Free energy

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Recall that $dS \geq \delta q/T$ so we have

$$dU \leq TdS$$

which leads to

$$dU - TdS \leq 0$$

Since T and V are constant we can write this as

$$d(U - TS) \leq 0$$

The quantity in parentheses is a measure of the spontaneity of the system that depends on known state functions.
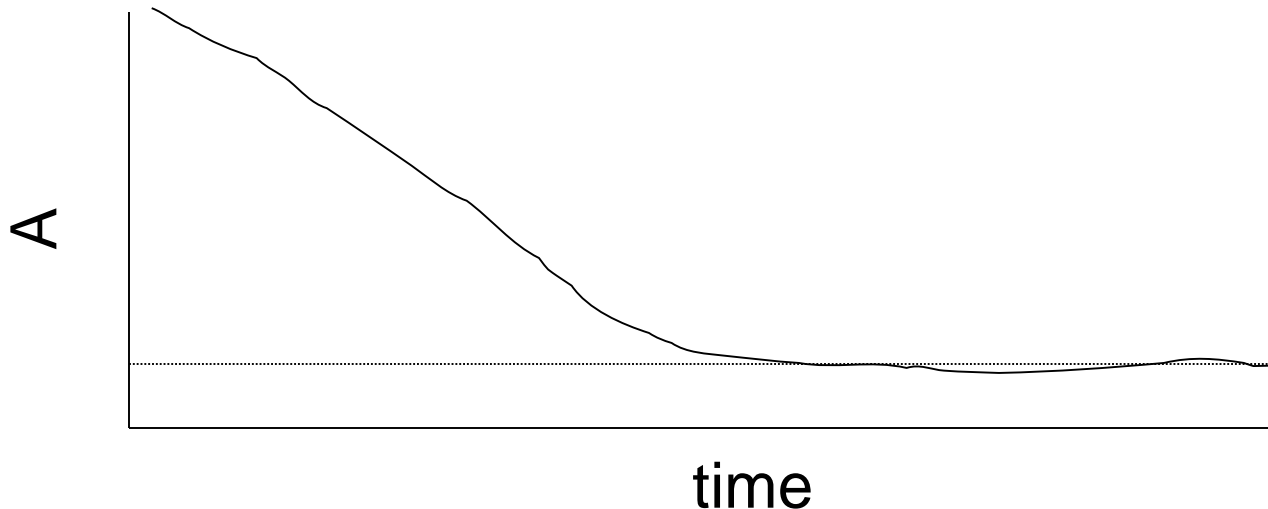
Definition of Helmholtz Free Energy

We define a new state function:
$A = U - TS$ such that $dA \leq 0$.
We call A the Helmholtz free energy.
At constant T and V the Helmholtz free energy will decrease until all possible spontaneous processes have occurred. At that point the system will be in equilibrium.
The condition for equilibrium is $dA = 0$.

Definition of Helmholtz Free Energy

Expressing the change in the Helmholtz free energy we have

$\Delta A = \Delta U - T\Delta S$

for an isothermal change from one state to another.
The condition for spontaneous change is that ΔA is less than zero and the condition for equilibrium is that $\Delta A = 0$.
We write

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If ΔA is greater than zero a process is not spontaneous.
It can occur if work is done on the system, however. The
Helmholtz free energy has an important physical interpretation.
Noting the $q_{rev} = T\Delta S$ we have

$\Delta A = \Delta U - q_{rev}$

According to the first law $\Delta U - q_{rev} = w_{rev}$ so

$\Delta A = w_{rev}$ (reversible, isothermal)

A represents the maximum amount of reversible work that
can be extracted from the system.

Definition of Gibbs Free Energy

Most reactions occur at constant pressure rather than constant volume.
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We define a state function $G = U + PV - TS = H - TS$.

Thus, $dG \leq 0$ (at constant T and P)

The quantity G is called the Gibb's free energy.

In a system at constant T and P, the Gibb's energy will decrease as the result of spontaneous processes until the system reaches equilibrium, where $dG = 0$.

Comparing Gibbs and Helmholtz

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the relationship between enthalpy and internal energy. For chemical processes we see that

$\Delta G = \Delta H - T\Delta S \leq 0$ (at constant T and P)

$\Delta A = \Delta U - T\Delta S \leq 0$ (at constant T and V)