

An example of a constant temperature process is a phase transition such as the melting of a solid at constant pressure. This occurs reversibly at the normal freezing temperature, T_f because an infinitesimal change in external conditions (e.g. a lowering of the temperature) serves to reverse the process. The reversible heat when 1 mole of substance melts is $q_{rev} = H_{fus}$ and thus:

$$\boxed{S_{fus} = \frac{q_{rev}}{T_f} = \frac{H_{fus}}{T_f}} \quad \text{Similarly,} \quad \boxed{S_{vap} = \frac{q_{rev}}{T_b} = \frac{H_{vap}}{T_b}}$$

where S_{vap} is the molar entropy of vaporization of a liquid at constant pressure at the boiling temperature, T_b . Amazingly, most liquids have about the same molar entropy of vaporization. **Trouton's rule** states that the magnitude of this entropy change: $S_{vap} = 88 \pm 5 \text{ J mol}^{-1} \text{ }^{-1}$ (for most liquids)

$$\boxed{S = n c_v \ln (T_2/T_1) \quad \text{at constant V}}$$

$$\boxed{S = n c_p \ln (T_2/T_1) \quad \text{at constant P}}$$

The Second Law of Thermodynamics: In any spontaneous process, the entropy of the universe (i.e., the system plus its surroundings) increases. More simply: The entropy of the universe is increasing. Note that the entropy of a system can decrease if that of the surroundings increases. $S_{univ} = S_{sys} + S_{surr}$

Because $S = q_{rev} / T$ and $q_{rev} > q_{irrev}$ it follows that $S > q_{irrev} / T$. Combining these two equations yields:
 $S > q / T$ where the equality applies to a reversible process.

In an isolated system there is no transfer of heat into or out of the system, that is, $q=0$. In this case $S = 0$. The universe itself (the system plus its surroundings) is an isolated system. Thus, it follows that:

- 1) In a reversible process the total entropy of a system plus its surroundings is unchanged, $S_{univ} = 0$.
- 2) In an irreversible process the total entropy of a system plus its surroundings must increase, $S_{univ} > 0$.
- 3) A process for which $S_{tot} < 0$ is impossible. (The process is spontaneous in the opposite direction.)

- $S_{univ} > 0$ Spontaneous process in direction written.
- $S_{univ} < 0$ Impossible (the process is spontaneous in opposite direction).
- $S_{univ} = 0$ System at equilibrium. (Reversible)

Definition of Gibbs free Energy: $G = H - TS$ and thus, $\boxed{G = H - TS \quad \text{at constant T}}$

In your text (pg 418) it is shown that $S_{univ} = - G_{sys}/T$ at constant P and T, which implies the following:

G_{sys} relates to the spontaneity of a given process carried out at <u>constant P</u> and <u>constant T</u>	
$G_{sys} < 0$	for spontaneous processes
$G_{sys} > 0$	for nonspontaneous processes
$G_{sys} = 0$	when the system is at equilibrium (reversible processes)

Note: Because $G = H - TS$, an endothermic reaction ($H > 0$) can be spontaneous if $S > 0$ but only at sufficiently high temperatures such that $H < TS$ or $H - TS < 0$ and thus $G < 0$, indicating the reaction is spontaneous. **Note:** When subscripts are not included, it is assumed that all quantities refer to the system.

The Third Law of Thermodynamics: The entropy of a perfect crystal at 0 K is zero. Thus, we can assign absolute entropies, S° . For the reaction: $a A + b B \rightarrow c C + d D$ $S^\circ = [c S^\circ (C) + d S^\circ (D)] - [a S^\circ (A) + b S^\circ (B)]$

Gibbs Free Energy and Equilibrium:

$$G = G^\circ + RT \ln Q \quad \text{where } Q \text{ is the reaction quotient and } G^\circ = H^\circ - T S^\circ$$

At equilibrium, $G = 0$ and $Q = K$. Thus, $G^\circ = -RT \ln K$ and $\boxed{\ln K = -\frac{G^\circ}{RT} = -\frac{H^\circ}{RT} + \frac{S^\circ}{R}}$

A graph of $\ln K$ versus $1/T$ yields a straight line with a slope = $-H^\circ/R$ and intercept = S°/R

van't Hoff equation (pg 438, text):

Vapor Pressure (pg 788, text, Ch.16):

$$\boxed{\ln \left(\frac{K_2}{K_1} \right) = -\frac{H_{vap}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$\boxed{\ln \left(\frac{P_2}{P_1} \right) = -\frac{H_{vap}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

Given H° and K at one temperature, the van't Hoff equation can be used to calculate K at another temperature, assuming H° and S° are constant over the temperature range T_1 to T_2 . For the equilibrium, $H_2O(l) \rightleftharpoons H_2O(g)$, the equilibrium constant $K = P_{H_2O(g)}$, the van't Hoff equation is written in terms of vapor pressures P_1 and P_2 at temperatures T_1 and T_2 . If $P_1 = 1 \text{ atm}$ then $T_1 = T_b$, the normal boiling point.