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Entropy

1. Temperature, volume, pressure and energy are all **state variables**: their values depend only on the current state of the system, not on how it got there. *Neither heat nor work are state variables.*
2. The change in **entropy** for any process is defined by the integral of

$$dS = dQ / T.$$

where T is the temperature at which dQ is transferred.

S is a state variable, so we can evaluate the integral over any convenient path (ie., an isothermal path even if the process was *not* isothermal).

S differs from other state variables in that *for any real process*, $\Delta S > 0$. This is one statement of the **second law of thermodynamics**.

3. The **first law of thermodynamics** can then be written

$$dE = T dS - P dV.$$

Defining the **enthalpy** as $H \equiv E + P V$, it takes the form

$$dH = T dS + V dP.$$

Since chemical processes commonly take place at constant pressure, the enthalpy in a chemical reaction indicates whether the reaction is **exothermic** (releases heat) or **endothermic** (absorbs heat).

The **Helmholtz free energy** $F \equiv E - T S$, giving

$$dF = -S dT - P dV.$$

In an isothermal process, the Helmholtz free energy is the maximum amount of energy available to do work.

Finally, the **Gibbs free energy** $G \equiv E - T S + P V$ yields

$$dG = -S dT + V dP.$$

The Gibbs free energy can also be written as $H - T S$ or $F + P V$. The Gibbs free energy is constant during phase transitions in which both the temperature and pressure are constant.

By holding one variable constant, we can obtain a whole host of relations, such as

- $T = dE/dS_{\text{constant } V} = dH/dS_{\text{constant } P}$
- $P = -dE/dV_{\text{constant } S} = -dF/dV_{\text{constant } T}$
- $V = dH/dP_{\text{constant } S} = dG/dP_{\text{constant } T}$

$$\circ S = -dF/dT_{\text{constant } V} = -dG/dT_{\text{constant } P}$$

4. Microscopically, if Ω is the **number of accessible states**,

$$S = k \ln \Omega.$$

A useful analogy: if order is not an observable, Ω would correspond to the number of permutations, and S would correspond to the number of combinations.

Since entropy is associated with the transfer of heat, it is useful to think of an increase in entropy as the distribution of thermal energy into a larger number of degrees of freedom.

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