Lecture 16. *Thermodynamic potentials*

- The **internal energy** U of a system is a function of state, which means that a system undergoes the same change in U when we move it from one equilibrium state to another, irrespective of which route we take through parameter space.

- We can make a number of other functions of state, simply by adding to U various other combinations of the functions of state!

- Three of them are extremely useful and are given special symbols: $H = U + pV$, $F = U - TS$ and $G = U + pV - TS$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

Internal energy, U

- Changes (1st law of thermo): $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$
- This shows the **natural variables** are S and V, that is $U = U(S, V)$.
- d$U = 0$ (or "U is a constant") if S and V are fixed
- We also get a definition of T and p. $T = \left(\frac{\partial U}{\partial S}\right)_V$ $p = -\left(\frac{\partial U}{\partial V}\right)_S$
- Isochoric (same volume): $\mathrm{d}U = T\mathrm{d}S$
- Isochoric and reversible: $\mathrm{d}U = \text{đ}Q_{\mathrm{rev}} = C_V\,\mathrm{d}T$ $\Delta U = \int_{T_1}^{T_2} C_V\,\mathrm{d}T$

What if we want to keep pressure constant?

Enthalpy H

$$H = U + PV$$

$$\begin{aligned} \mathrm{d}H &= T\mathrm{d}S - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p \\ &= T\mathrm{d}S + V\mathrm{d}p. \end{aligned}$$

The natural variables for H are thus S and p, and we have that $H = H(S,p)$.

We can therefore immediately write down that for a **isobaric process**, $\mathrm{d}H = T\mathrm{d}S$

and for a reversible isobaric process:

so that

This shows the importance of H, that for reversible isobaric processes the enthalpy represents the **heat absorbed by the system**.

Isobaric conditions are relatively easy to obtain: an experiment that is open to the air in a laboratory is at constant pressure (atmospheric pressure)

We also conclude that if both S and p are constant, we have that $\mathrm{d}H = 0$.

We also have:

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

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

Both U and H suffer from the drawback that one of their natural variables is the entropy S, which is not a very easy parameter to vary in a lab.

It would be more convenient if we could substitute that for the temperature T, which is an easier quantity to control.

We can fix this with the **Helmholtz** and **Gibbs functions**.

Helmholtz function, F

$$F = U - TS$$

$$\begin{aligned} \mathrm{d}F &= T\mathrm{d}S - p\mathrm{d}V - T\mathrm{d}S - S\mathrm{d}T \\ &= -S\mathrm{d}T - p\mathrm{d}V. \end{aligned}$$

This implies that the natural variables for F are V and T, and we can therefore write $F = F(T, V)$.

For an **isothermal process** (constant T) we can write:

$$\mathrm{d}F = -p\mathrm{d}V$$

and hence

$$\Delta F = -\int_{V_1}^{V_2} p \mathrm{d}V$$

Hence a positive change in F represents reversible work done on the system by the surroundings, while a negative change in F represents reversible work done on the surroundings by the system.

F actually represents the maximum amount of work you can get out of a system at constant temperature, since the system will do work on its surroundings until its Helmholtz function reaches a minimum. We also have

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

and the pressure p as

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

If T and V are constant, we have that $\mathrm{d}F = 0$ and F is a constant.

Gibbs function, G

$$G = H - TS$$

Thermodynamic potentials: Summary

Function of state		Differential	Natural variables	First derivatives	
Internal energy	U	$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$	$U = U(S, V)$	$T = \left(\frac{\partial U}{\partial S}\right)_V$,	$p = -\left(\frac{\partial U}{\partial V}\right)_S$
Enthalpy	$H = U + pV$	$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$	$H = H(S, p)$	$T = \left(\frac{\partial H}{\partial S}\right)_p$,	$V = \left(\frac{\partial H}{\partial p}\right)_S$
Helmholtz function	$F = U - TS$	$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$	$F = F(T, V)$	$S = -\left(\frac{\partial F}{\partial T}\right)_V$,	$p = -\left(\frac{\partial F}{\partial V}\right)_T$
Gibbs function	$G = H - TS$	$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$	$G = G(T, p)$	$S = -\left(\frac{\partial G}{\partial T}\right)_p$,	$V = \left(\frac{\partial G}{\partial p}\right)_T$

Show that $U = -T^2 \left(\frac{\partial}{\partial T}\right)_V \frac{F}{T}$ and $H = -T^2 \left(\frac{\partial}{\partial T}\right)_p \frac{G}{T}$

Using the expressions

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_p$$

we can write down

and

These equations are known as the **Gibbs-Helmholtz equations** and are useful in chemical thermodynamics.

Why do we all this?

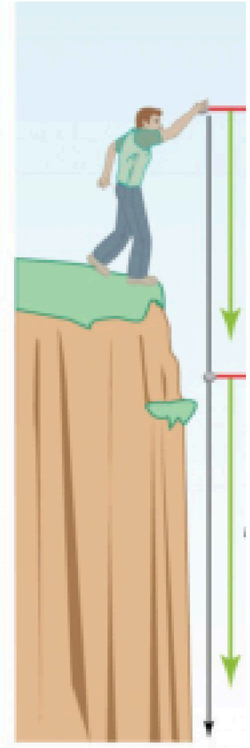
We have seen that the thermodynamic potentials are valid functions of state and have particular properties.

But we have not yet seen how they might be useful!

Are H, F and G just artificial objects whereas U, the internal energy, is the only natural one?

It all depends on the context of the problem, and in particular on the type of **constraint** that is applied to the system.

Free energy



Consider a mass on top of a cliff, near the edge.

This system has the potential to provide useful work

When the mass is at the bottom of the cliff, no more useful work can be obtained.

How can one quantify the amount of available useful work a system can provide? How do constraints affect it?

Free energy?

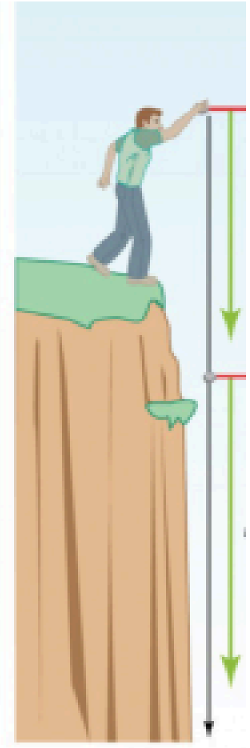
Consider a system with fixed volume, held at a temperature T

If heat $\mathrm{d}Q$ enters the system, we have

By the first law, and so the work added to the system must satisfy

What we have shown is that adding work to the system increases the system's Helmholtz function (which we may now call a Helmholtz free energy).

In a reversible process, $\mathrm{d}W = \mathrm{d}F$ and the work added to the system goes directly into an increase of Helmholtz free energy. If we extract a certain amount of work from the system ( ), then this will be associated with at least as big a drop in the sample's Helmholtz free energy (equality only being obtained in a reversible process).



Adding work to the system hauls the mass up to the top of the cliff and gives it the potential to do work in the future (adding free energy to the system), extracting work from the system occurs by letting the mass drop down the cliff and reduces its potential to provide work in the future (subtracting free energy from the system).

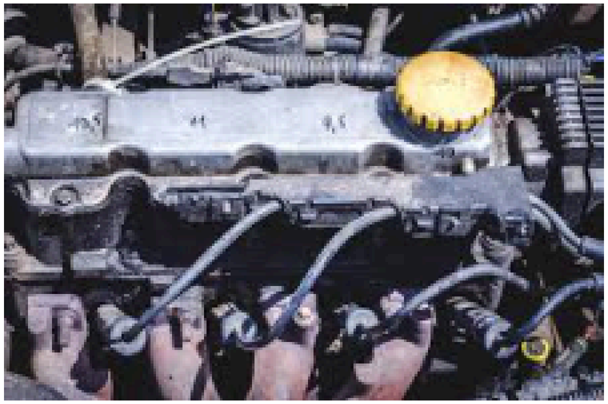
Oil : free energy that can be released when it is burned

How that free energy is defined depends on how the oil is burned.

If it burns inside a sealed drum containing only oil and air, then the combustion will take place in a fixed volume.

In this case, the relevant free energy is the **Helmholtz function**.

However, if the oil is burned in the open air, then the combustion products will need to push against the atmosphere and the **free energy will be the Gibbs function**!



If **the system is mechanically isolated from its surroundings**, so that no work can be applied (to the system) or extracted (from the system), then $\mathrm{d}W = 0$ and we have:

Thus any change in will be negative.

As the system settles down towards equilibrium, all processes will tend to force downwards. Once the system has reached equilibrium, will be constant at this minimum level.

Hence equilibrium can only be achieved by minimizing

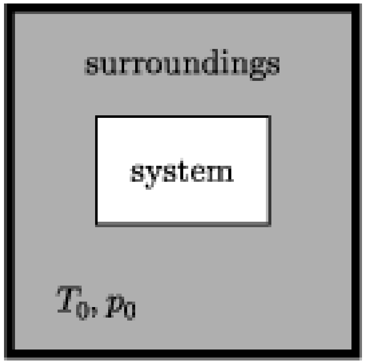
More general constraints

In general, a system is able to exchange heat with its surroundings and also, if the system's volume changes, it may do work on its surroundings.

Let us now consider a system in contact with surroundings at temperature T_0 and pressure p_0.

If heat $\text{đ}Q$ enters the system, the entropy change of the system satisfies . In the general case we write the first law as

More general constraints



Putting this all together gives

$$\text{đ}W \geq \mathrm{d}U + p_0\mathrm{d}V - T_0\mathrm{d}S$$

We now define the availability by

and because and are constants, we have

Changes in availability provide free energy "available" for doing work. A will change its form depending on the type of constraint, as shown below.

First, note that just as we found for the specific case of fixed V and T, in the general case the availability can be used to express a general minimization principle. If the system is mechanically isolated, then

$$\mathrm{d}A \leq 0$$

We have derived this inequality from the second law of thermodynamics. It demonstrates that changes in are always negative. All processes will tend to force downwards towards a minimum value.

Once the system has reached equilibrium, will be constant at this minimum level. Hence equilibrium can only be achieved by minimizing

However, the type of equilibrium achieved depends on the nature of the constraints!

System thermally isolated and with fixed volume

$$A = U + p_0 V - T_0 S$$

No heat can enter the system and the system can do no work on its surroundings, $\mathrm{d}U = 0$.

It follows that $\mathrm{d}A = -\,T_0 \mathrm{d}S$ and therefore $\mathrm{d}A \leq 0$ implies that $\mathrm{d}S \geq 0$

Thus we must maximize S to find the equilibrium state.

System with fixed volume at constant temperature:

$\mathrm{d}A = \mathrm{d}U - T_0\mathrm{d}S \leq 0$, but the temperature is fixed, $\mathrm{d}T = 0$, and

$$\mathrm{d}F = \mathrm{d}U - T_0\mathrm{d}S - S\mathrm{d}T = \mathrm{d}U - T_0\mathrm{d}S$$

so we must minimize   to find the equilibrium state.

System at constant pressure and temperature:

$\mathrm{d}A = \mathrm{d}U - T_0\mathrm{d}S + p_0\mathrm{d}V \leq 0$.

We can write

(from the definition) as

since , and

so we must minimize to find the equilibrium state.

If a chemical reaction is carried out at constant pressure, we have

$$\Delta H = \Delta Q$$

and hence is the reversible heat added to the system, i.e., the heat absorbed by the reaction.

- If the reaction is called exothermic and heat will be emitted.
- If the reaction is called endothermic and heat will be absorbed.

However, this does not tell you whether or not a chemical reaction will actually proceed. Usually reactions occur at constant and so if the system is trying to minimize its availability, then we need to consider The second law of thermodynamics therefore implies that a chemical system will minimize so that if , the reaction may spontaneously occur.

Maxwell's relations

In this section, we are going to derive four equations, which are known as Maxwell's relations. These equations are very useful in solving problems in thermodynamics, since each one relates a partial differential between quantities that can be hard to measure to a partial differential between quantities that can be much easier to measure.

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right)$$

Because f is an exact differential

Hence writing

$$F_x = \left(\frac{\partial f}{\partial x}\right)_y \quad \text{and} \quad F_y = \left(\frac{\partial f}{\partial y}\right)_x ,$$

we have

$$\left(\frac{\partial F_y}{\partial x}\right) = \left(\frac{\partial F_x}{\partial y}\right) .$$

Example: Application to G

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$$

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p \quad \Longrightarrow \quad S = -(\partial G/\partial T)_p \text{ and } V = (\partial G/\partial p)_T.$$

$$\left(\frac{\partial^2 G}{\partial T \partial p}\right) = \left(\frac{\partial^2 G}{\partial p \partial T}\right) \qquad -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

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

Find expressions for $\left(\partial C_p/\partial p\right)_T$ and $\left(\partial C_V/\partial V\right)_T$ in terms of p, V and T

By definition we have: $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$ and $C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$.

Therefore:

$$\begin{aligned}\left(\frac{\partial C_p}{\partial p}\right)_T &= \left(\frac{\partial}{\partial p}T\left(\frac{\partial S}{\partial T}\right)_p\right)_T \\ &= T\left(\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_p\right)_T \\ &= T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T\right)_p\end{aligned} \quad \Rightarrow \quad \left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_p\right)_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

We also have: $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$.

Procedure to solve problems

(1) Write the thermodynamic potential in terms of particular variables

(2) Use Maxwell's relations to transform partial differential into what you need

(3) Invert Maxwell's relation using the reciprocal theorem

(4) Combine partial differentials using the reciprocity theorem

(5) Identify heat capacity $\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V$ and $\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p$

(6) Identify a general susceptibility

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

General susceptibility

A generalized susceptibility quantifies how much a particular variable changes when a generalized force is applied.

A generalized force is a variable such as T or p which is a differential of the internal energy with respect to some other parameter.

An example of a generalized susceptibility is $\left(\frac{\partial V}{\partial T}\right)_x$ which answers the question "keeping x constant, how much does the volume change when you change the temperature?"

Thermal expansivity under a specific constraint

The **isobaric expansivity** β_p is defined as

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

while the **adiabatic expansivity** is defined as

Compressibility

This quantifies how large a fractional volume change you achieve when you apply pressure. The isothermal compressibility κ_T is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

while the adiabatic compressibility is defined as

By considering $S = S(T, V)$, show that $C_p - C_V = VT\beta_p^2/\kappa_T$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V.$$

$$\Downarrow$$

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

Entropy of one mole of ideal gas

$$\mathrm{d}S \quad = \quad \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

$$\Downarrow$$

$$S = \int \frac{C_V}{T}\mathrm{d}T + \int \frac{R\mathrm{d}V}{V}$$

Ratio of the isothermal and adiabatic compressibilities

$$
\begin{aligned}
\frac{\kappa_T}{\kappa_S} &= \frac{\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}{\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S} && \text{Definitions} \\
&= \frac{-\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V}{-\left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_V} && \text{Reciprocity theorem} \\
&= \frac{\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial S}{\partial V}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial S}{\partial p}\right)_V} && \text{Reciprocal theorem} \\
&= \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V} && \text{Simplification} \\
&= \frac{C_p/T}{C_V/T} \\
&= \gamma
\end{aligned}
$$

Summary

We define the following thermodynamic potentials:

$$U, \quad H = U + pV, \quad F = U - TS, \quad G = H - TS$$

which are then related by the following differentials: