partial^2 A}{\partial \xi^2} \right)_{T=T^*, V, \underline{N}} \geq 0$$

any fluctuation in a system at Equilibrium will increase A at fixed $T, V, \underline{N}$.



Isothermal, Isobaric Processes

Consider a closed, non-rigid system, in thermal & mechanical contact with a reservoir at fixed T^* & P^*.

General Extremum Principle:

$$\Delta S - \frac{1}{T^*}\Delta U - \frac{P^*}{T^*}\Delta V \geq 0$$

or

$$\Delta U - T^*\Delta S - P^*\Delta V \leq 0$$

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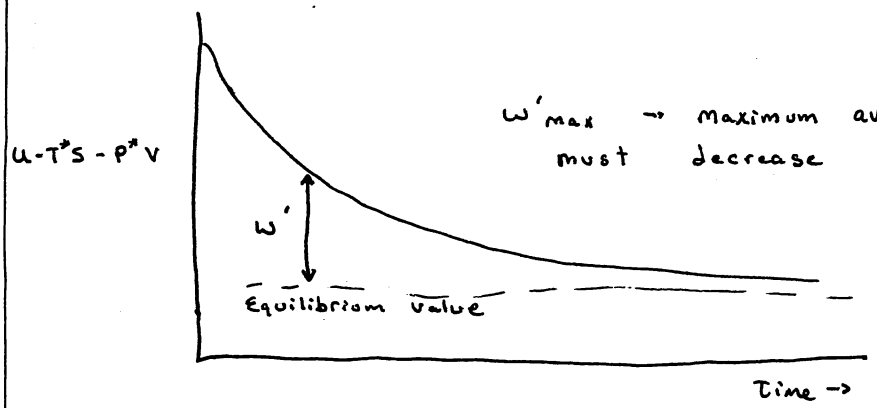
if T^* & P^* are fixed,

$\Delta(U - T^*S - P^*V) \leq 0$ for all spontaneous processes

&

$U - T^*S - P^*V$ is a minimum at the final Equil. state



w'_{max} → maximum available work @ T^* & P^*, must decrease for all spontaneous processes.

At Equilibrium we will also have $T=T^*$ & $P=P^*$ so that $G(T=T^*, P=P^*, \xi)$ will be a minimum value. Thus, to predict the final Equil. state, we can limit our search to those states where $T=T^*$ & $P=P^*$

Summary

For simple closed systems, the general Extremum principle can be written as:

General Extremum Principle

$$dS - \frac{1}{T^*}\,dU - \frac{P^*}{T^*}\,dV \geq 0$$

or

$$dU - T^*\,dS + P^*\,dV \leq 0$$

Entropy Maximum Principle: (fixed $U, V, \underline{N}$)

For a system with fixed $U, V, \underline{N}$,

$$\Rightarrow \Delta S \geq 0$$ for any spontaneous process

Thus, the final Equilibrium state for any isolated system (i.e, $U, V, \underline{N}$ fixed) is that state which maximizes the Entropy of the System.

Energy Minimum Principle: (fixed $S, V, \underline{N}$)

From the general Extremum principle we see that,

$$\Rightarrow \Delta U \leq 0$$ for any spontaneous process

The final Equilibrium state for any system where $S, V, \& \underline{N}$ are fixed is that state which minimizes the Energy of the System.

In summary, we have found that the 2nd law provides an Extremum principle which can be used to determine the final Equilibrium state of a system when any of its internal Constraints are removed. All of these Extremum principles simply boil down to the fact that a system will ultimately seek a final state which maximizes the Total Entropy of the system + surroundings. The various Thermodynamic potentials recast this statement in terms of System variables, i.e., the Entropy change of the Surroundings under certain conditions (i.e., P^* or T^* fixed) can be Expressed as changes in system variables.

Variables Constrained	Thermodynamic Extremum
$U, V, \underline{N}$	S maximized
$S, V, \underline{N}$	U minimized
$T^*, V, \underline{N}$	A minimized
$T^*, P^*, \underline{N}$	G "
$S, P^*, \underline{N}$	H "

It is important to note that these Extremum principles are fundamental. That is, they are valid for any general system regardless of the number of chemical components or phases present within the system. Our only restriction at this point is that the System be simple ($P^* dV$ work only) and closed ($\underline{N}$ fixed). The Extremum principle can easily be extended to situations where other types of work are allowed and also open systems.

We will see how the Extremum principle can be used to determine the final Equilibrium state of the system, i.e., how the Energy, mass & volume is distributed both within the system and between the system and surroundings.