

PREVIOUSLY ON

...*Thermodynamics*

Only two independent variables \implies Maxwell and other Relations

Equation of state as a 2D surface in a non-Euclidean space

Second Law in terms of properties of the system: Potentials U,H,F,G

Max's Maxwell Mnemonic

"Good Physicists Have Studied Under Very Fine Teachers"



Max Born (1882-1970, UoE 1936-52)
P and S have negative signs.

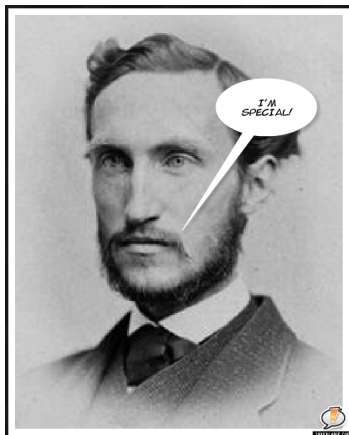
- S	U	V
H		F
- p	G	T

Potentials: coefficients in opposite corners, differentials adjacent. Sign goes with coefficient. e.g. $dF = -SdT - PdV$

Maxwell: Use corners, signs and constants from the bottom variables. e.g.

$$\frac{dS}{-dP_T} = \frac{dV}{dT_P}$$

System minimises its Gibbs free energy at equilibrium



System in equilibrium with itself.
Mechanical and Thermal Equilibrium...
... between any two parts.
Pressure temperature “boundary”

System in contact with a T_0 & P_0 reservoir, $dG=0$

Consider a system held at T_0 , P_0 , initially out of equilibrium.
Heat flows, and work is done as it equilibrates.

Change in surroundings

$$\Delta S_0 = -Q/T_0,$$

$$\Delta V_0 = \Delta V = W/P_0$$

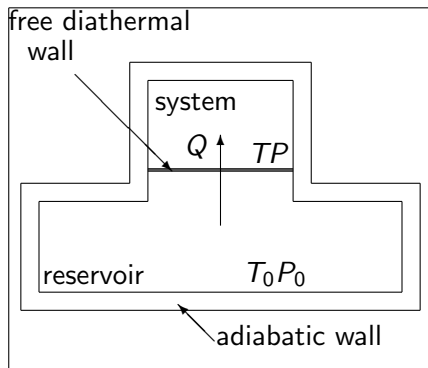
Eventually system reaches equilibrium.

2nd law $\Delta S_{\text{sys}} + \Delta S_0 \geq 0$.

1st law $Q = \Delta U + P_0 \Delta V$

Combined:

$$\Delta U + P_0 \Delta V - T_0 \Delta S \leq 0$$



System goes to Equilibrium

Combined Laws: $\Delta U + P_0\Delta V - T_0\Delta S \leq 0$

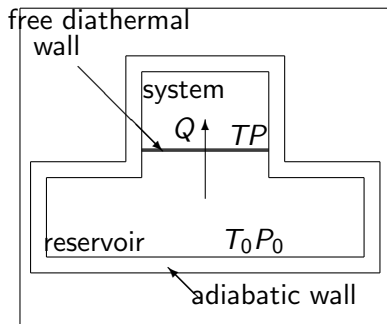
Since $P_0 = P_i = P_f$ and $T_0 = T_i = T_f$

$$\Delta U + (P_f V_f - P_i V_i) - (T_f S_f - T_i S_i) \leq 0$$

$$\Rightarrow \Delta U + \Delta(PV) - \Delta(TS) \leq 0$$

$$\Rightarrow \Delta(U + PV - TS) \leq 0$$

$$\Rightarrow \Delta G \leq 0$$



Any change moving towards equilibrium must reduce G_{sys}

Minimising G_{sys} is equivalent to maximising $S_{\text{sys}} + S_0$: i.e. obeys 2nd law.

Two questions

Evaluate $\left(\frac{\partial V}{\partial P}\right)_S$?



What's the difference between a duck?

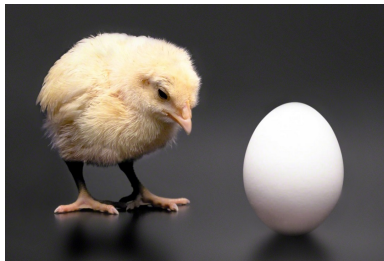
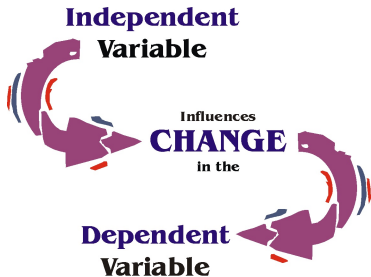
Answer: One of its legs are both the same.

$$(dV/dP)_s = ???$$

Compressibility of a particular substance?
Half a Maxwell relation?
Adiabatic change in volume as pressure increases?
Something to do with Power and Voltage?



Dependent and Independent Variables



In thermodynamic derivations, it is not obvious what to choose as the dependent variable.

This is the *physics* of the question. The rest is just maths.



Ewe chews

Example: The difference in heat capacities, $C_P - C_V$

- What is the general relation between C_P and C_V ?
- $C_P - C_V = nR$ is valid only for an Ideal gas
- Constant volume \implies no work. $dU = TdS - PdV = TdS$

$$C_V = \delta Q_V/dT = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

This suggests working with the entropy : $S = S(T, V)$

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

For $C_P = (\partial H/\partial T)_P = T(\partial S/\partial T)_P$, differentiate wrt T at constant P.

$$C_P = T \left(\frac{\partial S}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Identify terms which are materials properties

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

Introducing heat capacity

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

and isobaric thermal expansivity:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$C_P - C_V = TV\beta \left(\frac{\partial S}{\partial V} \right)_T$$

Eliminate the unmeasurable

$$C_P - C_V = TV\beta \left(\frac{\partial S}{\partial V} \right)_T$$

Recall S is not readily measurable, so use Maxwell to eliminate S .

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

and introduce the isothermal bulk modulus and thermal expansivity (again)

$$= -V \left(\frac{\partial P}{\partial V} \right)_T \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} KV\beta = K\beta$$

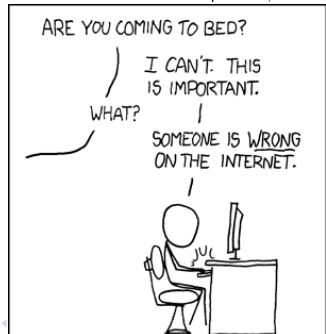
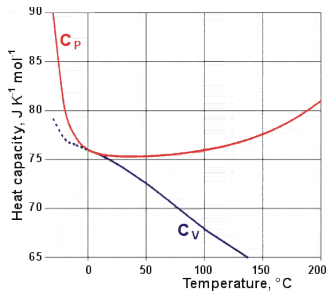
$$K = -V \left(\frac{\partial P}{\partial V} \right)_T \text{ and } \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$C_P - C_V = TV\beta^2 K = TV\beta^2 / \kappa$$

where $\kappa = 1/K$ is the isothermal compressibility.

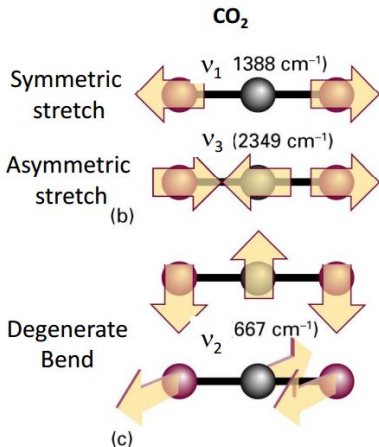
Deconstruct $C_P - C_V = TV\beta^2 K = TV\beta^2 / \kappa$

- $C_P - C_V \propto V \implies$ extensive quantity.
- K is positive for all known substances.
- β^2 is positive.
- $C_P > C_V$, even for negative thermal expansion.
- Difference is NOT due to work done expanding the material.
- $C_V = C_P$ at the density maximum in water.
- β is small except for gases, so $C_P \approx C_V$.
- So for solids and liquids we often (lazily) just give "heat capacity"





Ways and heat capacities: \hat{c}



Gas	C_v (J·K ⁻¹ ·mol ⁻¹)	C_p	$C_p - C_v$	γ
Monatomic gases				
He	12.5	20.8	8.33	1.67
Ar	12.5	20.8	8.33	1.67
Ne	12.7	20.8	8.12	1.64
Kr	12.3	20.8	8.49	1.69
Diatomic gases				
H ₂	20.4	28.8	8.33	1.41
N ₂	20.8	29.1	8.33	1.40
O ₂	21.1	29.4	8.33	1.40
CO	21.0	29.3	8.33	1.40
Cl ₂	25.7	34.7	8.96	1.35
Polyatomic gases				
CO ₂	28.5	37.0	8.50	1.30
SO ₂	32.4	40.4	9.00	1.29
H ₂ O	27.0	35.4	8.37	1.30

Entropy and heat capacity depend on how many degrees of freedom are available for heat.

1000cm⁻¹ = 1439K: Not active at room temperature!

Variations in C_V and C_P (Third derivatives)

What is $\left(\frac{\partial C_V}{\partial V}\right)_T$?

$$\begin{aligned}\left(\frac{\partial C_V}{\partial V}\right)_T &= T \left(\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T}\right)_V\right)_T = T \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T\right)_V \\ &= T \left(\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial T}\right)_V\right)_V = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V\end{aligned}$$

using a Maxwell relation. An analogous analysis for C_P yields

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

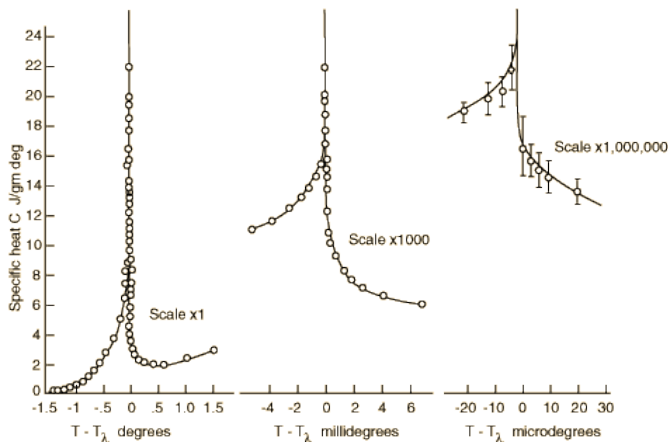
\hat{C}_V derivatives come directly from equation of state!

e.g. $\left(\frac{\partial C_P}{\partial P}\right)_T = 0$ for Ideal Gas $V=RT/P$. (regardless of monatomic/diatomic etc.)

Aside: Latent heats and the Lambda Function

Formally, c_p is infinite at a phase transition ($\Delta V \neq 0$, $\Delta T = 0$).

e.g. liquid He: the integral under the delta-function is the Latent Heat.



$$L = \int_{T-\delta T}^{T+\delta T} c_v dT$$

The “energy equation”. Why demonstrations don't work.

Relate the volume and pressure derivatives of the internal energy to material properties and gradients of equation of state.

Differentiate $dU = TdS - PdV$, wrt dV and eliminate S using a Maxwell relation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P = T \left(\frac{\partial P}{\partial T}\right)_V - P = \frac{T\beta}{\kappa} - P$$

Is force the derivative of energy? Compare $F = -\nabla U$, $P = -\left(\frac{\partial U}{\partial V}\right)_S$

Increasing energy under pressure

Similarly, differentiate $dU = TdS - PdV$, wrt dP and eliminate S using a Maxwell relation:

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T = -TV\beta + PV\kappa_T$$

The ratio of heat capacities C_P/C_V

In the tutorial you will show

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}$$

where κ_T and κ_S are the isothermal and adiabatic compressibilities:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{and} \quad \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$$

Another link between thermal and mechanical properties of materials.

The entropy of an ideal gas, again

For entropy per mole $s = s(T, V)$, we can always write

$$ds = \left(\frac{\partial s}{\partial T} \right)_V dT + \left(\frac{\partial s}{\partial V} \right)_T dV = c_V \frac{dT}{T} + \beta K dV$$

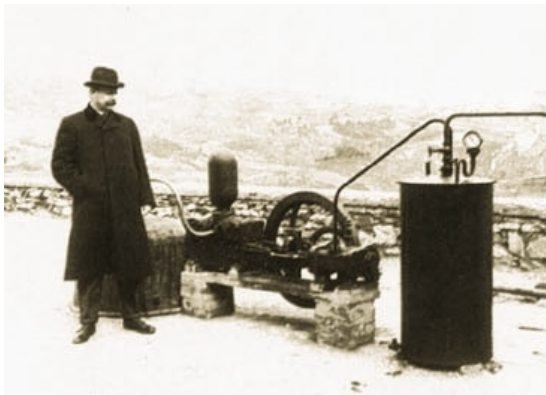
This equation applies to any fluid. β is thermal expansivity, K bulk modulus.

For an Ideal gas $\beta K = R/v$ and c_V is a constant. Integration then gives

$$s = c_V \ln T + R \ln v + s_0$$

Similarly $s = c_P \ln T - R \ln P + s_0$.

Again, we relate *changes* in entropy to measurable quantities via the equation of state.



1904 Prince Piero Ginori Conti. generating electric energy from geothermal steam

- How much work can be extracted from a system?
- Depends on surroundings, but how?

Availability - non Infinite reservoirs

Second-law for system with surrounding reservoir at T_0 , P_0

$$\begin{aligned}\Delta S + \Delta S_{surr} &\geq 0 \\ \Delta S - \frac{Q}{T_0} &\geq 0\end{aligned}$$

Q is heat transferred from the reservoir into the system.

First law for *system* gives $Q = \Delta U + P_0\Delta V$:

$$\Delta U + P_0\Delta V - T_0\Delta S \leq 0$$

Define a new function called the Availability, A ,

$$A = U - T_0S + P_0V$$

Availability $A = U - T_0S + P_0V$

- Availability is **not** Gibbs free energy.
- Depends on both the system *and* surroundings. $A(S, V, P_0, T_0)$,
- Spontaneous changes in availability are always negative
 $\Delta A = \Delta U - T_0\Delta S + P_0\Delta V \leq 0$
- At equilibrium, nothing more can change: Availability is minimised
-

$$dA = dU - T_0dS + P_0dV = 0$$

Availability incorporates all potentials

At equilibrium ($T = T_0$, $P = P_0$), $dA = 0$

If $T = T_0$	&	$P = P_0$	$A = U - TS + PV$	\therefore	G is minimum
If $T = T_0$	&	$V = \text{const}$	$A = U - TS + \text{const}$	\therefore	F is minimum
If S is const.	&	$V = \text{const}$	$A = U + \text{const}$	\therefore	U is minimum
If S is const.	&	$P = P_0$	$A = U - \text{const} + PV$	\therefore	H is minimum
If U is const.	&	$V = \text{const}$	$A = \text{const} - T_0S$	\therefore	S is maximum

- Minimising Availability maximises entropy of the Universe.
- Availability is minimised when system is in equilibrium with surroundings.
- Availability tells us how far from equilibrium we are

Useful Work

The work $P_0\Delta V$, is used to push back the environment.

The heat transfer could run an engine producing *useful work*.

$$\Delta U = Q - W = Q - W^{useful} - P_0\Delta V \quad (1)$$

where Q is the heat transported from the surroundings to the system,

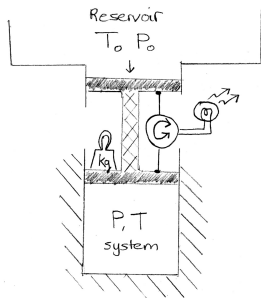
$$\Delta U + P_0\Delta V - T_0\Delta S + W^{useful} = W^{useful} - \Delta A \leq 0$$

Maximum useful work is $W_{max} = -\Delta A$. (iff all changes are reversible).

Likewise, with a small differential change of A :

$$\begin{aligned} dW_{useful} &\leq -dA = -dU + T_0dS - P_0dV \\ &= (T_0 - T)dS + (P - P_0)dV \end{aligned}$$

Available for work



$$dW_{\text{useful}} \leq (T_0 - T)dS + (P - P_0)dV$$

Useful work could come from

- moving entropy (heat) from hot body (T) to cold body (T_0).
- pushing a piston against a pressure (P_0)

Once the availability is used up - no more work.

n.b. the system T changes as it equilibrates

Idealised engines had two infinite T -reservoirs, hot and cold.

Real engines need continual supply of energy to maintain the temperatures.