



Lecture TOPIC 8 (Finn: 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.8, 6.9)

Synopsis: The thermodynamic potentials: internal energy U , enthalpy H , Helmholtz function F and the Gibbs function G . Maxwell's relations. $dG = 0$ as the condition for equilibrium.

Equilibrium and the Thermodynamic Potentials

The Second Law tells us that entropy increases in the universe as a whole. So it must increase in any isolated system. But generally, 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	Maxwell relation	natural variables
internal energy U	$dU = TdS - PdV$	$(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$	S, V
enthalpy H $H \triangleq U + PV$	$dH = TdS + VdP$	$(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P$	S, P
Helmholtz free energy F $F \triangleq U - TS$	$dF = -PdV - SdT$	$(\frac{\partial P}{\partial T})_V = (\frac{\partial S}{\partial V})_T$	T, V
the Gibbs free energy G $G \triangleq H - TS$	$dG = VdP - SdT$	$(\frac{\partial V}{\partial T})_P = -(\frac{\partial S}{\partial P})_T$	T, P

Maxwell Relations

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. They are most conveniently 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; this is required since the potentials are state functions.

e.g. $dU = TdS - PdV$ implies that: $\partial^2 U / \partial V_s \partial S_v = (\partial T / \partial V)_s = \partial^2 U / \partial S_v \partial V_s = -(\partial P / \partial S)_v$

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.

Derivations based on Internal Energy U

The central equation of thermodynamics $dU = TdS - PdV$ suggests putting $U = U(S, V)$. Then $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$, equate coefficients to get:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad -P = \left(\frac{\partial U}{\partial V}\right)_S$$

For isochoric process (constant volume) & no other work is done, for ANY changes:

$$\Delta U = Q \quad \therefore \quad dU|_V = TdS|_V, \quad (\text{no work, REVERSIBLE process})$$

Heat capacity: For reversible, isochoric (constant volume) heat flows:

$$C_V \triangleq \frac{dQ_V}{dT} = \frac{dU_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and so} \quad C_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

From partial derivatives for T and P : $\left(\frac{\partial T}{\partial V}\right)_S \left[= \frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \right] = -\left(\frac{\partial P}{\partial S}\right)_V$

U is minimised for system at equilibrium with constant V and S boundaries.

Derivations based on Enthalpy $H = U + PV$

$dH = dU + PdV + VdP = TdS + VdP$ suggests putting $H = H(S, P)$. Then $dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$, equate coefficients to get:

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad \text{and} \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

For isobaric process (constant pressure) if no work done other than mechanical:

$$\Delta H = Q \quad (P_f = P_i = P_0, \text{ no W except PdV})$$

$$\therefore dH|_P = T dS|_P \quad (|_P, \text{ no W except PV, REV})$$

Heat capacity For reversible, isobaric (constant pressure) heat flows:

$$C_P \triangleq \frac{dQ_P}{dT} = \frac{dH_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P \quad \text{and so} \quad C_P = T \frac{dS_P}{dT} = T \left(\frac{\partial S}{\partial T}\right)_P$$

From partial derivatives for T and V : $\left(\frac{\partial T}{\partial P}\right)_S \left[= \frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P} \right] = \left(\frac{\partial V}{\partial S}\right)_P$,

H is minimised for system at equilibrium with constant P and S boundaries.

Derivations based on Helmholtz free energy $F = U - TS$

$dF = dU - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT$ suggests putting $F = F(V, T)$. Then $dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$, equate coefficients to get:

$$-P = \left(\frac{\partial F}{\partial V}\right)_T \quad \text{and} \quad -S = \left(\frac{\partial F}{\partial T}\right)_V$$

From partial derivatives for $-P$ and $-S$: $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$,

F is minimised for system at equilibrium with constant V and T boundaries.

Derivations based on the Gibbs free energy $G = H - TS$

$dG = dH - TdS - SdT = dU + PdV + VdP - TdS - SdT = VdP - SdT$ suggests $G = G(P, T)$. Then $dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$, equate coefficients to get:

$$V = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{and} \quad -S = \left(\frac{\partial G}{\partial T}\right)_P$$

From partial derivatives for V and $-S$. $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$,

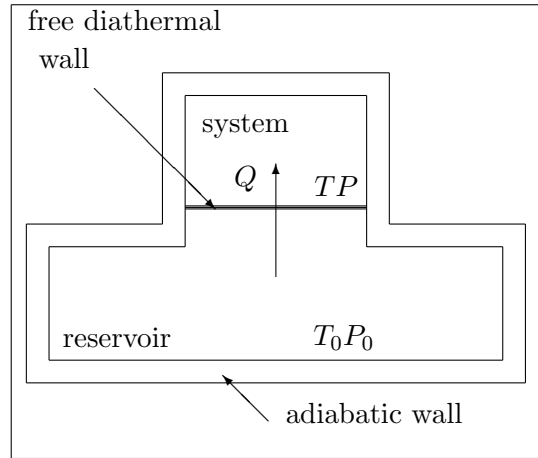
G is minimised for system at equilibrium with constant P and T boundaries.

Equilibrium condition for System in contact with T & P reservoirs: $dG = 0$

Many systems are constrained to operate or evolve when they are open to the atmosphere, and so are subject to (very nearly) constant pressure and temperature at their boundaries.

Gibbs free energy has special status because two parts of a system with no fixed boundary will come into mechanical and thermal equilibrium with constant P and T throughout.

Consider a process in a system is initially at the temperature (T_0) and pressure (P_0) of the heat and pressure reservoir.



If the system evolves, possibly by chemical reaction, its temperature and pressure will, in general, both vary with time. If the system cools, heat Q (assumed measurable) will flow into it from the reservoir. The entropy of the reservoir will change by $\Delta S_0 = -Q/T_0$. If the system expands, it will do work $P_0\Delta V$ on the reservoir.

Suppose that the system eventually returns to a new equilibrium state with temperature T_0 and pressure P_0 , but with its composition somehow changed (possibly its chemical composition). Then, in general, the values of some of its state functions will have changed, possibly the Gibbs free energy and the entropy, amongst others. The change in value of the Gibbs free energy can be found using the principle of increasing entropy, and the 1st law of thermodynamics.

In what follows, symbols with the subscript "0" denote properties of the reservoir and no subscript is used for properties of the system. We examine the ensemble of the system and a sufficiently large volume of reservoir such that the ensemble can be considered to be thermally isolated from the 'rest of the universe'.

	entropy increase	First Law
	$\Delta S + \Delta S_0 \geq 0$	$\Delta U = Q - P_0\Delta V$
→	$\Delta S + \frac{-Q}{T_0} \geq 0$	$Q = \Delta U + P_0\Delta V$
→	$T_0\Delta S - Q \geq 0$	
→	$Q - T_0\Delta S \leq 0$	

Combining the above,

$$\begin{aligned} \Delta U + P_0\Delta V - T_0\Delta S &\leq 0 \\ \Rightarrow \Delta U + P_0(V_f - V_i) - T_0(S_f - S_i) &\leq 0 \end{aligned}$$

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

$$\begin{aligned} \Delta U + (P_f V_f - P_i V_i) - (T_f S_f - T_i S_i) &\leq 0 \\ \Rightarrow \Delta U + \Delta(PV) - \Delta(TS) &\leq 0 \\ \Rightarrow \Delta(U + PV - TS) &\leq 0 \\ \Rightarrow \Delta G &\leq 0 \end{aligned}$$

A system in thermal and mechanical contact with a heat and pressure reservoir is in equilibrium when the Gibbs free energy is a minimum

This means that spontaneous changes in a system in contact with a heat and pressure reservoir are accompanied by a decrease in the value of its Gibbs free energy. Further if any infinitesimal changes are somehow induced in a system already in an equilibrium state, the changes are reversible and $dG = 0$.

Equilibrium condition for different system boundaries

From the boxed equations below, we can identify the natural variables for each potential.

$$\begin{aligned}
 U & \quad \boxed{dU = TdS - PdV} \Rightarrow U(S, V) \\
 \boxed{H = U + PV} & \Rightarrow dH = TdS + VdP \Rightarrow H(S, P) \\
 \boxed{F = U - TS} & \Rightarrow dF = -SdT - PdV \Rightarrow F(T, V) \\
 \boxed{G = U - TS + PV} & \Rightarrow dG = -SdT + VdP \Rightarrow G(T, P)
 \end{aligned}$$

Be aware that if there are additional thermodynamic variables and conjugate forces (i.e. non-PdV work), more potentials can be defined eg. for $dU = TdS - PdV + xdx$ it may be useful to define a new potential $G'(T, P, x) = U - TS + PV - xX$

If the boundary constraints fix the natural variables for a particular potential, that potential is at an extremum at equilibrium with respect to changes of all internal degrees of freedom (eg fixing $P = P_0$ & $T = T_0$ requires $dG = 0$ at equil^m for all possible internal changes of composition). For U, H, F, G the extremum is a minimum. For $S(U, V)$ the extremum is a maximum. The proof in each case follows the same line of argument as was given on the previous page for G .

There are an infinite number of state variables

Any partial derivative of a state variable with respect to another state variable, while holding a third constant, $(\frac{\partial X}{\partial Y})_Z$ is itself a state variable. Any product of state variables is a state variable. Adding together two state variables with the same dimensions produces a state variable. An infinite number, but *all* of them can be derived from the equation of state for *any* of the thermodynamic potentials for the substance.

Example derivation of a Maxwell relation

Suppose we need to re-express $(\frac{\partial S}{\partial P})_T$ in terms of other derivatives, because we don't know about S . A Maxwell relation might help.

1. The relevant independent variables can be identified as P, T . Since the Maxwell relations just reverse the order of differentiation, the above derivative can be related to a partial derivative with respect to T with P held constant. We could also work with the reciprocal $(\frac{\partial P}{\partial S})_T$ and relate this to a partial derivative with respect to T with S held constant.
2. The cross multiplication 'rule' tells us that the derivative it is related to is $(\frac{\partial V}{\partial T})_P$. At this stage it should be apparent whether the application of a Maxwell relation is a useful step in solving a particular problem or not.
3. We know that G has natural variables (T, P) therefore look at $dG = -SdT + VdP$:

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

Thus a negative sign is required in this case: $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$.

This Maxwell relation relates a derivative that does not correspond to a common type of measurement to the isobaric thermal expansivity, $\beta = (\partial \ln(V) / \partial T)_P$, which is easily measured or can be written down directly from the equation of state if the latter is known.