



Lecture TOPIC 9 (Finn: 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8)

Synopsis: Relationship between state variables, including applications of Maxwell's relations. Heat capacities and entropy. Interdependence of thermal and mechanical properties:

TdS equations

Entropy is hard to measure, so we would like equations which relate it to measurable quantities, e.g. to find $S(T, V)$:

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

From Central Equation $c_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$
and use the Maxwell relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$

Which gives a relationship between entropy and more easily measured quantities.

$$TdS = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

A similar derivation gives: $TdS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$

How to find the difference in heat capacities, $C_P - C_V$

The first step is to decide what should be chosen as independent variables. Heat capacity is *defined* in terms of easily measurable properties: $C_V = dQ_V/dT$; $C_P = dQ_P/dT$.

The central equation gives equivalent expressions in terms of state variables

$$C_V = (\partial U / \partial T)_V = T(\partial S / \partial T)_V$$

$$C_P = (\partial H / \partial T)_P = T(\partial S / \partial T)_P$$

These expressions emphasise the relationship between entropy and heat capacity: they even have the same units! Measuring heat capacity enables us to infer changes in entropy.

To relate C_v to C_P consider $S = S(T, V)$, and its differential by T at constant P .

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

Now we have a general expression for C_P involving C_V

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

Where one partial derivative was identified as the volume thermal expansivity β :

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

The partial derivative $(\partial S/\partial V)_T$ can be re-expressed with the help of a Maxwell relation to eliminate S. The final result in terms of standard measurable properties is then obtained with the cyclical rule:

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

with $K = -V\left(\frac{\partial P}{\partial V}\right)_T$ the isothermal bulk modulus (a mechanical parameter) and β the thermal expansion coefficient again. Inserting the above result:

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

where $\kappa = 1/K$ is the isothermal compressibility. Because K is positive for all substances (as required for mechanical stability) it is always true that $C_P > C_V$.

The dependence of C_V on volume V , and of C_P on pressure P

The internal energy U and $C_V = dU/dT$ of an Ideal Gas are functions of temperature T only, but this is not generally true. A real material's capability of absorbing heat changes with its density, due to the stretching of interatomic bonds, described by a material property $\left(\frac{\partial C_V}{\partial V}\right)_T$.

Thermodynamics can be used to relate $\left(\frac{\partial C_V}{\partial V}\right)_T$ directly to any equation of state:

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

Where a Maxwell relation was used in the penultimate equality. You can easily check that for an ideal gas or even the van der Waals fluid, this is zero. An analogous analysis for C_P yields

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

The Force-energy relation

Taking the derivative of the central equation of thermodynamics, $dU = TdS - PdV$, with respect to dV and replacing the derivative of the entropy using a Maxwell relation gives:

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

For a body in motion, if we write V as length (x) times area (A), and P as force over area.

$$F = P \times A = -\left(\frac{\partial U}{\partial x}\right)_T + AT\beta K_T$$

“Force = -gradient of potential energy + something else”

Note if we consider an *isentropic* process rather than an *isothermal* one, we will recover the normal laws of dynamics. Newton's Laws only hold for objects unable to exchange heat with their surroundings. Similarly, the force is equal to the differential of the appropriate *Free energy* for the boundary condition.

Energy stored as pressure

A similar analysis can be made to re-express the pressure derivative of the internal energy:

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

The various differentials can be related to physical properties, e.g. thermal expansivity $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, Bulk Modulus $K = -V\left(\frac{\partial P}{\partial V}\right)_T$ and Gay-Lussac coefficient $\left(\frac{\partial P}{\partial T}\right)_V = \beta K_T$

Relating thermal and mechanical properties

It can also be shown using Maxwell relations (see tutorial examples) that

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

where κ_T and κ_S are, respectively, the isothermal and adiabatic compressibilities:

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

This provides another useful link between thermal and mechanical properties of materials, enabling us to measure one thing and calculate an apparently unrelated one.

The entropy of an ideal gas, again

For entropy $S = S(T, V)$,

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

which for 1 mole becomes $ds = c_v \frac{dT}{T} + \beta K dv$

The above equation applies to any fluid. For an Ideal gas $\beta K = R/v$ and c_v is a constant. Integration from a reference state (0) then gives $s = c_v \ln T/T_0 + R \ln v/v_0 + s_0$.

Starting with $S = S(T, P)$ a parallel set of steps yields $s = c_P \ln T/T_0 - R \ln P/P_0 + s_0$.

In very general terms, an increase in volume means a positive $\ln(v/v_0)$ implying an increase in the number of ways of arranging particles [because the molecules have more space to occupy]. This gives an increase in the value of entropy. An increase in P (proportional to density) means positive $\ln P/P_0$ meaning that the gas is constrained to occupy a smaller volume, hence the minus sign in $-R \ln P/P_0$. In either case, note that as $T \rightarrow 0$ it seems that $S \rightarrow -\infty$. This is a sign that the classical notions behind the ideal gas are breaking down at low T.

Availability - what is minimised as a system goes to equilibrium?

Consider a system out of equilibrium with surroundings at (T_0, P_0) . Heat Q flows into the system until it reaches equilibrium, and in principle that heat flow can be used to generate work.

The second-law tells us that total entropy increases in a process:

$$\Delta S_{sys} + \Delta S_{surr} \geq 0 \tag{1}$$

$$\Delta S - \frac{Q}{T_0} \geq 0 \quad \text{because} \quad \Delta S_{surr} = \frac{1}{T_0} \int dQ \tag{2}$$

The reservoir is assumed to be much larger than the system, so we take (T_0, P_0) as constants.

In our derivation of the increasing entropy principle EQN 2 was derived directly from the Clausius inequality. EQN 1 can be obtained by considering the surroundings and system as a combined system thermally isolated from the rest of the universe or alternatively from EQN 2 assuming that a reservoir is always considered to be internally in equilibrium.

Using the first law applied to the system is $\Delta U = Q - P_0 \Delta V$, to eliminate Q :

$$\Delta U + P_0 \Delta V - T_0 \Delta S \leq 0 \tag{3}$$

We can define a function called the Availability, $A = U - T_0 S + P_0 V$. Availability depends on both the system and surroundings $A(S, V, P_0, T_0)$, unlike the thermodynamic potentials U, H, F, G , which depend only on the system variables. Availability is not a state variable.

Spontaneous changes in availability as a system equilibrates are always negative (see EQN 3).

$$\Delta A = \Delta U - T_0\Delta S + P_0\Delta V \leq 0 \quad (4)$$

The availability will therefore be at a minimum at equilibrium where no further spontaneous changes can occur. The general condition that A is minimised is a unifying principle which simplifies depending on the boundary conditions of the system.

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

How much useful Work can we get from bringing a finite system to equilibrium?

In the previous section the system did work in expanding against the environment $P_0\Delta V$. This cannot be used for another purpose, but in general, the “system” could incorporate e.g. a heat engine producing additional useful work. In that case work done *by* the system is: $W = W^{useful} + P_0\Delta V$. And the First Law becomes

$$\Delta U = Q - W = Q - W^{useful} - P_0\Delta V \quad (5)$$

where some heat engine is part of the system, so Q is now only the heat transported from the surroundings to the system. Combining (EQN 2 and 5) gives

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

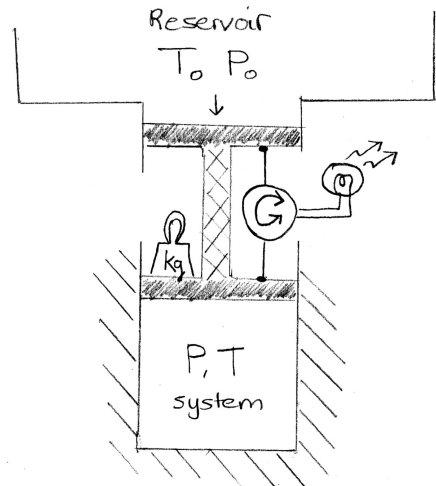
So the maximum useful work that can be obtained is $W_{max}^{useful} = -\Delta A$. This is achieved when all the changes are carried out reversibly. This explains why A is called the availability.

This is also clearly seen if we look at a small differential change of A :

$$\begin{aligned} dW_{useful} &\leq -dA = -dU + T_0dS - P_0dV \\ &= (T_0 - T)dS + (P - P_0)dV \end{aligned} \quad (6)$$

In principle the pressure difference can be used to do mechanical work as the piston moves. For a spontaneous process both $(P - P_0)dV$ and $(T_0 - T)dS$ are positive: a system will expand if its pressure reduces, and increased temperature always increases entropy.

If the changes in dV and dS are reversible the work done by the piston *plus* the work done by the engine, is the maximum that can be extracted from a change (see figure). The maximum useful work is simply $-\Delta A$. We do not have to worry about details of the piston motion or heat engine: we can evaluate $-\Delta A$ however we choose. For example, Supposing the system was one mole of cold ideal gas, initially at (T_i, P_i) . $\Delta U = c_v(T_0 - T_i)$ and $\Delta V = R(T_0/P_0 - T_i/P_i)$. For ΔS , we can use the expression above (being careful with signs) so that in total



$$\Delta A = c_v(T_0 - T_i) - T_0[c_P \ln T_0/T_i - R \ln P_0/P_i] + P_0R(T_0/P_0 - T_i/P_i)$$

Notice each term may be positive or negative, depending on whether the system is initially hotter/colder or higher/lower pressure than the surroundings. Only the total is unambiguously negative. It is always possible to do useful work before reaching equilibrium, which you can prove using the fun function $f(y) = \ln(y) + 1 - y$ which is ALWAYS negative for $y > 0$.