Thermodynamics: The Direction of Chemical Reactions
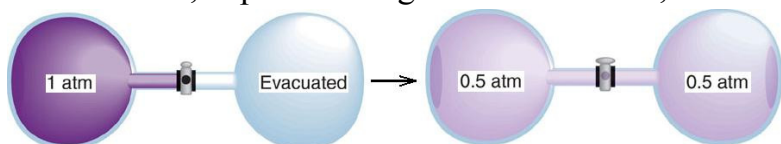
– Thermodynamics has two major aspects:
  • Conservation of energy (1st law)
  • Direction of processes (2nd law)

20.1 The 2nd Law of Thermodynamics

• **Spontaneous changes** – occur without any external influence

Examples: Aging, rusting, heat transfer from hot to cold, expansion of gases into vacuum, etc.
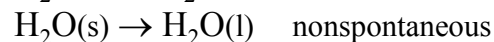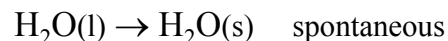

• **Nonspontaneous changes** – require an external force or energy in order to occur
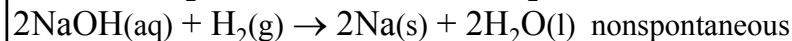
Examples: Refrigeration (heat transfer from cold to hot), evacuation of flasks by vacuum pumps, etc.

• If a process is spontaneous in one direction, it is not spontaneous in the other

Example: At -20°C, water freezes spontaneously, but ice does not melt spontaneously:

$H_2O(l) \rightarrow H_2O(s)$ spontaneous
$H_2O(s) \rightarrow H_2O(l)$ nonspontaneous

Example: At 25°C:

$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$ spontaneous
$2NaOH(aq) + H_2(g) \rightarrow 2Na(s) + 2H_2O(l)$ nonspontaneous

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Limitations of the 1st Law

➤ The **1st law** states that **the total energy of the universe is constant** (E_{univ} = const.)

→ E_{univ} can be separated into two parts, energy of the system, E_{sys}, and energy of its surroundings, E_{surr}
  $\Rightarrow E_{univ} = E_{sys} + E_{surr} \Rightarrow \Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr}$

→ Since E_{univ} = const., $\Delta E_{univ} = 0$
  $$\Rightarrow \Delta E_{sys} + \Delta E_{surr} = 0 \quad \Rightarrow \quad \Delta E_{sys} = -\Delta E_{surr}$$

→ Since $\Delta E = q + w$ $\quad \Rightarrow (q + w)_{sys} = -(q + w)_{surr}$

  → Energy (heat and/or work) released by the system is absorbed by its surroundings and vice versa

  → The 1st law doesn't explain the direction of spontaneous processes since energy conservation can be achieved in either direction

The Sign of ΔH and Spontaneity

➤ The sign of ΔH has been used (especially by organic chemists) to predict spontaneous changes – **not a reliable indicator**

  ➤ In most cases spontaneous reactions are **exothermic** ($\Delta H < 0$) → combustion, formation of salts from elements, neutralization, rusting, …

  ➤ In some cases, spontaneous reactions can be **endothermic** ($\Delta H > 0$) → dissolution of many salts, melting and vaporization at high T, …

→ A common feature of all **spontaneous endothermic reactions** is that their products are less ordered than the reactants (**disorder**↑ during the reaction)

Example: Solid → Liquid → Gas
                most ordered   least ordered

The Meaning of Disorder and Entropy

➤ **Macro-state** – the macroscopic state of a system described by its parameters (*P, V, n, T, E, H*, etc.)

  ➤ Spontaneous processes proceed from macro-states that are less probable toward ones that are more probable

➤ **Micro-state** – one of the possible microscopic ways through which the macro-state can be achieved

  ➤ Refers to one of the possible ways the total energy can be distributed over the quantized energy levels of the system

  ➤ This includes energy levels related to all possible motions of the molecules (translational, rotational, vibrational, etc.)

➤ More probable macro-states are those that can be achieved in a larger number of different ways (micro-states), and therefore, are more disordered

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➤ In thermodynamics, the disorder of a macro-state is measured by the **statistical probability**, $W \rightarrow$ the number of different ways the energy can be distributed over the quantized energy levels of the system while still having the same total energy, or simply the number of micro-states through which the macro-state can be achieved

Example: Arrangement of 2 particles (**x** and **o**) in 3 possible positions $\rightarrow$ | 1 | 2 | 3 |

$\rightarrow$ There are 6 possible arrangements ($W = 6$)

$\rightarrow$ Increasing the # of possible positions increases W

$\uparrow W \Leftrightarrow \uparrow$Disorder

• **Entropy** (*S*) – a state function related to the disorder of the system

  – **Boltzmann equation** $\rightarrow$ $\boxed{S = k \ln(W)}$

   $\rightarrow k = 1.38 \times 10^{-23}$ J/K (Boltzmann constant)

   $$\boxed{\uparrow W \Leftrightarrow \uparrow \text{Disorder} \Leftrightarrow \uparrow S}$$

  – *S* is a state function – depends only on the present state of the system and not on the way it arrived in that state

  $\Rightarrow$ The entropy change, $\Delta S = S_{final} - S_{initial}$, is path independent

  $\Rightarrow$ If $\Delta S > 0$, the entropy and the disorder increase

  $\Rightarrow$ If $\Delta S < 0$, the entropy and the disorder decrease

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• The entropy and the disorder of a system can be increased in two basic ways:

  – Heating (increases the **thermal disorder**)

  – Expansion, mixing or phase changes (increase the **positional disorder**)

  Note: Both thermal and positional disorder have the same origin (the number of possible micro-states)

Example: Gases expand spontaneously in vacuum.

$\rightarrow$ During the expansion the total energy does not change (no heat is exchanged and no work is done since $P_{ext} = 0$)

$\rightarrow$ The volume increases so the number of possible positions available to the particles increases $\Rightarrow W \uparrow$

$\Rightarrow$ The process is driven by increase in the positional disorder and thus increase in the entropy

Entropy and the 2nd Law

➢ The entropy of the system alone can not be used as a criterion for spontaneity

  ➢ Spontaneous processes can have $\Delta S > 0$ or $\Delta S < 0$

➢ The true criterion for spontaneity is the entropy of the universe (S_{univ})

• **The 2nd law of thermodynamics** – for any spontaneous process, the entropy of the universe increases ($\Delta S_{univ} > 0$)

$$\Rightarrow \Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

  – There are no restrictions on the signs of ΔS_{sys} and ΔS_{surr} as long as the sum of the two is greater than zero

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Standard Molar Entropies and the 3rd Law

• **The 3rd law of thermodynamics** – the entropy of a perfect crystal at the absolute zero is zero (As $T \rightarrow 0K$, $S_{sys} \rightarrow 0$)

  – At the absolute zero, the particles of the crystal achieve the lowest possible energy and there is only one way they can be arranged ($W = 1$)

$$\Rightarrow S_{sys} = k \ln(1) = k\,(0) = 0$$

  – The 3rd law allows the use of **absolute entropies**

  $\Rightarrow$ The entropy of a substance at a given T is equal to the entropy increase accompanying the heating of the substance from 0 K that T

• **Standard molar entropy** (S^o) – the entropy of 1 mol of a substance in its standard state and a specified temperature (usually 298 K)

  – **Standard state** – 1 atm for gases, 1 M for solutions, pure for liquids and solids

  – Units of $S^o \rightarrow$ J/mol·K

• S^o can be affected by changing the thermal and positional disorder in different ways

  ➢ **Temperature changes** – for a given substance, S^o increases as the temperature is increased

$$\uparrow T \Rightarrow \uparrow S^o$$

  $\rightarrow$ As $T\uparrow$, the average E_k of the molecules $\uparrow$ and the # of ways to distribute E_k among the particles $\uparrow$ so W and $S^o\uparrow$

➢ **Phase changes** – for a given substance, S^o increases as the substance is converted from solid to liquid to gas

$$S^o_{(solid)} < S^o_{(liquid)} < S^o_{(gas)}$$

$\rightarrow$ In the liquid and especially in the gas phase, the particles have more freedom to move around an thus higher positional disorder

$\Rightarrow$ Within each phase, the entropy increases gradually with increasing T

$\Rightarrow$ Since phase changes occur at constant T, a sharp change in entropy is observed as the T passes through the melting or boiling points

$\Rightarrow$ Since the gas phase has much higher S^o than the liquid and solid phases, $\Delta S^o_{vap} >> \Delta S^o_{fus}$