

An example of a constant temperature reversible 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 $q_{rev} = \Delta H_{fus}$.

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

where ΔS_{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: $\Delta S_{vap} = 88 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ (for most liquids)

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

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. $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

Because $\Delta S = q_{rev} / T$ and $q_{rev} > q_{irrev}$ it follows that $\Delta S > q_{irrev} / T$ Combining these two equations yields:
 $\Delta S \geq q / T$ 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 $\Delta S \geq 0$. 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, $\Delta S_{univ} = 0$.
- 2) In an irreversible process the total entropy of a system plus its surroundings must increase, $\Delta S_{univ} > 0$.
- 3) A process for which $\Delta S_{tot} < 0$ is impossible. (The process is spontaneous in the opposite direction.)
 $\Delta S_{univ} > 0$ Spontaneous process in direction written.
 $\Delta S_{univ} < 0$ Impossible (the process is spontaneous in opposite direction).
 $\Delta S_{univ} = 0$ System at equilibrium. (Reversible)

Definition of Gibbs free Energy: $G = H - TS$ and thus, $\Delta G = \Delta H - T\Delta S$ at constant T

It can be shown that $\Delta S_{univ} = -\Delta G_{sys}/T$ at constant P and T, which implies the following:

$$\begin{aligned} \Delta G_{sys} \text{ and the spontaneity of a given process carried out at } \underline{\text{constant P}} \text{ and } \underline{\text{constant T}} \\ \Delta G_{sys} < 0 & \quad \text{for spontaneous processes} \\ \Delta G_{sys} > 0 & \quad \text{for nonspontaneous processes} \\ \Delta G_{sys} = 0 & \quad \text{when the system is at equilibrium (reversible processes)} \end{aligned}$$

Note: Because $\Delta G = \Delta H - T\Delta S$, an endothermic reaction ($\Delta H > 0$) can be spontaneous if $\Delta S > 0$ but only at sufficiently high temperatures such that $\Delta H < T\Delta S$, $\Delta H - T\Delta S < 0$ and thus $\Delta G < 0$, indicating the reaction is spontaneous. **Note:** When subscripts are not included, it is assumed that all quantities refer to the system. See Table 10.6 pg 424 of your text.

The Third Law of Thermodynamics: The entropy of a perfect crystal at 0 K is zero. Thus, the absolute entropies, S° , for all substances at a given temperature greater than 0 K will be great than zero. Values of S° at 25°C are tabulated in Appendix 4. S° increases as the complexity of a molecule increases.

$$\text{For the reaction: } a A + b B \rightarrow c C + d D \quad \Delta S^\circ = [c S^\circ (C) + d S^\circ (D)] - [a S^\circ (A) + b S^\circ (B)]$$

Gibbs Free Energy and Equilibrium:

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

At equilibrium, $\Delta G = 0$ and $Q = K$. Thus, $\Delta G^\circ = -RT \ln K$ and

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

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

van't Hoff equation

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

Vapor Pressure

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

Given ΔH° and K at one temperature, the van't Hoff equation can be used to calculate K at another temperature, assuming ΔH° and ΔS° 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.