

PREVIOUSLY ON

...*Thermodynamics*

Entropy: The state function for the Second Law

$$\text{Entropy } \int dS = \int \frac{\delta Q}{T}$$

$$\text{Central Equation } dU = TdS - PdV$$

$$\text{Ideal gas entropy } \Delta s = c_v \ln T/T_0 + R \ln v/v_0$$

$$\text{Boltzmann entropy } S = k \log W$$

$$\text{Statistical Entropy } S = -k_B \sum_i p_i \ln(p_i)$$

Fewer entropy with chickens

Counting Things

You can't count a continuum.



This includes states which may never be actually realised.
This is where the ideal gas entropy breaks down

Boltzmann's entropy *requires* Quantum Mechanics.

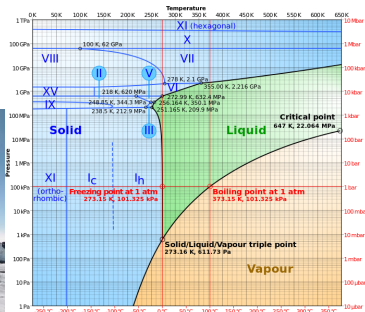
Equilibrium and the thermodynamic potentials

- Second Law : entropy increases in any isolated system.
- Entropy of **system+surroundings** must increase.
- A **system** can reduce its entropy, provided the entropy of the **surroundings** increases by more.



Equilibrium and boundary conditions

- Main postulate of thermodynamics: systems tend to “equilibrium”.
- Equilibrium depends on boundary conditions.



A function for every boundary condition

Another statement of 2nd Law...

System+surroundings maximise S

Compare with mechanical equilibrium

System minimises energy

In thermodynamic equilibrium

System minimises ...



Free energy

Willard Gibbs 1839-1903:

A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces, 1873

Equation of state plotted as a surface of energy vs T and P.

Volume, entropy are *slopes* of this surface

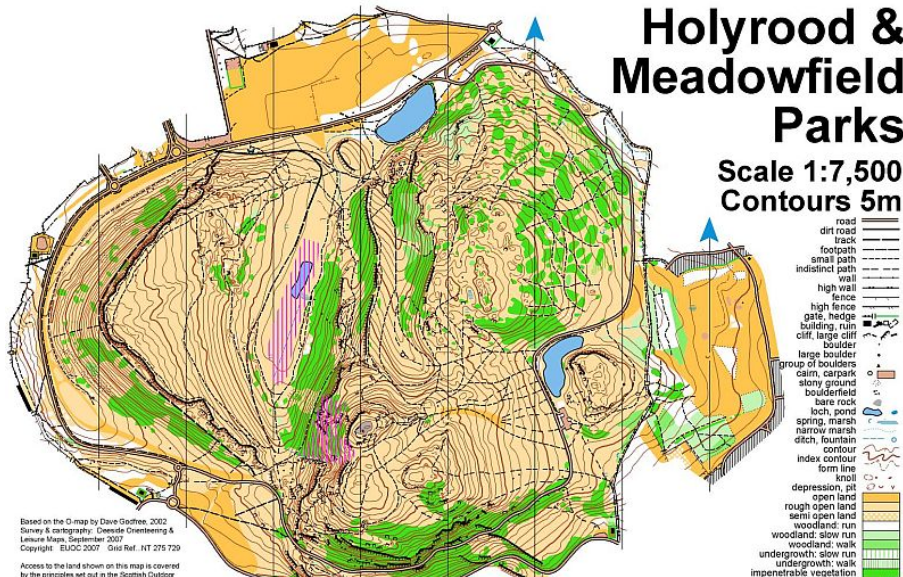
Heat capacity, compressibility are *curvatures*.



Surface and Slopes: Not like this

Holyrood & Meadowfield Parks

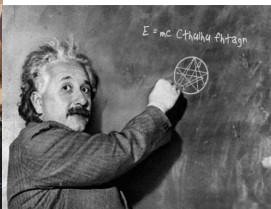
Scale 1:7,500
Contours 5m



Based on the O map by Dave Godfree, 2002
Survey & cartography: Geesde Centrelineing &
Leisure Maps, September 2007
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Access to the land shown on this map is covered
by the principles set out in the Scottish Outdoor

Surfaces and slope: More like something from Lovecraft



H.P.Lovecraft 1928 “The Call of Cthulhu”

PV or TS “space” is completely non-euclidean.

Einstein 1928: [on general relativity] *“The fact that the metric tensor is denoted as geometrical is simply connected to the fact that this formal structure first appeared in the area of study denoted as geometry. However, this is by no means a justification for denoting as geometry every area of study in which this formal structure plays a role,”*

Why *Free* energy

Different axes: different function

Unmeasurable “entropy” axis is awkward

Equilibrium depends on boundary conditions.

Different Definition of Free energy for every boundary condition.

Depends on the dependent variables.

Maximum work available from a system.

Free energies are all state variables.

Also referred to as thermodynamic potentials.

The thermodynamic potentials

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

Hamiltonians, Lagrangians and all that

- Physicists often lazily think we can start with the Hamiltonian (“energy”).
- This makes a hidden assumption about boundary conditions
- In reality, careful thought is needed about what “energy” to use.
- e.g. Particle moving in a potential: S, V boundary, use $U = PE + KE$
- e.g. Air as sound wave passes: S, P boundary, use H
- e.g. Reagents dissolved in water: T, V boundary, use F
- e.g. Water exposed to atmosphere : T, P boundary, use G

Maxwell Relations

- State functions have TWO independent variables.
- Must be relationships between P , V , T and S .
- Equation of state is one - material specific.
- Also general mathematical relationships: Maxwell

Derivation of Maxwell's relations

- The four *Maxwell's relations* are identities involving P , V , T and S .
- They are most conveniently derived from U, H, F, G
- State functions: second derivatives do not depend on the order of differentiation.

e.g. $dU = TdS - PdV$

$$\frac{\partial^2 U}{\partial V_S \partial S_V} = \frac{\partial^2 U}{\partial S_V \partial V_S} \implies \frac{\partial T}{\partial V_S} = -\frac{\partial P}{\partial S_V}$$

etc.

Derivation of Maxwell's relations

To recall the Maxwell relations from their derivation it can be seen that:

- 1 The independent (natural) variables of the potential from which each Maxwell relation is derived appear in the denominators of the relation.
- 2 Cross multiplication of numerators and denominators yields products of pairs of conjugate variables, $\partial S \partial T$ and $\partial P \partial V$.
- 3 The sign can be deduced by recourse to the appropriate potential function.

potential	differential	Maxwell relation
internal energy U	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_U$
enthalpy H $H = U + PV$	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
Helmholtz free energy F $F = U - TS$	$dF = -PdV - SdT$	$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
the Gibbs free energy G $G = H - TS$	$dG = VdP - SdT$	$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

Worth remembering!

TdS equations

To relate entropy changes to measurable quantities.

$$Tds = c_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dv$$

$$Tds = c_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$Tds = c_P \left(\frac{\partial T}{\partial V} \right)_P dV + c_V \left(\frac{\partial T}{\partial P} \right)_V dP$$

such as Heat capacities, thermal expansion, compressibility and Gay-Lussac coefficient

Gay Lussac Coefficient



Louis Joseph Gay-Lussac;
1778 1850

Gay-Lussac, or Amonton's "Law"
"greater pressure causes more hot air"

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

"or maybe not" - unspoken isothermal
assumption.

$$k_{GL} = \frac{P}{T}$$
$$k_{GL} = \left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_P$$

These k_{GL} are *properties of the material*.

iso- is a prefix from the Greek isos, meaning "equal."

- **Equal in all parts/directions** isotropic
- **Equal element** isotopic
- **Equal Temperature:** isothermal
- **Equal Pressure:** isobaric
- **Equal Volume:** isochoric = isovolumetric
- **Equal Enthalpic:** isenthalpic
- **Equal Energy:** isoenergetic
- **Equal Entropy:** isentropic
- **Equal Heat:** adiabatic

Internal Energy for processes involving entropy and volume

$$\begin{aligned}dU &= TdS - PdV \\ &= \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV\end{aligned}$$

Equate coefficients to get:

- 1 $T = \left(\frac{\partial U}{\partial S}\right)_V$
- 2 $-P = \left(\frac{\partial U}{\partial V}\right)_S$

TdS equation

$$Tds = c_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dv$$

If no work is done (V constant)

$$\Delta U = Q \quad (\text{isochoric, no work})$$

note: $\delta q_R = TdS$ for any REVERSIBLE change with no restriction on dV

Heat capacity

For reversible, isochoric heat flows:

$$\begin{aligned}C_V &= \frac{\delta Q_V}{dT} = \frac{dU_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \\ \text{and } C_V &= T \frac{dS}{dT}_V = T \left(\frac{\partial S}{\partial T}\right)_V\end{aligned}$$

From partial derivatives

$$\left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V,$$

a Maxwell's relation.

Enthalpy for processes involving entropy and pressure $H=U+PV$

$$\begin{aligned}dH &= dU + PdV + VdP \\ &= TdS + VdP\end{aligned}$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

Equate coefficients to get:

① $T = \left(\frac{\partial H}{\partial S}\right)_P$

② $V = \left(\frac{\partial H}{\partial P}\right)_S$

TdS equation

$$Tds = c_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$$

Constant P_0 , only P_0V work:

$$\Delta H = Q \quad (P_f = P_i = P_0),$$

$\therefore dH = TdS$ for isobaric process.

note $\delta q_R = T dS$ for any REVERSIBLE changes with no restriction on dP .

Heat capacity

$$C_P = \frac{\delta Q_P}{dT} = \frac{dH_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\text{and } C_P = T \frac{dS_P}{dT} = T \left(\frac{\partial S}{\partial T}\right)_P$$

From partial derivatives

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P,$$

another Maxwell's relation.

Helmholtz for processes involving volume and temperature $F=U-TS$



e.g. Chemicals in a closed container, reactants dispersed in water.

$$\begin{aligned}dF &= dU - TdS - SdT \\ &= -PdV - SdT \\ &= \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT\end{aligned}$$

Equate coefficients to get:

- 1 $-P = \left(\frac{\partial F}{\partial V}\right)_T$
- 2 $-S = \left(\frac{\partial F}{\partial T}\right)_V$

Finally, second derivatives of F .
 $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$,
another Maxwell's relation.

Gibbs for processes involving temperature and pressure.



For systems open to pressure transmitting medium, no exchanging material.

$$\begin{aligned}dG &= dH - TdS - SdT \\ &= VdP - SdT \\ &= \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT\end{aligned}$$

Equate coefficients to get:

- 1 $V = \left(\frac{\partial G}{\partial P}\right)_T$
- 2 $-S = \left(\frac{\partial G}{\partial T}\right)_P$

from partial derivatives

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

another Maxwell's relation.