Thermodynamics, Part 3

Last time

Entropy

Second law of thermodynamics

Today

Open systems

Free energy

Spontaneity

Next time

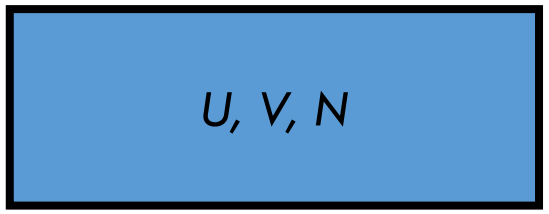
Ideal gases

Simple solids

Thermodynamics so far

- There are four laws of thermodynamics, and they can be derived from statistical mechanics
- First law: energy is conserved
- Second law: entropy always increases in an isolated system

Open systems: Constraints and reservoirs



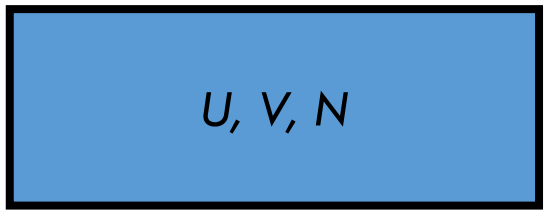
An isolated system is characterised by the energy, volume and particle number, which are fixed



What properties are fixed in an open system?

When we allow exchange of a system quantity with the *surroundings,* we will assume that the surroundings are so much larger than our system that the state of the surroundings remains unchanged, i.e., the surroundings are infinite reservoirs.

Open systems: Constraints and reservoirs



An isolated system is characterised by the energy, volume and particle number, which are fixed



What properties are fixed in an open system?

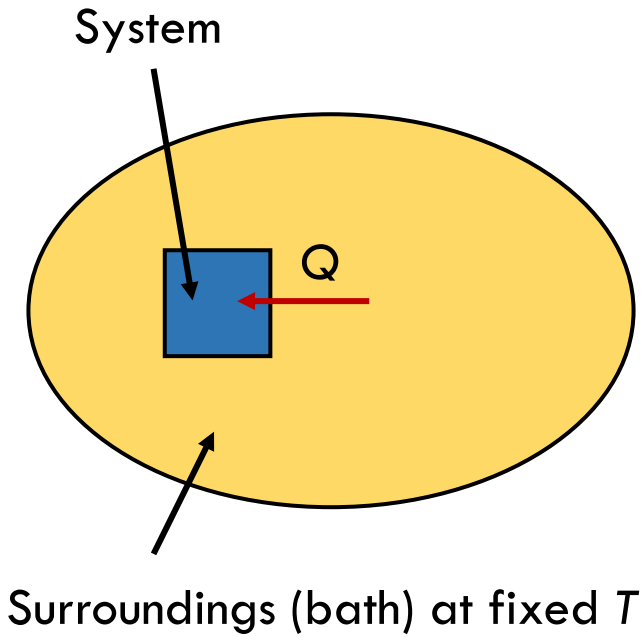
If the system can exchange heat with the surroundings, then its **energy** U is no longer fixed. At equilibrium, the system **temperature** T will equal that of the surroundings.

If the system can expand or contract, its **volume** V is no longer fixed. At equilibrium, the system **pressure** p will equal that of the surroundings.

(The same argument applies for any kind of work, i.e., any pair of generalized displacement and force).

If we allow particle exchange, particle **number** N is no longer fixed. At equilibrium, the **chemical potential** μ will equal that of the surroundings.

System at constant temperature



We start with

$$dS_{\text{total}} = dS + dS_{\text{bath}} \geq 0$$

A large bath is always close to equilibrium,

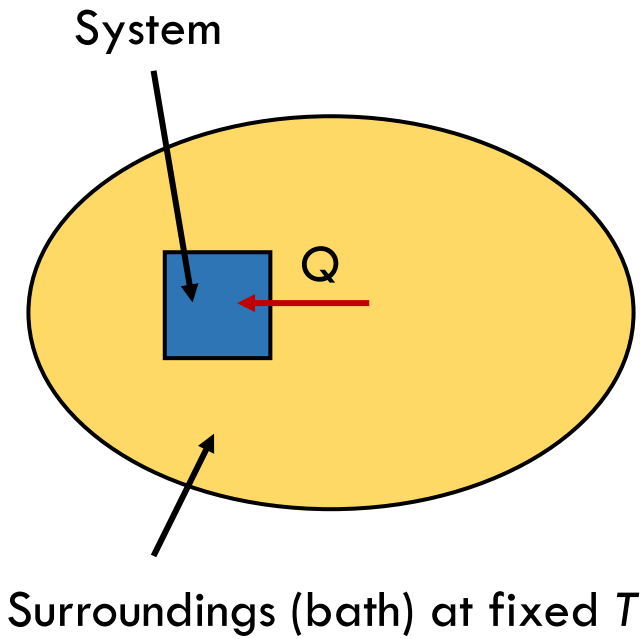
$$dS_{\text{bath}} = -dQ/T$$

Therefore,

$$dS \geq dQ/T$$

This is the Clausius version of the second law

System at constant temperature



$$dS \geq dQ/T$$

Next, we note that

$$dQ = dU - dW$$

Plugging in, we get

$$dS \geq dU/T - dW/T$$

$$dU - TdS \leq dW$$

Free energy

$$dU - TdS \leq dW$$

We define the *Helmholtz free energy*

$$A \equiv U - TS$$

At constant *T*,

$$dA = dU - TdS$$

Still at constant *T*,

$$dA \leq dW$$

Therefore: the Helmholtz free energy is the maximum amount of work that can be extracted from a system at constant *T*. (*A* is for *Arbeit*, German for work).

Spontaneity at constant *T* and *V*

In general, at constant *T*,

$$dA \leq dW$$

If we also add the constraint of constant *V*, i.e., no *pV* work (d*W* = -*p* d*V*), and also no non-*pV* work,

$$dA \leq 0$$

Therefore: at constant *T* and *V*, the condition for spontaneity is d*A* ≤ 0.

The system will try to minimise its free energy.

NB: we are still maximising the entropy of the universe, but we are only tracking the properties of the system.

Important thermodynamic state functions

The free energy is one of several important *state functions.*

State functions depend only on the equilibrium state of the system, and not its history.

For example: internal energy (in the absence of non-expansion work):

$$dU = TdS - pdV$$

At constant volume:

$$dU = dQ_{\mathrm{rev}}$$

Mentimeter

Derivatives of state functions

Derivatives of state functions are sometimes convenient.

For example, given

$$dU = TdS - pdV$$

it follows that

$$\left(\frac{dU}{dS}\right)_V = T$$

Constant pressure and enthalpy

Most chemical reactions take place at constant *pressure*, not volume, so we want a state function analogous to *U* for that circumstance.

We define the enthalpy: $H \equiv U + pV$

$$\begin{aligned} dH &= d(U + pV) \\ &= TdS - pdV + pdV + Vdp \\ &= TdS + Vdp \end{aligned}$$

Then, at constant *p* (and no non-*pV* work), $dH = dQ_{rev}$

When we describe a reaction as exothermic or endothermic, we are usually talking about ΔH, not ΔU.

Gibbs free energy

The analogue of the Helmholtz free energy that is useful at constant pressure is the Gibbs free energy,

$$G \equiv U - TS + pV = H - TS = A + pV$$

From before,

$$dA \leq dW$$

$$dG \leq dW + pdV + Vdp$$

At constant *T* and p,

$$dG \leq dW + pdV = dW_{\text{non-expansion}}$$

If there's no non-*pV* work, we get the condition for spontaneity at constant *T* and *p*:

$$\Delta G \leq 0$$

Mentimeter

Spontaneity summarised

	$dQ = 0$ (adiabatic)	$dT = 0$ (isothermal)
$dV = 0$ (isochoric)	$dS \geq 0$	$dA \leq 0$
$dp = 0$ (isobaric)	$dH \leq 0$	$dG \leq 0$

Connections of state functions to stat. mech.

All thermodynamic state functions can be expressed in terms of the partition function, allowing them to be calculated from microscopic considerations

For example (see book for derivations and other examples):

$$G = -NkT \ln \frac{q}{N}$$

At constant *T* and *N*, *G* is proportional to –ln *q*

This means that equilibrium maximises the number of accessible energy states

Mentimeter

Summary

Key points:

- Open systems shift constraints, e.g., from const. *U* to const. *T*, or from const. *V* to const. *p*
- The state functions *A*, *G*, and *H* govern spontaneity in different kinds of open systems
  - But in all cases, they are just system-based measures of whether the entropy of the universe is increasing
- Statistical mechanics allows all state functions to be expressed in terms of the partition function

Next time

Next time, we'll look at some concrete examples of how to calculate thermodynamic properties using statistical mechanics, with a focus on ideal gases and simple solids.

Reading:

E&R *Phys. Chem.* 31.3, 31.4, 31.7, 32.2.1, 32.3

or E&R *Thermo.* 14.3, 14.4, 14.7, 15.2.1, 15.3