Thermodynamics Notes

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Contents

1 Definitions **2**
- 1.1 Spontaneous process . . . 2
- 1.2 State function . . . 2
- 1.3 Enthalpy change (ΔH) . . . 2
- 1.4 Entropy (S) . . . 2
- 1.5 Exothermic . . . 2
- 1.6 Endothermic . . . 2
- 1.7 First law of thermodynamics . . . 2
- 1.8 Second law of thermodynamics . . . 3
- 1.9 Third law of thermodynamics . . . 3
- 1.10 Standard molar entropy (S°) . . . 3
- 1.11 Thermodynamic standard state . . . 3

2 Formulas **4**
- 2.1 Change in entropy (ΔS) . . . 4
- 2.2 Entropy (S) . . . 5
- 2.3 Standard molar entropy (S°) . . . 8
- 2.4 Change in entropy and the 2nd law of thermodynamics . . . 8
- 2.5 Free energy (G) . . . 9
- 2.6 Standard free energy of formation . . . 9
- 2.7 Free energy changes under non-standard conditions . . . 10
- 2.8 Free energy and chemical equilibrium . . . 10

1 Definitions

1.1 Spontaneous process

A spontaneous process is a process that, once started, proceeds on its own without a continuous external influence.

A spontaneous reaction occurs slowly if it has a high activation energy E_a.

1.2 State function

A state function is a function or property whose value depends only on the present state, or condition, of the system, not on the path used to arrive at that state.

1.3 Enthalpy change (ΔH)

Enthalpy change is the heat change in a reaction or process at constant pressure.

$$\Delta H = \Delta E + P\Delta V$$

1.4 Entropy (S)

Entropy is the amount of molecular randomness in a system.

1.5 Exothermic

A process is considered exothermic if its $\Delta H < 0$. In other words, the reaction releases energy.

1.6 Endothermic

A process is considered endothermic if its $\Delta H > 0$. In other words, the reaction takes in energy.

1.7 First law of thermodynamics

The first law of thermodynamics states that in any process, regardless of the process' spontaneity, the total energy of a system and its surroundings is constant.

1.8 Second law of thermodynamics

The second law of thermodynamics states that in any **spontaneous** process, the total entropy of a system and its surroundings always increases.

1.9 Third law of thermodynamics

The third law of thermodynamics states that the entropy of a perfectly ordered crystalline substance at 0 K is zero.

1.10 Standard molar entropy (S°)

The entropy of 1 mole of a pure substance at 1 atm pressure and a specified temperature.

1.11 Thermodynamic standard state

The thermodynamic standard state is the most stable form of a substance. The conditions are:

- Pressure of 1 atm
- Temperature of 25 °C
- Concentration of 1 M for all substances in solution

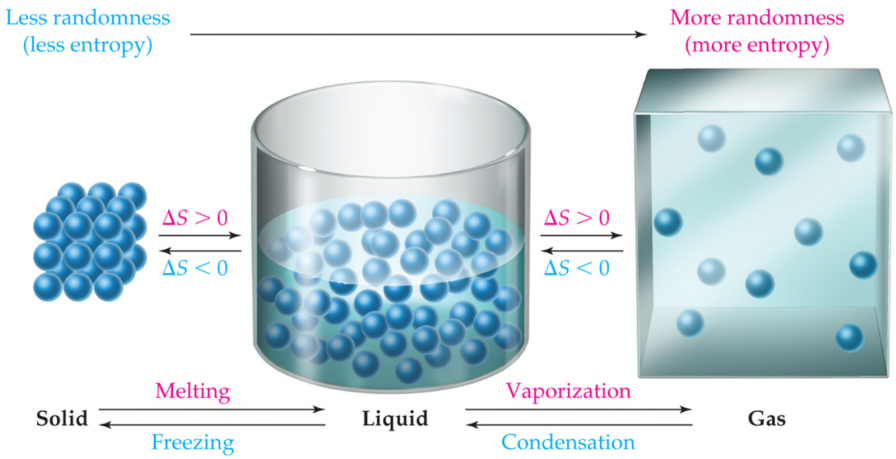
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

2 Formulas

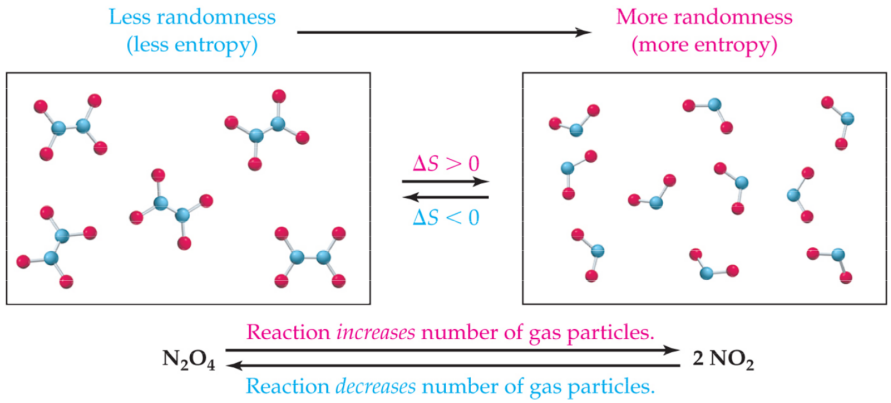
2.1 Change in entropy (ΔS)

$$\Delta S = S_{final} - S_{initial}$$

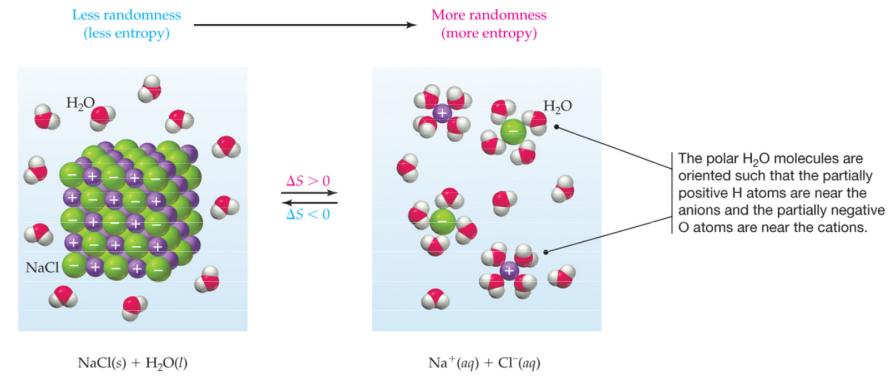
2.1.1 Entropy change for a change in state



2.1.2 Entropy change for a gas reaction



2.1.3 Entropy change for the dissolution of an ionic compound



Disruption of the crystal increases the entropy, but the hydration process decreases the entropy. For the dissolution of NaCl, the net effect is an entropy increase.

2.2 Entropy (S)

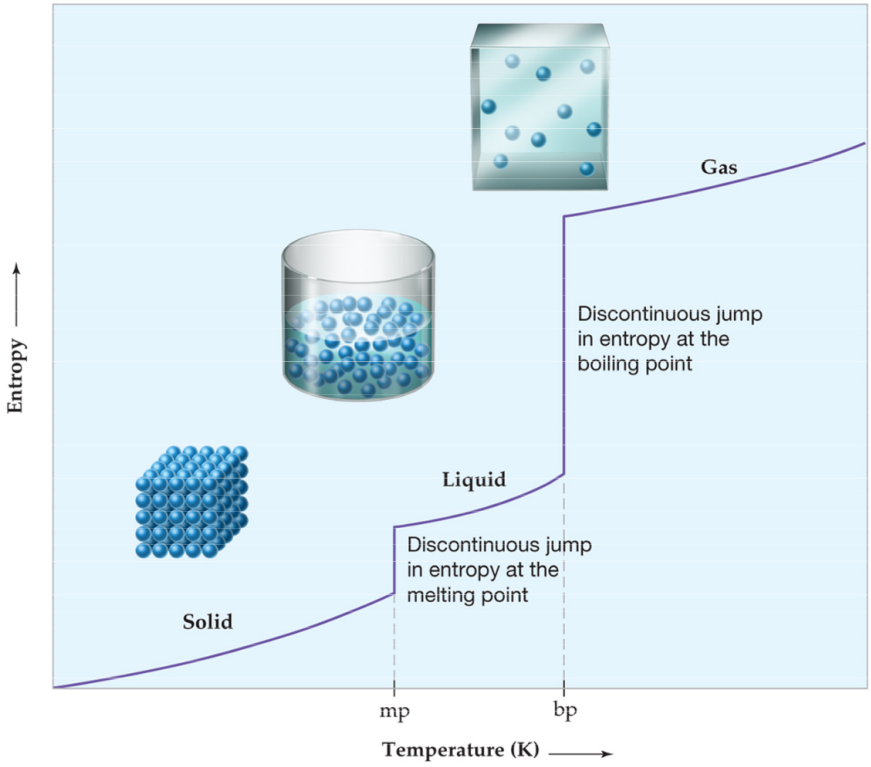
$$S = k \ln W$$

Where:

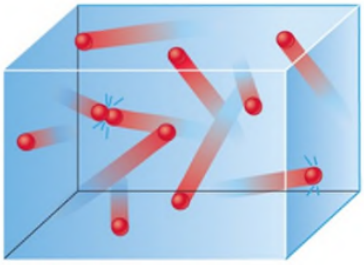
$$k = \text{Boltzmann's constant}$$
$$= 1.38 \times 10^{-23}\ \text{J K}^{-1}$$

W = The number of ways that the state can be achieved

2.2.1 Entropy at various temperatures

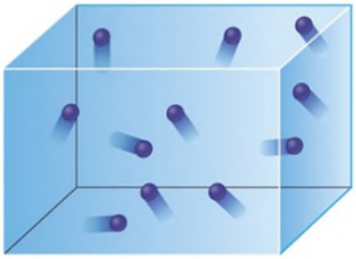


2.2.2 Entropy at high temperatures



Higher temperature:
- Greater molecular speeds
- Broader distribution of individual kinetic energies
- More randomness
- Higher entropy

2.2.3 Entropy at low temperatures



Lower temperature:
- Lesser molecular speeds
- Narrower distribution of individual kinetic energies
- Less randomness
- Lower entropy

2.3 Standard molar entropy (S°)

$$\Delta S^\circ = S^\circ(\text{Products}) - S^\circ(\text{Reactants})$$

$$aA + bB \rightarrow cC + dD$$

$$\Delta S^\circ = \underbrace{[cS^\circ(C) + dS^\circ(D)]}_{\text{Products}} - \underbrace{[aS^\circ(A) + bS^\circ(B)]}_{\text{Reactants}}$$

2.4 Change in entropy and the 2nd law of thermodynamics

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$\Delta S_{total} > 0$	The reaction is spontaneous.
$\Delta S_{total} < 0$	The reaction is not spontaneous.
$\Delta S_{total} = 0$	The reaction mixture is at equilibrium.

$$\Delta S_{surr} \propto -\Delta H$$

$$\Delta S_{surr} \propto \frac{1}{T}$$

$$\Delta S_{surr} \propto \frac{-\Delta H}{T}$$

2.5 Free energy (G)

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$\begin{aligned}
\Delta S_{total} &= \Delta S_{sys} + \Delta S_{surr} \\
&= \Delta S_{sys} + \frac{-\Delta H}{T} \quad (\because \Delta S_{surr} = \frac{-\Delta H}{T}) \\
&= \Delta S - \frac{\Delta H}{T} \quad (\because \Delta S = \Delta S_{sys})
\end{aligned}$$

Hence:

$$\Delta S = \Delta S_{total} + \frac{\Delta H}{T}$$

Substituting into the formula for the change in Gibbs free energy

$$\begin{aligned}
\Delta G &= \Delta H - T\Delta S \\
&= \Delta H - T\left(\Delta S_{total} + \frac{\Delta H}{T}\right) \\
&= \Delta H - T\Delta S_{total} + \Delta H \\
&= -T\Delta S_{total}
\end{aligned}$$

Using the second law of thermodynamics and $\Delta G = -T\Delta S_{total}$:

$\Delta G > 0$	The reaction is spontaneous.
$\Delta G < 0$	The reaction is not spontaneous.
$\Delta G = 0$	The reaction mixture is at equilibrium.

2.6 Standard free energy of formation

$$\Delta G^\circ = \Delta G_f^\circ(\text{Products}) - \Delta G_f^\circ(\text{Reactants})$$

$$aA + bB \rightarrow cC + dD$$

$$\Delta G^\circ = \underbrace{[cG_f^\circ(C) + dG_f^\circ(D)]}_{\text{Products}} - \underbrace{[aG_f^\circ(A) + bG_f^\circ(B)]}_{\text{Reactants}}$$

2.7 Free energy changes under non-standard conditions

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Where ΔG is the free energy change under non-standard conditions.
For example, the Haber synthesis of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$Q_p = \frac{(P_{NH_3})^2}{(P_{N_2})^2 (P_{H_2})^3}$$

2.8 Free energy and chemical equilibrium

$$\Delta G = \Delta G^\circ + RT \ln Q$$

When the reaction mixture is mostly **reactants**:

$$Q << 1$$

$$RT \ln Q << 0$$

$$\Delta G < 0$$

The total free energy decreases as the reaction proceeds spontaneously in the **forward** direction.

When the reaction mixture is mostly **products**:

$$Q >> 1$$

$$RT \ln Q >> 0$$

$$\Delta G > 0$$

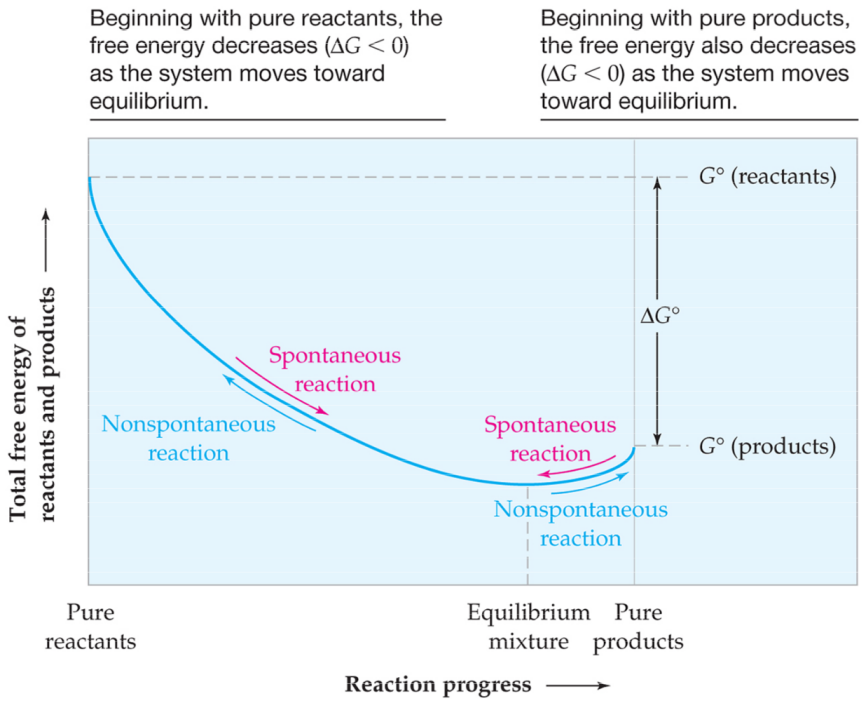
The total free energy decreases as the reaction proceeds spontaneously in the **reverse** direction.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium, $\Delta G = 0$ and $Q = K$:

$$\Delta G^\circ = -RT \ln K$$

2.8.1 A diagram to explain the relationship between free energy and chemical equilibrium



2.8.2 Relationship between the standard free energy change and the equilibrium constant

$\Delta G°$	$\ln K$	K	Comment
$\Delta G° < 0$	$\ln K > 0$	$K > 1$	The equilibrium mixture is mainly products.
$\Delta G° > 0$	$\ln K < 0$	$K < 1$	The equilibrium mixutre is mainly reactants.
$\Delta G° = 0$	$\ln K = 0$	$K = 1$	The equilibrium mixture contains comparable amounts of reactants and products.