

Another statement of 2nd Law...

Maxmise Entropy

System+surroundings maximise Entropy S

Compare with mechanical equilibrium

Minimise Energy

System minimises energy

In thermodynamic equilibrium

Minises energy

System minimises energy **Free Energy**

Free energy or Gibbs free energy G , is the energy available in a system to do useful work and is different from the total energy change of a process. Thus, total energy = utilizable energy + non-utilizable energy

Potentials

We want to know the equilibrium behaviour of a material system, for specified surroundings.

We can define state functions, U , H , F and G which are useful for determining thermodynamic equilibrium under different external conditions, and the maximum work that can be extracted from a system when those boundary conditions are changed. They all involve state functions and are independent of the process applied to the system.

Potential	Differential	Variables
entropy S	$TdS = dU + PdV$	U, V
internal energy U	$dU = TdS - PdV$	S, V
enthalpy $H = U + PV$	$dH = TdS + VdP$	S, P
Helmholtz free energy $F = U - TS$	$dF = -PdV - SdT$	T, V
the Gibbs free energy $G = H - TS$	$dG = VdP - SdT$	T, P

Maxwell Relations

Kinetic Theory of Gases

Thermodynamics

State Variables

Zeroth law of thermodynamics

Reversible and Irreversible processes

First law of Thermodynamics

Second law of Thermodynamics

Entropy

Thermodynamic Potential

- State functions have TWO independent variables.
- Must be relationships between P, V, T and S.
- Equation of state is one - material specific.
- Also there are general mathematical relationships: Maxwell
- The four Maxwell's relations are general thermodynamic relations involving P, V, T and S which establish links between different measurable properties of substances; specific heat capacities, compressibilities etc.

Maxwell Relations

- Derived from the requirement that the second derivatives of U,H,F,G with respect to their natural variables do not depend on the order of differentiation; – the potentials are state functions.
- $dU = TdS - PdV$: $\frac{\partial^2 U}{\partial V_S \partial S_V} = \left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial S_V \partial V_S} = -\left(\frac{\partial P}{\partial S}\right)_V$
- Independent variables of the potential from which each Maxwell relation is derived appear in the denominators.
- Cross multiplication of numerators and denominators yields products of pairs of conjugate variables, $\partial S \partial T$ and $\partial P \partial V$.
- The sign can be deduced by recourse to the appropriate potential function.

Differential	Maxwell relation
$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$dF = -PdV - SdT$	$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
$dG = VdP - SdT$	$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

Derivations based on Internal Energy U

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- $dU = TdS - PdV$ suggests putting $U = U(S,V)$.
- $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$
- equate coefficients to get: $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $-P = \left(\frac{\partial U}{\partial V}\right)_S$. U is minimised for system at equilibrium with constant V and S boundaries.
- For isochoric process (constant volume) & no other work is done: $dU|_V = TdS|_V = dQ|_V$
- Heat capacity: For reversible, isochoric (constant volume) heat flows: $C_V = \frac{dQ_V}{dT} = \frac{dU_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$

Derivations based on Enthalpy H

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- $H = U + P V$, $dH = dU + PdV + VdP = TdS + VdP$ suggests putting $H = H(S, P)$.
- $dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$
- equate coefficients to get: $T = \left(\frac{\partial H}{\partial S}\right)_P$ and $V = \left(\frac{\partial H}{\partial P}\right)_S$. H is minimised for system at equilibrium with constant P and S boundaries.
- For isobaric process (constant pressure) & no other work is done expect mechanical: $dH|_P = TdS|_P = dQ|_P$
- Heat capacity: For reversible, isobaric (constant pressure) heat flows: $C_P = \frac{dQ_P}{dT} = \frac{dH_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$

Derivations based on Helmholtz free energy F and Gibbs free energy G

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- $F = U - TS$, $dF = dU - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT$ suggests $F = F(V, T)$
- $dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$
- equate coefficients to get: $-P = \left(\frac{\partial F}{\partial V}\right)_T$ and $-S = \left(\frac{\partial F}{\partial T}\right)_V$. F is minimised for system at equilibrium with constant V and T boundaries.
- $G = H - TS$, $dG = dH - TdS - SdT = dU + PdV + VdP - TdS - SdT = VdP - SdT$ suggests $G = G(P, T)$
- $dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$
- equate coefficients to get: $V = \left(\frac{\partial G}{\partial P}\right)_T$ and $-S = \left(\frac{\partial G}{\partial T}\right)_P$. G is minimised for system at equilibrium with constant P and T boundaries.

TdS Equation

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- Entropy is hard to measure, so we would like equations which relate it to measurable quantities, e.g. to find $S(T,V)$.
- $TdS = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV$.
- Knowing $C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$ and using Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ gives the relation between entropy and more easily measured quantities
- $TdS = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$
- Similarly, $TdS = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$