

Spontaneous Change: Entropy and Free Energy

2nd and 3rd Laws of Thermodynamics

Problem Set: Chapter 20 questions 29, 33, 39, 41, 43,
45, 49, 51, 60, 63, 68, 75

The second law of thermodynamics looks mathematically simple but it has so many subtle and complex implications that it makes most chemistry majors sweat a lot before (and after) they graduate. Fortunately its practical, down-to-earth applications are easy and crystal clear. We can build on those to get to very sophisticated conclusions about the behavior of material substances and objects in our lives.

Frank L. Lambert

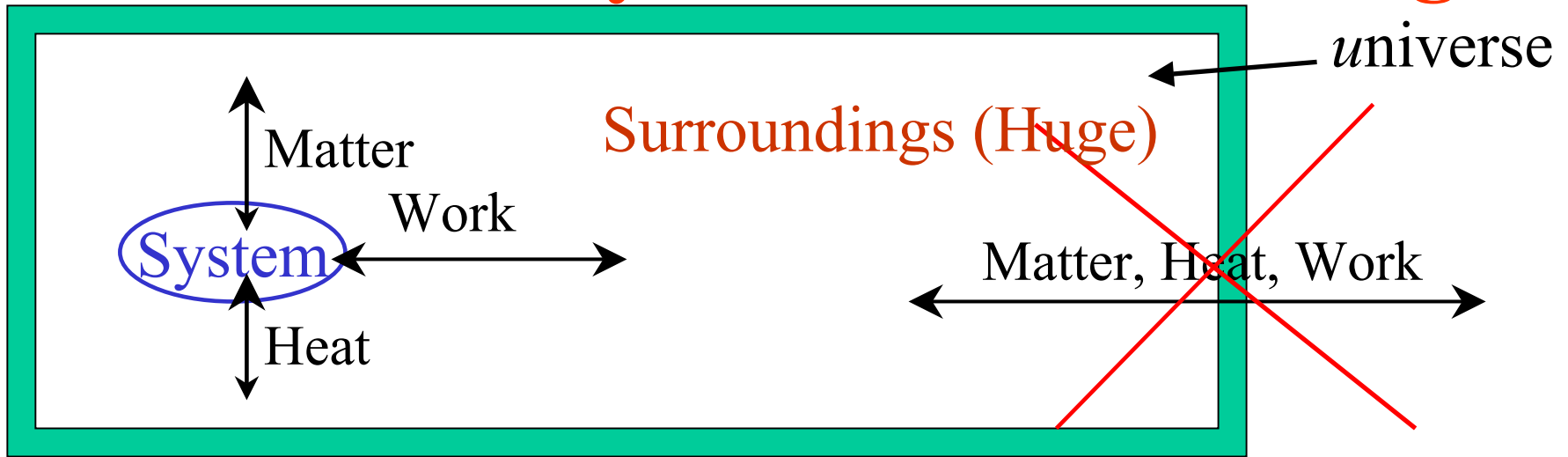
Experimental Observations that Led to the Formulation of the 2nd Law

- 1) It is impossible by a cycle process to take heat from the hot system and convert it into work without at the same time transferring some heat to cold surroundings. *In the other words, the efficiency of an engine cannot be 100%. (Lord Kelvin)*
- 2) It is impossible to transfer heat from a cold system to a hot surroundings without converting a certain amount of work into additional heat of surroundings. *In the other words, a refrigerator releases more heat to surroundings than it takes from the system. (Clausius)*

Note 1: Even though the need to describe an engine and a refrigerator resulted in formulating the 2nd Law of Thermodynamics, this law is universal (similarly to the 1st Law) and applicable to all processes.

Note 2: To use the Laws of Thermodynamics we need to understand **what the system and surroundings are.**

Universe = System + Surroundings



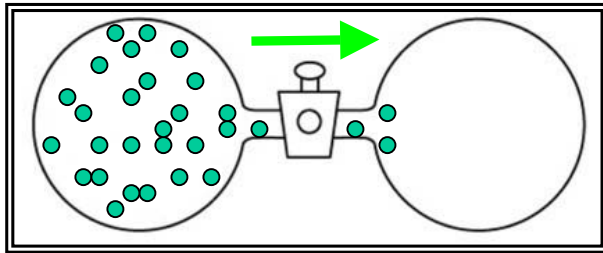
1. The **system** is a part of the universe (and a subject of study).
2. **Surroundings** are everything else (but the system) in the universe.
3. The system (*in general*) can exchange matter, heat and work with surroundings.
4. **Universe is isolated**: the amount of matter and energy in the universe is conserved.

Note: Our **Universe** is a questionable example of the **universe** since we do not know whether or not it is isolated.

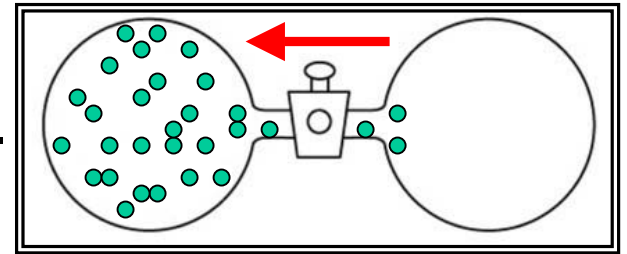
Definition of Spontaneity

- **Definition:** A process is spontaneous if it occurs when it is left to itself in a universe. A process is non-spontaneous if it requires action from outside a universe to occur.
- **Consequences:**
 1. *If a process is spontaneous, the reverse one is non-spontaneous.*
Example: gas expanding to vacuum is spontaneous, the reverse process is non-spontaneous:

Spontaneous



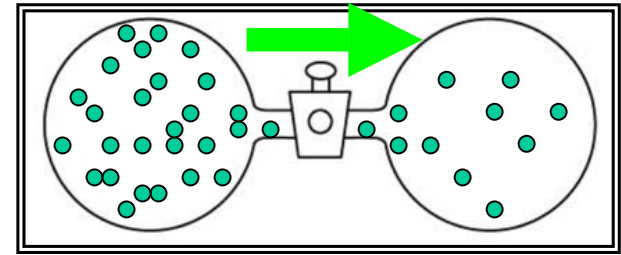
Non-spontaneous



2. *A non-spontaneous process can occur if it is coupled with another process that is spontaneous.* **Example:** If we add to the universe a pump powered by an electrical motor and a battery then gas flowing to a full reservoir becomes a part of overall spontaneous process in the universe that includes: (i) gas flowing to a full reservoir, (ii) battery discharge, and (iii) heating of surroundings.

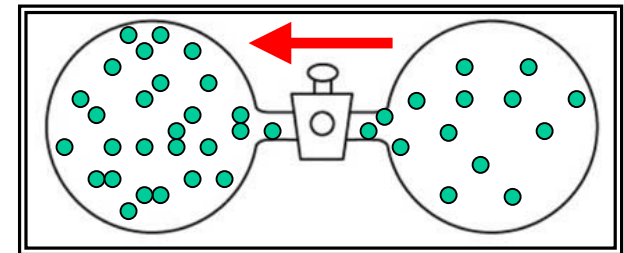
Probabilistic Definition of Spontaneity

A process is spontaneous if its probability to occur by itself in a universe is greater than 50%.



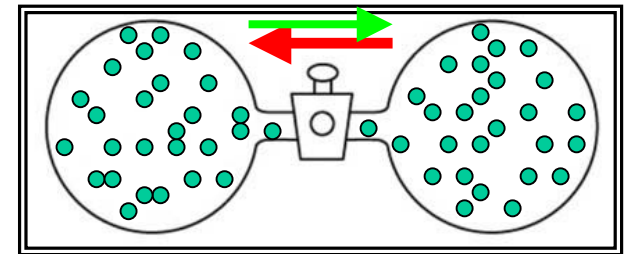
$P > 50\%$: Spontaneous

A process is non-spontaneous if its probability to occur by itself in a universe is less than 50%.



$P < 50\%$: Nonspontaneous

The system is at equilibrium if the probabilities of the forward and reverse processes are equal.



$P = 50\%$: Equilibrium

Retrospective: The 1st Law of Thermodynamics

- The 1st Law of Thermodynamics is often called “The conservation principle”:

$$\Delta U_{\text{univ}} = \Delta U_{\text{sys}} + \Delta U_{\text{sur}} = 0$$

- The 1st Law of Thermodynamics allows us to determine the energy change in a system without knowing the details of processes. This is done through measuring the energy change in the surroundings (calorimeter):

$$\Delta U_{\text{sys}} = - \Delta U_{\text{sur}}$$

In chemical applications of the 1st Law we use enthalpy instead of internal energy:

$$\Delta H = \Delta U - w \quad (w \text{ is work the system does to its surroundings, } w = - P\Delta V)$$

And the first Law can be written as:

$$\Delta H_{\text{sys}} = - \Delta H_{\text{sur}}$$

What the 1st Law Can and Cannot Do

- The 1st Law **CAN** help us determine whether the process in the system is **exothermic** ($\Delta H_{\text{sys}} < 0$, the system exports energy to the surroundings) or **endothermic** ($\Delta H_{\text{sys}} > 0$, the system imports energy from surroundings).
- The 1st Law **CANNOT** help us to determine whether or not the process in the system will occur **spontaneously**.
- We **tend** to think that (i) exothermic processes are spontaneous and (ii) endothermic are not. We also tend to think that (iii) if the energy of the system does not change then the process does not occur. **In general it is not true** as demonstrated in the following examples.

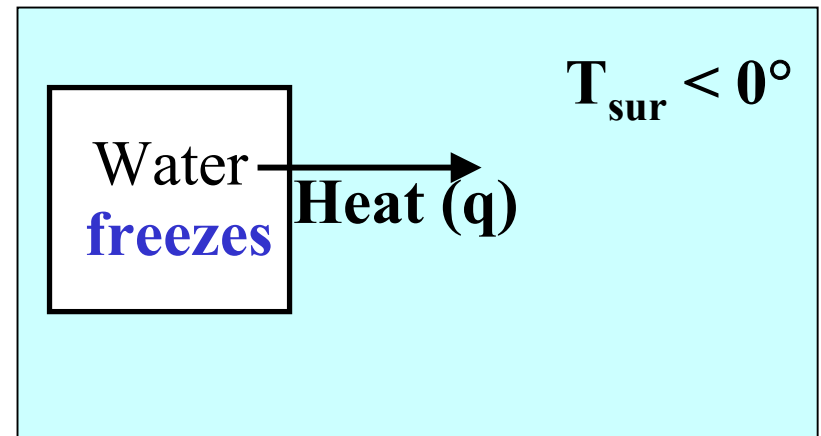
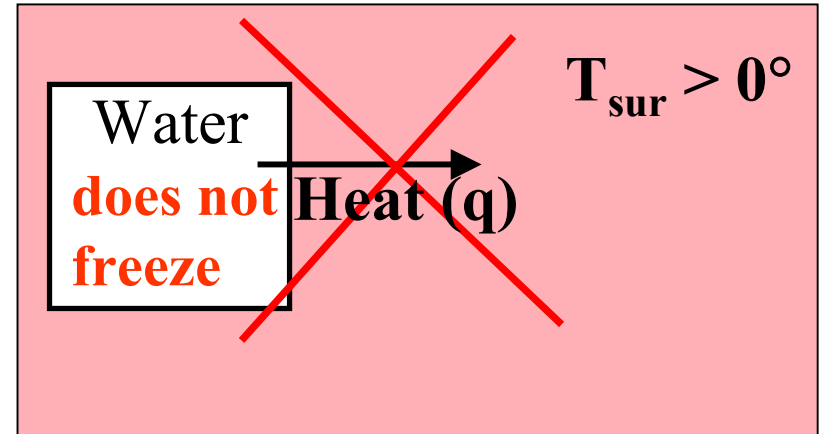
Examples Demonstrating that the 1st Law Says Nothing about Spontaneity

1. Freezing of water is **exothermic** ($\Delta H_{\text{sys}} < 0$) but it is **not spontaneous** at $T > 0\text{ }^{\circ}\text{C}$.
2. Melting of ice is **endothermic** ($\Delta H_{\text{sys}} > 0$) but it is **spontaneous** at $T > 0\text{ }^{\circ}\text{C}$.
3. Gas expanding to vacuum under isothermal conditions **does not change gas' internal energy** ($\Delta H_{\text{sys}} = 0$) but it is **spontaneous**

Conclusion: The thermodynamic function of enthalpy, H , does not define the spontaneity of a process. The first two examples show that **spontaneity depends on the ability of heat exchange at different temperatures of surroundings.**

Spontaneity Depends on the Ability of Heat Exchange between the System and Surroundings

- Water freezing is an exothermic process. Thus water has to dissipate heat of reaction to freeze.
- Heat dissipation is impossible at $T_{\text{sur}} > 0\text{ }^{\circ}\text{C}$
- Water does not freeze at $T_{\text{sur}} > 0\text{ }^{\circ}\text{C}$
- In contrast heat dissipates from water easily if $T_{\text{sur}} < 0\text{ }^{\circ}\text{C}$
- Water freezes at $T_{\text{sur}} < 0\text{ }^{\circ}\text{C}$



Entropy

- We will introduce a new thermodynamic function, **entropy (S)**, that is dependent on heat flow between the system and surroundings and temperature. It will be used to determine spontaneity.
- **Entropy is a function of state** (does not depend on the path)
- Entropy is an additive function : the entropy of a universe is a sum of entropies of a system and its surroundings:

$$S_{\text{univ}} = S_{\text{sys}} + S_{\text{sur}},$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

If surroundings are much larger than the system then $T_{\text{sur}} \approx \text{const}$ and we define the change of entropy in surroundings as:

$$\Delta S_{\text{sur}} = q_{\text{sur}}/T_{\text{sur}} \quad (q_{\text{sur}} = -q_{\text{sys}})$$

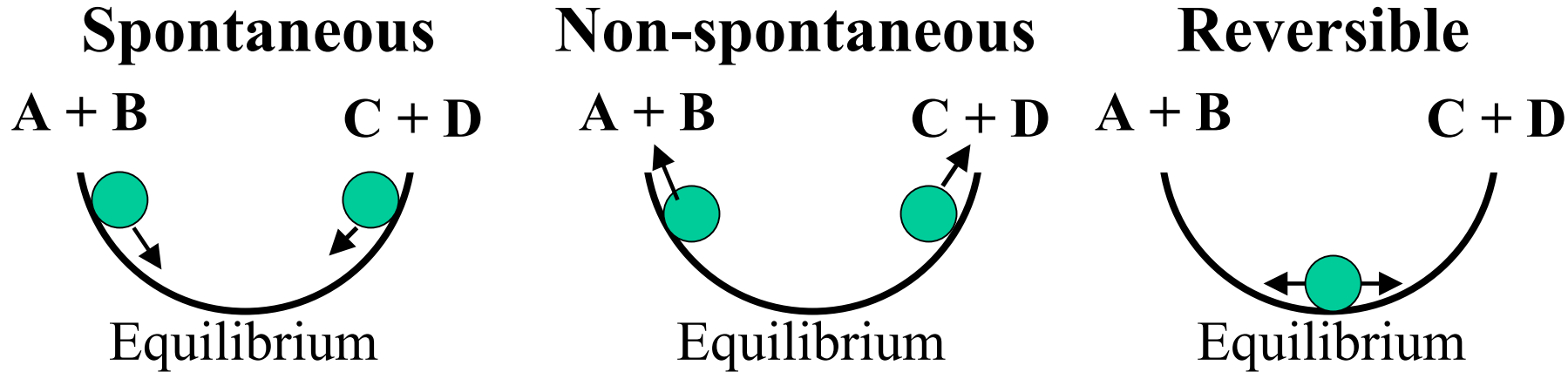
Note: $q_{\text{sur}} > 0$ for heat flowing from the system to surroundings to produce $\Delta S_{\text{sur}} > 0$. In the 1st Law, $q_{\text{sys}} < 0$ for the same direction of heat flow to produce $\Delta U_{\text{sys}} < 0$ or $\Delta H < 0$.

Determination of the change of entropy in the system is not trivial:

$$\Delta S_{\text{sys}} = ?$$

We will understand how to determine ΔS_{sys} after we (i) define spontaneous and reversible processes and (ii) introduce the 2nd law of thermodynamics

Spontaneity and Equilibrium:



- **Spontaneous process:** the system is far from equilibrium and the process is directed towards the equilibrium: infinitesimal action cannot stop the process.
- **Non-spontaneous process:** improbable. Non-spontaneous process may become spontaneous **only** by redefining a universe, e.g. including in a universe something that can change equilibrium.
- **Reversible process:** the system is at equilibrium: infinitesimal action can move the process in any direction from the equilibrium (*extremely important for determination ΔS_{sys}*).

Spontaneity, Reversibility and the 2nd Law of Thermodynamics

The 2nd Law of Thermodynamics:

- In spontaneous processes, the S_{univ} increases:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$$

- In reversible processes, S_{univ} does not change:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$$

Alternative definition:

- In an isolated system (universe) $\Delta S \geq 0$.
 $\Delta S > 0$ if the system is far from equilibrium and
 $\Delta S = 0$ if the system is at equilibrium

What Do We Need to Know to Find Out If a Process Is Spontaneous?

- According to the 2nd Law of Thermodynamics, in order to determine whether the process is spontaneous or not we need to find out the sign of $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$. **For this we need to know the values ΔS_{sys} and ΔS_{sur} .**
- **ΔS_{sur} can be found easily** due to its definition: $\Delta S_{\text{sur}} = q_{\text{sur}}/T_{\text{sur}}$, in an experiment where a system is placed in a calorimeter (large one to keep $T_{\text{sur}} = \text{const}$)
- **Finding ΔS_{sys} is trickier** but possible using the second part of the 2nd Law: In reversible processes, S_{univ} does not change:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$$

Determining ΔS_{sys}

Recall: The 1st Law of Thermodynamics allowed us to find the change in the energy of the system through that in surroundings: $\Delta U_{\text{sys}} = -\Delta U_{\text{sur}}$

Similarly, we will use the 2nd Law to find the change of entropy in the system ΔS_{sys} through that in surroundings ΔS_{sur} . As we know ΔS_{sur} can be easily determined:

$$\Delta S_{\text{sur}} = q_{\text{sur}}/T_{\text{sur}}$$

For reversible processes (very slow processes that are close to equilibrium throughout the entire process):

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$$

Thus, for **reversible** processes (only):

$$\Delta S_{\text{sys}}^{\text{rev}} = -\Delta S_{\text{sur}}^{\text{rev}} = -q_{\text{sur}}/T = q_{\text{sys}}/T$$

$$\Delta S_{\text{sys}}^{\text{rev}} = q_{\text{sys}}^{\text{rev}}/T \quad (\text{for revers. proc. } T_{\text{sur}} \approx T_{\text{sys}} = T)$$

Note: the $\Delta S_{\text{sys}}^{\text{rev}}$ decreases when heat is transferred from the system to surroundings and increases when heat transferred from surroundings to the system.

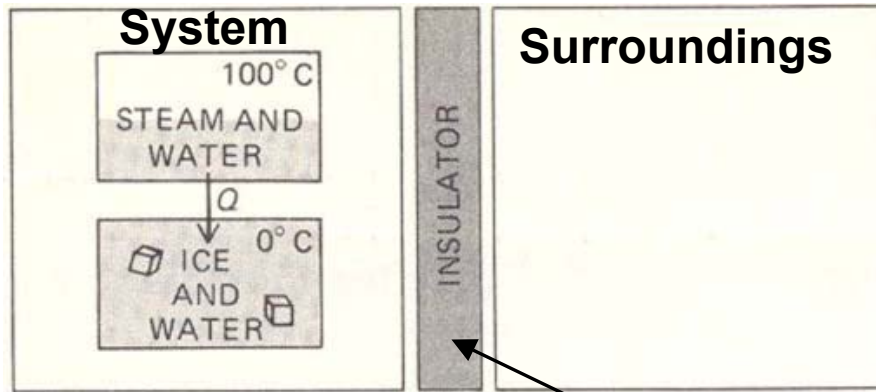
Carrying Processes in a Reversible Manner

- ΔS_{sys} can be easily measured through ΔS_{sur} only for a reversible process. Therefore, if we need to determine ΔS_{sys} in an irreversible (spontaneous) process we need to construct an artificial reversible process that would lead to the same final state, hence it would produce the same ΔS_{univ} . We can determine ΔS_{sys} from this artificial reversible process. It will be the same as ΔS_{sys} in an irreversible process since S is a state function.
- **Note:** here is the difference between the 1st and the 2nd Laws of Thermodynamics; the 1st Law does not require reversibility in measurements of ΔU_{sys} .

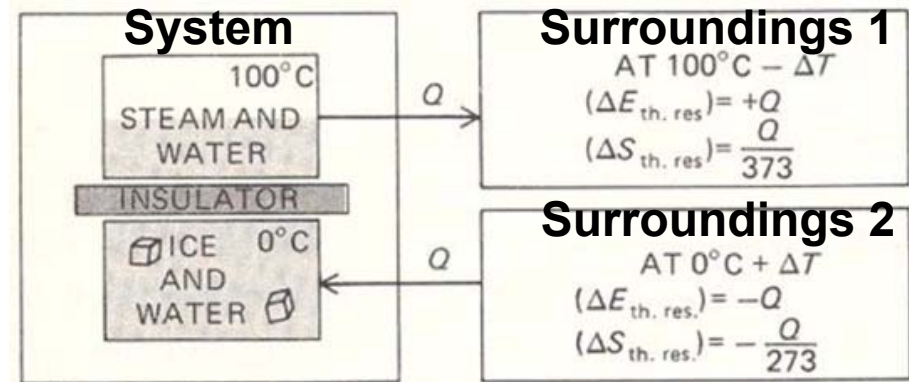
Example of an Artificial Reversible Process

What is ΔS_{sys} for transferring heat q from a “steam/water” mixture at $T_1 = 100^\circ\text{C}$ to a “ice/water” mixture at $T_2 = 0^\circ\text{C}$?

Irreversible process ($T_1 \gg T_2$)



Artificial reversible process



In the artificial process: 1) the steam/water mixture transfers q to “surroundings 1” at $T = T_1 - \Delta T$ and 2) the ice/water mixture gets q from “surroundings 2” at $T = T_2 + \Delta T$. If $\Delta T \rightarrow 0$ then both processes are reversible. Therefore for steam/water $\Delta S_{\text{sys}}^{\text{steam}} = -q/T_1$ and for ice/water $\Delta S_{\text{sys}}^{\text{ice}} = q/T_2$. The total entropy change in the system is:

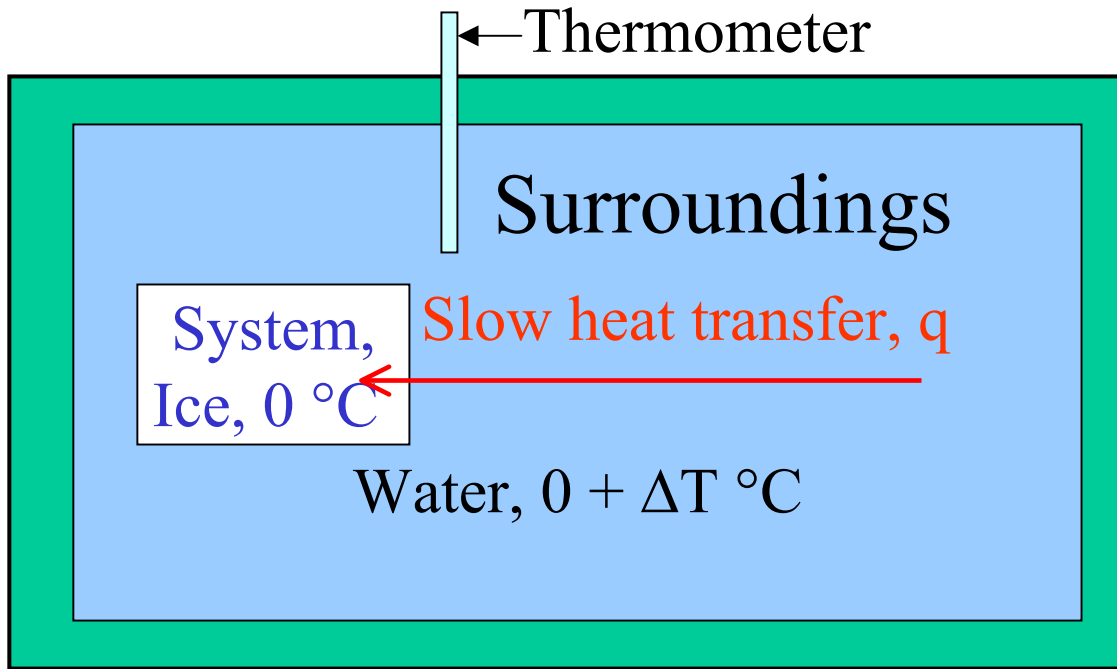
$$\Delta S_{\text{sys}} = \Delta S_{\text{sys}}^{\text{steam}} + \Delta S_{\text{sys}}^{\text{ice}} = -q/T_1 + q/T_2 = q(-1/T_1 + 1/T_2) = 0.00982q.$$

$$\Delta S_{\text{sur}} = 0 \text{ (in the irreversible process the system is isolated)}$$

Thus, $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0.00982q > 0$ (since q is defined as being positive)

Note: ΔS_{univ} is positive. Thus, if we did not know that the irreversible process is spontaneous, we would conclude that it is now.

Apparatus for Reversible Phase Transfer (melting, fusion, vaporization, condensation) is Simple. It is a Calorimeter.



System: ice at 0 °C;
Surroundings: water at
0 °C + ΔT (ΔT → 0)

Process: melting of ice

Melting of ice in such a process is reversible because the system is in equilibrium with surroundings and heat transfer between water reservoirs is slow.

ΔS_{sys} in Phase Transitions (melting, fusion, vaporization, condensation)

- First, let's define standard entropy change, ΔS° , as entropy change at 1 atm. Also, standard (and non-standard) entropy change depends on the amount of substances involved and usually expressed on a per-mole basis called **standard molar entropy change**.
- Standard molar entropy change of phase transition (melting, fusion, vaporization, condensation) carried out reversibly is:

$$\Delta S^\circ_{\text{sys trans}} = - q_{\text{sur}}^{\text{rev trans}} / T_{\text{sur}} = q_{\text{sys}}^{\text{rev trans}} / T_{\text{sur}} = \overset{\text{P = const}}{\Delta H^\circ_{\text{trans}} / T_{\text{trans}}}$$

Note: $\Delta S^\circ_{\text{sys melt}} > 0$, $\Delta S^\circ_{\text{sys vap}} > 0$, and

$\Delta S^\circ_{\text{sys fus}} < 0$, $\Delta S^\circ_{\text{sys cond}} < 0$. From either pair of inequalities we can get:

$$S^\circ(\text{g}) > S^\circ(\text{l}) > S^\circ(\text{s}) \quad (\text{REMEMBER THIS})$$

Practice Example: 20-2A

Q: What is the standard molar entropy of vaporization, $\Delta S^\circ_{\text{vap}}$, for CCl_2F_2 (used in old-style refrigerators). It's normal (at $P = 1 \text{ atm}$) boiling point is -29.79°C , and $\Delta H^\circ_{\text{vap}} = 20.2 \text{ kJ mol}^{-1}$?

Solution:

1. Formalization: $\text{CCl}_2\text{F}_2(l, 1 \text{ atm}, T_{\text{bp}}) \leftrightarrow \text{CCl}_2\text{F}_2(g, 1 \text{ atm}, T_{\text{bp}})$

$$\Delta H^\circ_{\text{vap}} = 20.2 \text{ kJ mol}^{-1},$$

$$T_{\text{bp}} = 273.15 - 29.79 = 243.36 \text{ K}$$

$$\Delta S^\circ_{\text{sys vap}} = ?$$

2. Formula/Equation/Calculations/Significant figures:

If vaporization is carried out at normal boiling point then it is a reversible process and:

$$\Delta S^\circ_{\text{sys vap}} = \Delta H^\circ_{\text{vap}} / T_{\text{bp}} = 20.2 \text{ kJ mol}^{-1} / 243.36 \text{ K} = 83.005 \text{ J mol}^{-1} \text{ K}^{-1} = \{3 \text{ significant figures}\} = 83.0 \text{ J mol}^{-1} \text{ K}^{-1}$$

Trouton's Rule: For many liquids at their normal boiling points, $\Delta S^\circ_{\text{sys vap}} \approx 80 \text{ to } 90 \text{ J mol}^{-1} \text{ K}^{-1}$

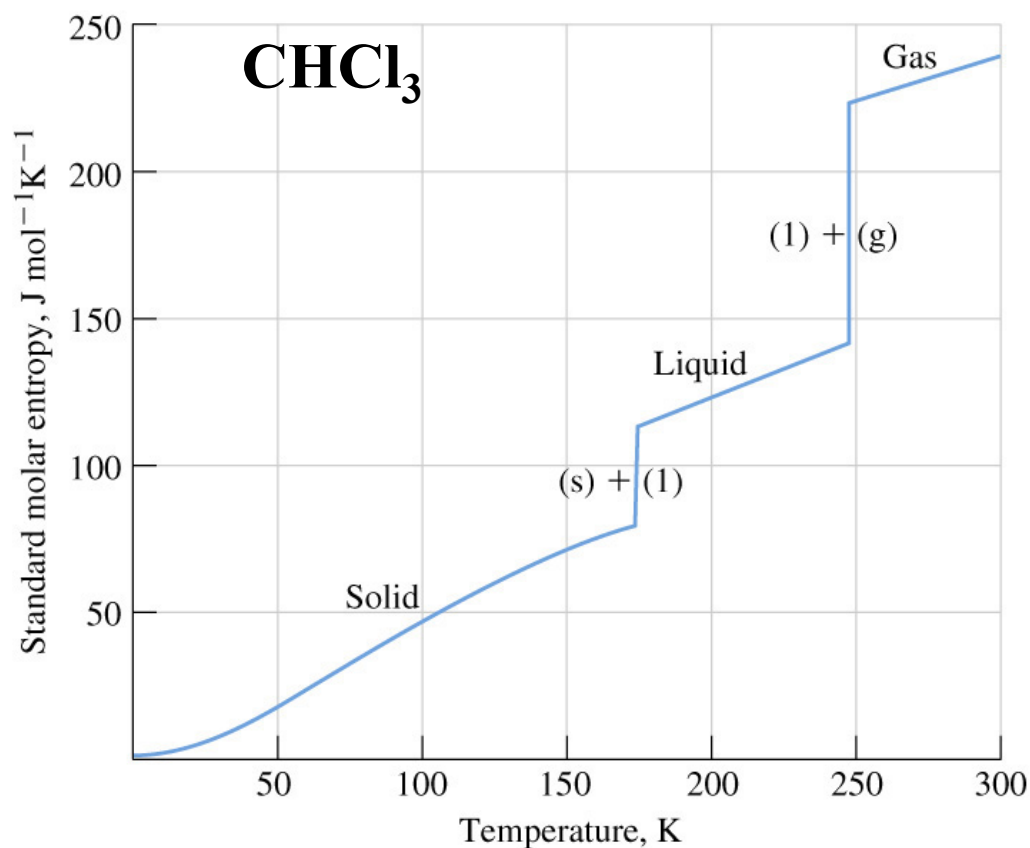
The rationale for this will be better to obtain from the microscopic definition of entropy: the entropy change is dominated by moving molecules from a semi-ordered liquid state to a gas state. Different molecules behave similarly in the same phase.

Substance	$\Delta H^\circ_{\text{vap}}, \text{ kJmol}^{-1}$	$T_{\text{bp}}, \text{ K}$	$\Delta S^\circ_{\text{vap}}, \text{ Jmol}^{-1} \text{ K}^{-1}$
Methane	9.27	111.75	83.0
Carbon tetrachloride	30	349.85	85.8
Cyclohexane	30.1	353.85	85.1
benzene	30.8	353.25	87.2
hydrogene sulphide	18.8	213.55	88.0
water	40.7	373.15	109

Note: Hydrogen bonds of water in liquid make it much better “structured” than molecules of other liquids

The 3rd Law of Thermodynamics: the Entropy of A Perfect Pure Crystal at 0K Is Zero

- Experimental observation that led to the formulation of the third law: Absolute zero temperature is unattainable.
- Consequence of the 3rd Law: we can assign absolute entropy values, S , to chemical compounds. The entropy of a pure perfect crystal at 0 K is zero
- **The absolute entropy of one mole of a substance in its standard state ($P = 1$ atm and specified T) is called the standard molar entropy, S° .**
- The values of S° have been measured and tabulated for many compounds. (see appendix D in the text)



The Change of Standard Molar Entropy

- The entropy change in the reaction ΔS° , can be calculated through standard molar entropies of reagents, $S^\circ(\text{reagents})$, and products, $S^\circ(\text{products})$:

$$\Delta S^\circ = \sum \nu_P S^\circ(\text{products}) - \sum \nu_R S^\circ(\text{reactants})$$

where ν_P and ν_R are corresponding stoichiometric coefficients of products and reagents.

Note: this expression is derived from the definition of the change of entropy:

$$\Delta S^\circ = S^\circ_{\text{final}} - S^\circ_{\text{initial}}$$

and from entropy being an extensive (additive) function:

$$S^\circ_{\text{final}} = \sum \nu_P S^\circ(\text{products}) \text{ and } S^\circ_{\text{initial}} = \sum \nu_R S^\circ(\text{reactant})$$

Example 20-3: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ $\Delta S^\circ_{298\text{K}} = ?$

Solution: $\Delta S^\circ = 2S^\circ_{\text{NO}_2(\text{g})} - 2S^\circ_{\text{NO}(\text{g})} - S^\circ_{\text{O}_2(\text{g})} =$
 $= 2 \times 240.1 - 2 \times 210.8 - 205.1 = -146.5 \text{ J mol}^{-1}\text{K}^{-1}$

Is the reaction spontaneous? We do not know since we found only ΔS of the system while for spontaneity we need to know ΔS of the universe

Microscopic Definition of Entropy

- So far we based our considerations on the MACROscopic definition of entropy through heat $\Delta S_{\text{sur}} = q_{\text{sur}}/T_{\text{sur}}$.
- What is the MICROscopic meaning of entropy?

Boltzmann gave the microscopic definition of entropy as:

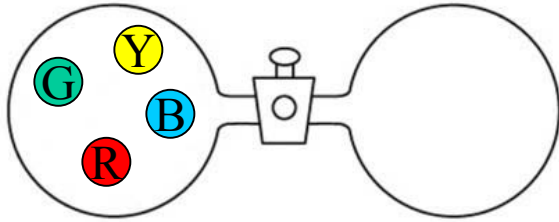
$$S = k \ln W, \text{ where}$$

k is the Boltzmann's constant, $k = R/N_A$, and

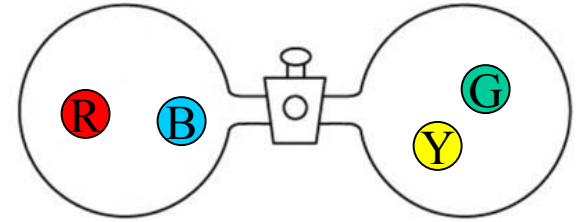
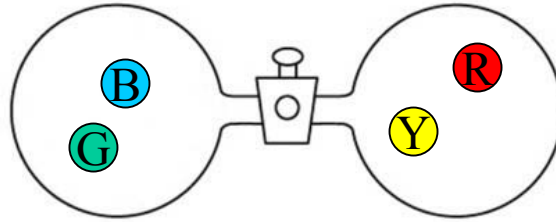
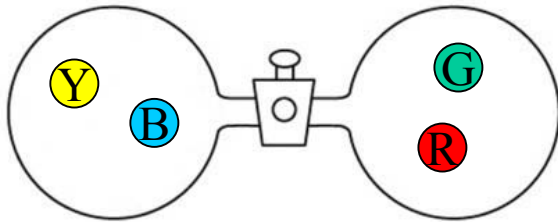
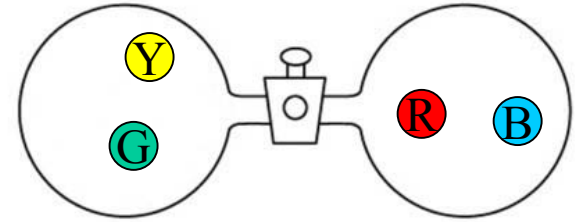
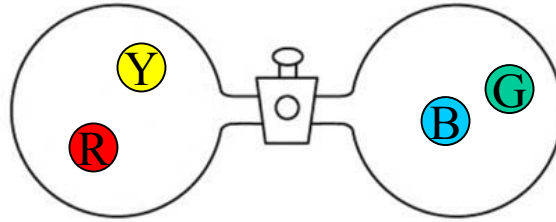
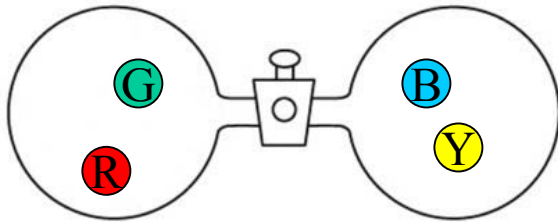
W is the number of accessible microstates in the system, that result in the same energy.

Entropy increases with increasing number of accessible microstates.

Positional Microstates

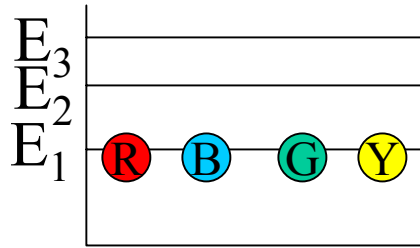


- All 4 particles in the left reservoir.
- Lower number of accessible microstates → Lower Entropy. Probability = $(1/2)^4 = 1/16$

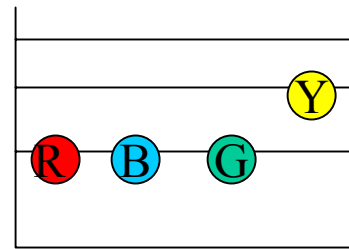
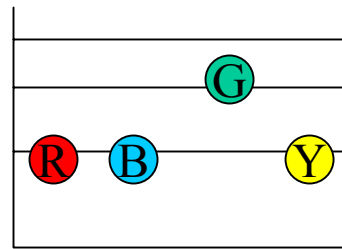
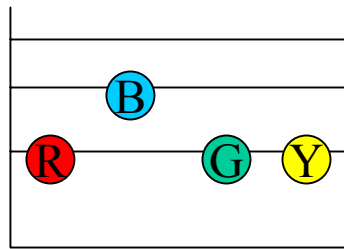
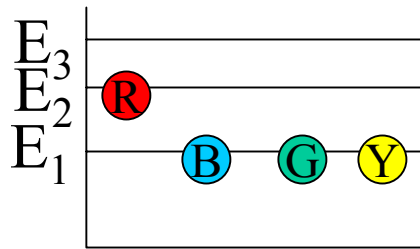


- 2 particles on the left and 2 particles on the right. Higher number of accessible microstates.
- **Conclusion:** 1) Entropy increases with increasing the volume that gas system occupies. 2) Entropy increases when the number of molecules of gas increases as a result of a chemical reaction.

Energy Microstates

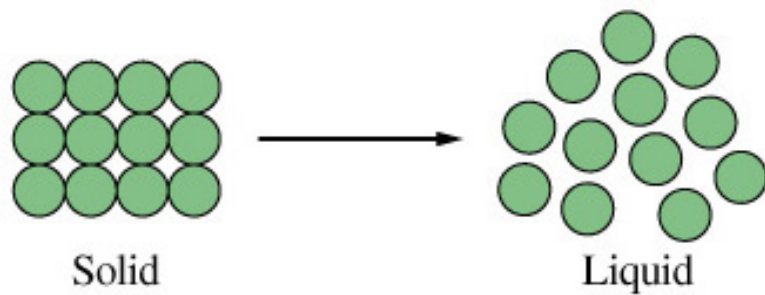


$T = 0$, only one energy level is accessible, one microstate exists

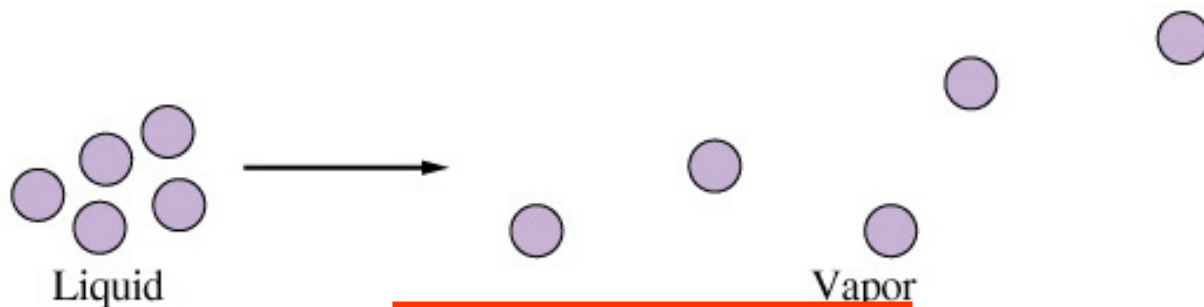


$T > 0$, more energy levels are accessible. There are many microstates. The number of accessible energy microstates, W , increases with temperature.

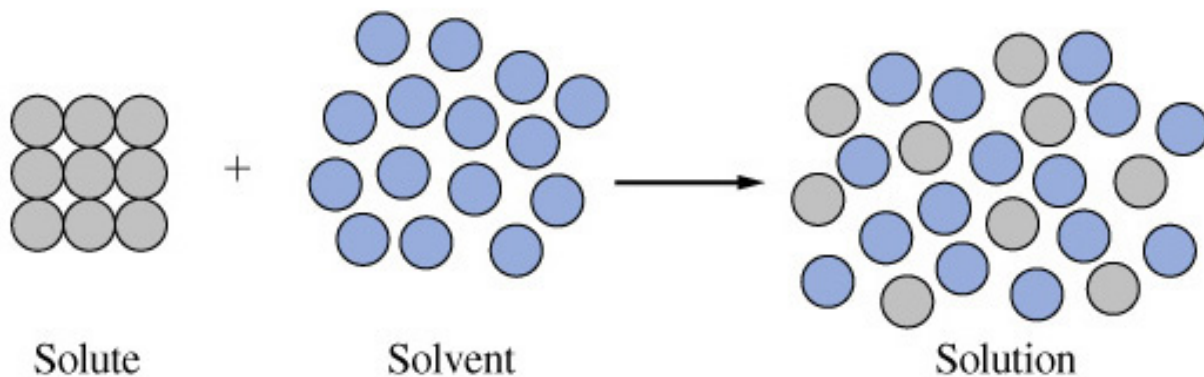
Conclusion: Entropy increases with temperature.



(a) Melting: $S_{\text{liquid}} > S_{\text{solid}}$



(b) Vaporization: $S_{\text{vapor}} > S_{\text{liquid}}$



(c) Dissolving: $S_{\text{soln}} > (S_{\text{solvent}} + S_{\text{solute}})$

**Entropy also increases
in these processes**

Retrospective Look at Entropy

- Entropy defined MICROscopically is the same as one defined MACROscopically (Note: macroscopic definition is for ΔS , while microscopic is for S .)
- Entropy is a state function. Therefore, $\Delta S = S_2 - S_1$ does not depend on the path from state 1 to state 2.
- The 2nd Law of Thermodynamics: in an isolated system (universe) $\Delta S \geq 0$. It can be paraphrased as “Spontaneous change in a universe is in the direction from highly concentrated energy to that of dispersed energy”.
- Entropy in an isolated system (universe) increases until the system reaches equilibrium. After that $\Delta S = 0$. **What is the thermodynamic future of our Universe? Is $\Delta S = 0$ the Ultimate Definition of Death?**

Concentrating on the System: the case of $P = \text{const}$, $T = \text{const}$

Using the criterion $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$ for determining spontaneity requires operating with both ΔS_{sys} and ΔS_{sur} . Although it is possible to determine ΔS_{sur} in an artificially created universe, it would be much easier to operate only with the system.

We will define the way of determining spontaneity based solely on the properties of the system for a limited set of most abundant processes carried out at $P = \text{const}$ and $T = T_{\text{sur}} = T_{\text{sys}} = \text{const}$ (e.g. biochemical processes in our body:

$T = 310 \text{ K}$, $P = 1 \text{ atm}$).

P = const: Lets recall the change of enthalpy, ΔH , that can be defined for $P = \text{const}$ from the 1st law of thermodynamics:

$$\Delta U = q_{\text{sys}} + w$$

$$\Delta U = q_{\text{sys } P} - P\Delta V$$

$$q_{\text{sys } P} = \Delta U + P\Delta V$$

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

Concentrating on the System:

the case of $P = \text{const}$, $T = \text{const}$ Continued

Heat that surroundings receive is negative of heat lost by the system:

$$q_{\text{sur } P} = - q_{\text{sys } P} = - \Delta H_{\text{sys}}$$

$$\Delta S_{\text{sur}} = q_{\text{sur } P} / T_{\text{sur}} = - q_{\text{sys } P} / T_{\text{sur}} = - \Delta H_{\text{sys}} / T_{\text{sur}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}} / T_{\text{sur}}$$

$T = T_{\text{sur}} = T_{\text{sys}} = \text{const}$ can be achieved if two conditions are satisfied: 1) surroundings are much larger than the system and 2) the process is carried out slowly enough to ensure good heat exchange. Lets replace T_{sur} with T_{sys} in the last expression:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}} / T_{\text{sys}}$$

Thus, if $P = \text{const}$ and $T = \text{constant}$ then the entropy in the universe, ΔS_{univ} , can be expressed through the parameters of the system only ΔS_{sys} , ΔH_{sys} , and T_{sys} . Therefore, we can drop the subscript denoting the system with understanding that all parameters on the right hand side are those of the system:

$$\Delta S_{\text{univ}} = \Delta S - \Delta H / T$$

Free Energy (Gibbs Function, G)

We can multiply both parts of the last expression by T:

$$T\Delta S_{\text{univ}} = T\Delta S - \Delta H = -(\Delta H - T\Delta S)$$

Definition:

Free energy function is:

$$G = H - TS$$

Free energy change is:

$$\Delta G = -T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

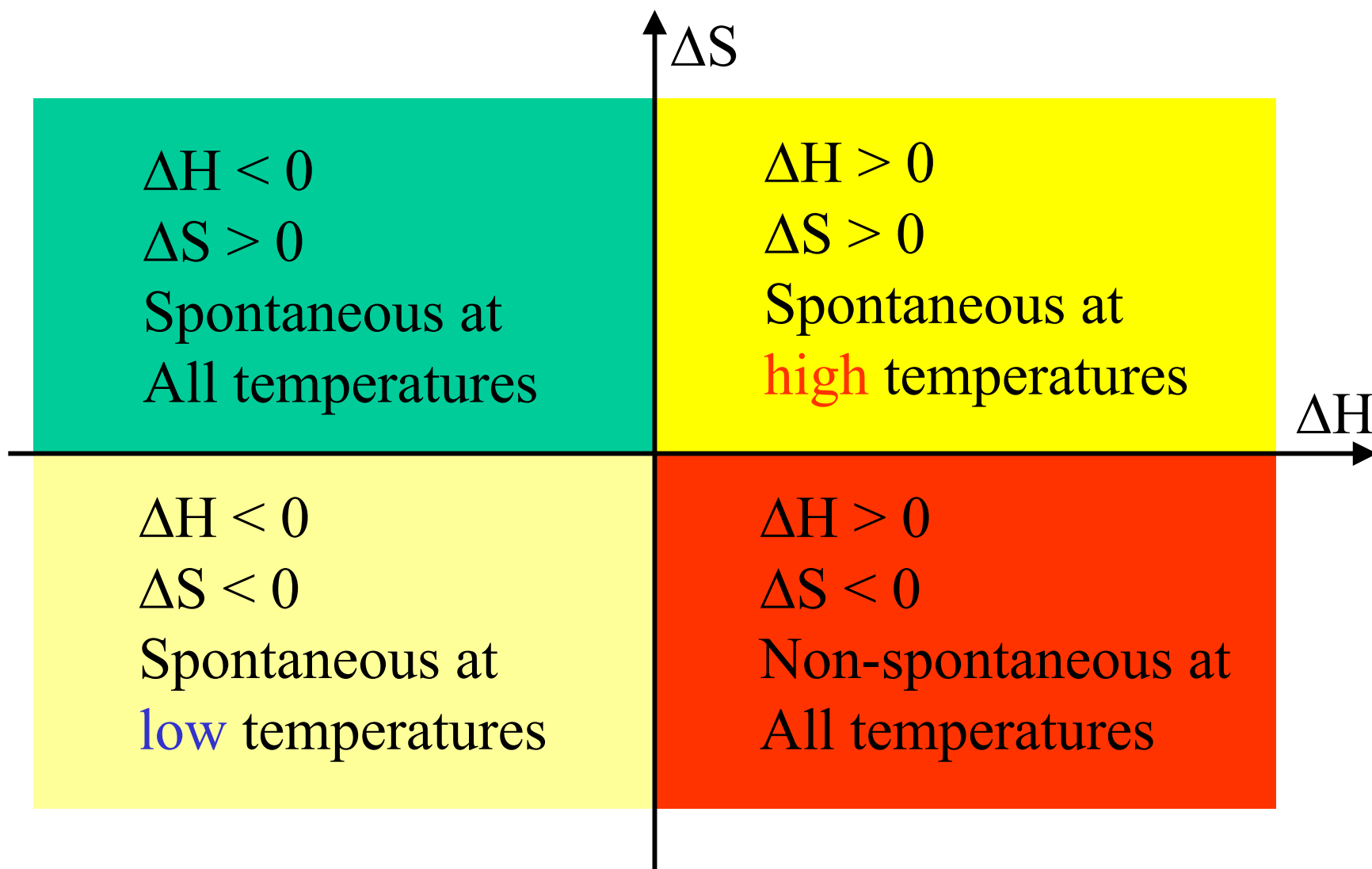
ΔG connects the change of entropy in the universe, ΔS_{univ} , with thermodynamic parameters of the system only, ΔH , ΔS , and T .

ΔG can be used to determine spontaneity

From $\Delta G = -T\Delta S_{\text{univ}}$ the sign of ΔG is opposite to that of ΔS_{univ} . Therefore, the following criteria can be used to determine spontaneity of a process:

ΔS_{univ}	ΔG (P = const, T = const)	Process
> 0	< 0	Spontaneous
< 0	> 0	Nonspontaneous
$= 0$	$= 0$	Equilibrium

The Sign of ΔG Depends on the Signs of ΔH and ΔS As Well As on the Value of T : $\Delta G = \Delta H - T\Delta S$



Examples

Reaction	ΔH	ΔS	ΔG
$2\text{N}_2\text{O}(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$	< 0	> 0	< 0 (all T)
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$	< 0	< 0	< 0 (low T) > 0 (high T)
$2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	> 0	> 0	< 0 (high T) > 0 (low T)
$3\text{O}_2(\text{g}) \rightarrow 2\text{O}_3(\text{g})$	> 0	< 0	> 0 (all T)

Free Energy Change, ΔG

- Entropy (S) has absolute values.
- Enthalpy (H), in contrast, does not have absolute values. Therefore we use the change of enthalpy, ΔH , instead.
- Since G is a function of H ($G = H - TS$) there are no absolute values of G. Therefore, best we can do is to operate with free energy change, ΔG .

Properties of ΔG (are similar to that of ΔH)

- 1. ΔG changes sign when a process is reversed.**
- 2. ΔG for an overall process can be obtained by summing the ΔG values for individual steps.**

Standard Free Energy Change, ΔG°

Since ΔG depends on reaction conditions, it is impossible to tabulate ΔG for all P and T ; therefore we use *standard free energy change ΔG° of reaction, that is defined for reactants and products in their standard states ($P = 1 \text{ bar} \approx 1 \text{ atm}$ at a T of interest).*

The standard free energy change can be also determined directly from the definition of ΔG :

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

We will calculate the standard free energy change in a chemical reaction as:

$$\Delta G^\circ = \sum v_P \Delta G_f^\circ(\text{products}) - \sum v_R \Delta G_f^\circ(\text{reactants})$$

{Similar to $\Delta H^\circ = \sum v_P \Delta H_f^\circ(\text{products}) - \sum v_R \Delta H_f^\circ(\text{reactants})$ }

ΔG_f° is the free energy change for a reaction in which a substance (in its standard state) is formed from its elements (in their standard states).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

can be used for any T if the values of ΔH° and ΔS° are known for this T.

$$\Delta G^\circ = \sum v_P \Delta G_f^\circ(\text{products}) - \sum v_R \Delta G_f^\circ(\text{reactants}) \quad (2)$$

can be used only at temperatures for which the data for ΔG_f° are available. The only tabulated data widely available are those for 25°C.

Conclusion: The expression $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ is more universal.

Example: Calculate ΔG° at 298.15 K for the reaction: $2\text{N}_2\text{O}(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$

1. Since the reaction takes place at 298.15K we can use formula (2) and tabulated data for ΔG_f° (appendix D):

$$\Delta G^\circ = 2\Delta G_f^\circ\text{N}_2 + \Delta G_f^\circ\text{O}_2 - 2\Delta G_f^\circ\text{N}_2\text{O} = 0 + 0 - 2 \times 104.2 = -208.4 \text{ kJ mol}^{-1}$$

2. Similar result can be obtained from using tabulated data for ΔG_f° and S° (appendix D) and formulas for calculating ΔH° and ΔS° along with formula (1):

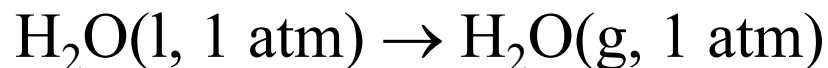
$$\Delta H^\circ = 2\Delta H_f^\circ\text{N}_2 + \Delta H_f^\circ\text{O}_2 - 2\Delta H_f^\circ\text{N}_2\text{O} = 0 + 0 - 2 \times 82.05 = -164.1 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\Delta S^\circ &= 2S^\circ\text{N}_2 + S^\circ\text{O}_2 - 2S^\circ\text{N}_2\text{O} = 2 \times 191.6 + 205.1 - 2 \times 219.9 = 148.5 \text{ J mol}^{-1}\text{K}^{-1} \\ &= 0.1485 \text{ kJ mol}^{-1}\text{K}^{-1}\end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -164.1 \text{ kJ mol}^{-1} - 298.15 \times 0.1485 = -208.4 \text{ kJ mol}^{-1}$$

The Need for Non-Standard Conditions ($P \neq 1 \text{ atm}$)

Lets consider vaporizations of water at $T = 298.15\text{K}$ trying to use standard conditions ($P_{\text{H}_2\text{O}} = 1 \text{ atm}$):



Using tabulated data (appendix D) we get:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -44.00 + 298.15 \times 0.1189 = 8.55 \text{ kJ/mol} \neq 0$$

That is at $T = 298.15 \text{ K}$ and $P_{\text{H}_2\text{O}} = 1 \text{ atm}$ the reaction is **always** out of equilibrium. Equilibrium exists only at temperature $T = 373.15 \text{ K}$:

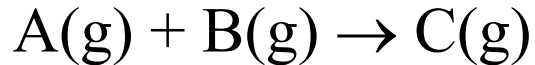
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -40.70 + 373.15 \times 0.1091 = 0 \text{ kJ/mol}$$

Equilibrium in this reaction will exist ($\Delta G = 0$) at $T = 298.15$ as well but at $P = 0.03126 \text{ atm}$. **Thus, to determine spontaneity at non-standard conditions we need to know ΔG at P of interest (very obvious even without this example).** Since the only tabulated data available are those for ΔG° ($P = 1 \text{ atm}$) it is important to know:

how to calculate ΔG (for P of interest) if we know ΔG° .

ΔG as a function of ΔG°

We will obtain this relationship for the reaction in gas phase assuming that: (i) gas is ideal and (ii) the process is reversible and isothermal ($T = \text{const}$):



For standard conditions ($P = 1 \text{ atm}$):

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

For non-standard conditions ($P \neq 1 \text{ atm}$):

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

To relate ΔG with ΔG° we will relate ΔH with ΔH° and ΔS with ΔS°

1. For an ideal gas, ΔH depends on T but not on P ($\Delta H \sim \Delta U \sim \Delta E_{\text{kin}}$ of molecules $\sim \Delta T$ but does not depend on P), thus:

$$\Delta H = \Delta H^\circ$$

2. For a reversible isothermal reaction ($\Delta T = 0$):

$$\Delta U = 0 \quad (\text{recall that } \Delta U \sim \Delta T)$$

Substituting this into one of the forms of the 1st Law of Thermodynamics

$$\Delta U = q_{\text{sys}} + w$$

we get:

$$q_{\text{sys}}^{\text{rev}} = -w = \int_{V_1}^{V_2} P dV$$

Recall that $PV = nRT \Rightarrow P = nRT/V$ and by substituting this in the previous equation we get:

$$q_{\text{sys}}^{\text{rev}} = -w = \int_{V_{\text{ini}}}^{V_{\text{fin}}} P dV = nRT \int_{V_{\text{ini}}}^{V_{\text{fin}}} \frac{dV}{V} = nRT(\ln V_{\text{fin}} - \ln V_{\text{ini}}) = nRT \ln \left(\frac{V_{\text{fin}}}{V_{\text{ini}}} \right)$$

By substituting this into $\Delta S_{\text{sys}}^{\text{rev}} = q_{\text{sys}}^{\text{rev}}/T$ for entropy change of the system we get:

$$\Delta S = \Delta S_{\text{sys}}^{\text{rev}} = nR \ln(V_{\text{fin}}/V_{\text{ini}})$$

For ideal gas, $V_{\text{fin}}/V_{\text{ini}} = P_{\text{ini}}/P_{\text{fin}}$ and for ΔS we get

$$\Delta S = nR \ln(V_{\text{fin}}/V_{\text{ini}}) = nR \ln(P_{\text{ini}}/P_{\text{fin}}) = -nR \ln(P_{\text{fin}}/P_{\text{ini}})$$

To get molar entropy we divide the right-hand side by n :

$$\Delta S = -R \ln(P_{\text{fin}}/P_{\text{ini}})$$

From a definition of S as a state function:

$$\Delta S = S_{\text{fin}} - S_{\text{ini}} = -R \ln(P_{\text{fin}}/P_{\text{ini}})$$

If we assume that $P_{\text{ini}} = 1 \text{ atm}$ (standard cond.) and $P_{\text{fin}} = P$, then $S_{\text{ini}} = S^\circ$ and $S_{\text{fin}} = S$. By substituting these four into the last expression we get:

$$\Delta S = S - S^\circ = -R \ln(P/1) \Rightarrow$$

$$S = S^\circ - R \ln P \quad (\text{P is dimensionless because it is defined as a ratio})$$

For the two reactants and one product we can express S as:

$$S_A = S^\circ_A - R \ln P_A, \quad S_B = S^\circ_B - R \ln P_B \quad \text{and} \quad S_C = S^\circ_C - R \ln P_C$$

The change of molar entropy in the reaction is:

$$\begin{aligned} \Delta S &= S_C - S_A - S_B = (S^\circ_C - R \ln P_C) - (S^\circ_B - R \ln P_B) - (S^\circ_A - R \ln P_A) = \\ &= S^\circ_C - S^\circ_B - S^\circ_A - R \ln P_C + R \ln P_B + R \ln P_A = \Delta S^\circ - R \ln \frac{P_C}{P_A P_B} \end{aligned}$$


P_C , P_A and P_B are dimensionless since they are defined as ratios; thus:

$$\Delta S = \Delta S^\circ - R \ln \frac{P_C}{P_A P_B} = \Delta S^\circ - R \ln Q_{\text{eq}}$$

Note 1: Q_{eq} is dimensionless since it is a logarithm of dimensionless pressures that can be considered as activities.

We can finally get the relationship between ΔG and ΔG° :

$$\Delta G = \Delta H - T\Delta S = \Delta H^\circ - (T\Delta S^\circ - RT\ln Q_{eq}) = \Delta G^\circ + RT\ln Q_{eq}$$

$$\underbrace{\hspace{10em}}_{\Delta G^\circ}$$


$$\Delta G = \Delta G^\circ + RT\ln Q_{eq}$$

It can be used to determine the spontaneity of a process that is carried out at $P = \text{const}$ ($\neq 1 \text{ atm}$), $T = \text{const}$.

Note 2: ΔG and ΔG° are for **this T**.

Note 3: Even though we used an ideal gas to obtain this formula, it works for any system at $P = \text{const}$, $T = \text{const}$.

Relationship between ΔG° and K_{eq}

At equilibrium (for P of interest) $\Delta G = 0$ and $Q_{eq} = K_{eq}$:

$$\Delta G = \Delta G^\circ + RT \ln Q_{eq}$$

$0 = \Delta G^\circ + RT \ln K_{eq}$

$$\Delta G^\circ = -RT \ln K_{eq}$$
$$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$$

Note: K_{eq} is a dimensionless equilibrium constant defined through activities.

Conclusions:

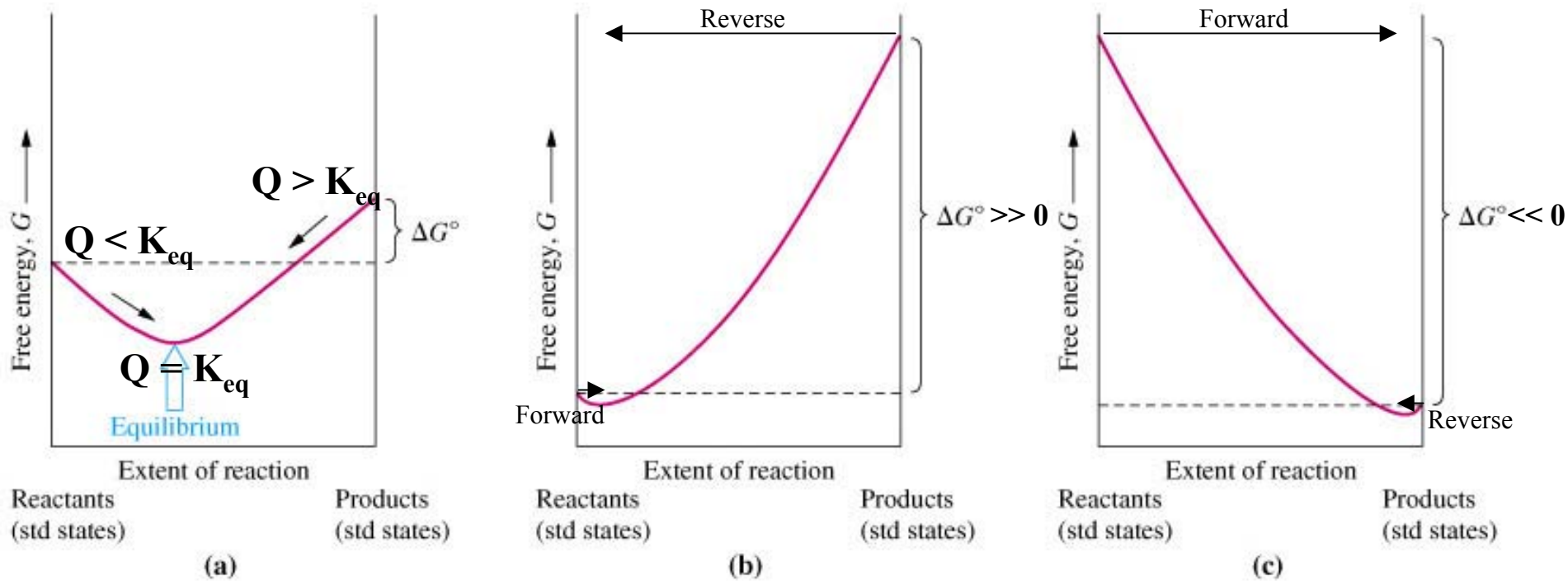
1. If we know ΔG° for T of interest, then we can find K_{eq} for this T.
2. Tabulated data for ΔG° (given for T = 298.15K) can be used to calculate K_{eq} at T = 298.15K:

$$K_{eq(298.15K)} = e^{-\frac{\Delta G^\circ_{298.15K}}{R \times 298.15}}$$

“*G vs Extent of Reaction*” Plot:

further analysis of $\Delta G = \Delta G^\circ + RT \ln Q_{eq}$ and $\Delta G^\circ = -RT \ln K_{eq}$

Even though in the formulas we operate with ΔG not G , we can still use G in graphs (similarly to what we did with enthalpy, H).



1. Equilibrium is the extent of reaction at which G is minimum.
2. Spontaneous processes are in the direction of decreasing G .
3. ΔG° determines the location of the equilibrium:
 - a) if ΔG° is close to 0, the the equilibrium is close to the middle
 - b) if $\Delta G^\circ > 0$ then the equilibrium is shifted to reactants
 - c) if $\Delta G^\circ < 0$ then the equilibrium is shifted to products

Significance of the Magnitude of ΔG°

ΔG°	$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$	
+200 kJ/mol	9.1×10^{-36}	No reaction
+100	3.0×10^{-18}	
+50	1.7×10^{-9}	
+10	1.8×10^{-2}	
+1.0	6.7×10^{-1}	
0	1.0	Equilibrium calculation is necessary
-1.0	1.5	
-10	5.6×10^1	Reaction goes to completion
-50	5.8×10^8	
-100	3.3×10^{17}	
-200	1.1×10^{35}	

Criteria for Predicting The Direction of Chemical Change

1. $\Delta G < 0$: the forward reaction is spontaneous *for the stated conditions*
2. $\Delta G^\circ < 0$: the forward reaction is spontaneous *for all reactants and products in their standard states*; $K_{eq} > 1$, whatever the initial concentrations (or pressures) of reactants and products
3. $\Delta G = 0$: the reaction is at equilibrium *for the stated conditions*
4. $\Delta G^\circ = 0$: the reaction is at equilibrium for all reactants and products in their standard states; $K_{eq} = 1$, which can occur only at a particular temperature (recall water vaporization at $P = 1 \text{ atm}$)
5. $\Delta G > 0$: the reverse reaction is spontaneous *for the stated conditions*
6. $\Delta G^\circ > 0$: the reverse reaction is spontaneous *for all reactants and products in their standard states*; $K_{eq} < 1$, whatever the initial concentrations (or pressures) of reactants and products
7. $\Delta G = \Delta G^\circ$: only when *all reactants and products in their standard states* ($Q_{eq} = 1$); otherwise, $\Delta G = \Delta G^\circ + RT \ln Q_{eq}$

Example: assessing spontaneity for non-standard conditions

Q: $A(g) \leftrightarrow B(g) + C(g)$, $K_{eq} = 0.5$ at $T = 500K$

- a) Is the **forward** reaction spontaneous under standard conditions?
- b) Will the **forward** reaction be spontaneous when $P_A = 1$ bar, $P_B = 0.2$ bar and $P_C = 0.1$ bar?

Solution (a): If the reaction is carried out under standard conditions then we have to use criteria 2, 4 or 6. We look either (i) at the sign of ΔG° , or (ii) at the value of K_{eq} whatever is known:

From criterion 6:

If $K_{eq} < 1$, then the reverse reaction is spontaneous under standard conditions or **the forward is non-spontaneous**

We can make the same conclusion by assessing the sign of ΔG° :

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_{eq} \\ &= -8.314 \text{ Jmol}^{-1}\text{K}^{-1} \times 500 \text{ K} \times \ln 0.5 = 2881 \text{ Jmol}^{-1}\end{aligned}$$

$\Delta G^\circ > 0$, thus the forward reaction is non-spontaneous

Solution (b): If the conditions are non-standard ($P_A = 1$ bar, $P_B = 0.2$ bar and $P_C = 0.1$ bar) then we have to use criteria 1, 3 or 5 to determine spontaneity. For this we have to determine the sign of ΔG :

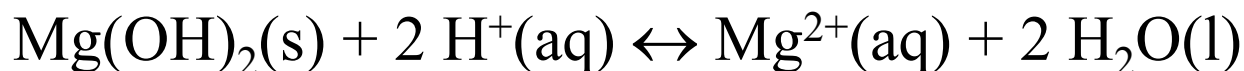
$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q_{eq} = \Delta G^\circ + RT \ln(P_B P_C / P_A) = \\ &= 2881 \text{ Jmol}^{-1} + 8.314 \text{ Jmol}^{-1}\text{K}^{-1} \times 500 \text{ K} \times \ln(0.2 \times 0.1/1) \\ &= -13.4 \text{ kJ/mol}\end{aligned}$$

From criterion 1:

$\Delta G < 0$, that is the forward reaction is spontaneous under the stated conditions

Example 20-8: Calculating K_{eq} from ΔG°

Q: Determine K_{eq} at $T = 298.15$ K for the dissociation of magnesium hydroxide in an acidic solution:



Solution: We will use the following formula to calculate K_{eq} :

$$K_{eq(298.15\text{K})} = e^{-\frac{\Delta G^\circ_{298.15\text{K}}}{R \times 298.15}}$$

To do those calculations we need to determine ΔG° of this reaction:

$$\Delta G^\circ = \Delta G_f^\circ \text{Mg}^{2+} + 2\Delta G_f^\circ \text{H}_2\text{O} - \Delta G_f^\circ \text{Mg(OH)}_2 - 2\Delta G_f^\circ \text{H}^+$$

The values of G_f° are found in Appendix D:

$$\Delta G^\circ = -454.8 + 2 \times (-237.1) - (-833.5) - 2 \times 0 = -95.5 \text{ kJ/mol}$$

By substituting this into the formula for K_{eq} we get:

$$K_{eq(298.15\text{K})} = e^{-\frac{-95.5 \times 10^3}{8.314 \times 298.15}} = 5.392 \times 10^{16}$$

Thermodynamic Equilibrium Constant: Activities

Recall these two lines from our derivations:

$$\Delta S = S - S^\circ = -R \ln(P/1) \Rightarrow$$

$$S = S^\circ - R \ln P \quad (\text{note that } P \text{ is dimensionless because it is defined as a ratio})$$

Dimensionless P is *per se* the activity, a :

$$S = S^\circ - R \ln a$$

This expression can be used not only for gases but also for solutions

The activity, a , can be defined as usually:

$$a = \frac{\text{the concentration of a substance in the system}}{\text{the concentration of this substance in its standard reference state}}$$

Note: It is important to define the standard reference state.

- For gases, standard reference state is that at $P = 1 \text{ bar}$ (10^5 Pa) $\approx 1 \text{ atm}$
- For solutions, standard reference state is that at $C = 1 \text{ M}$
- For solids (liquids), standard reference state is pure solid (liquid)

Activities of Ideal Gases and Solutions

Thus,

1. **For a gas component in an ideal gas mixture** (no electrodynamic interactions between molecules and ions) the activity of a reaction component is equal to its partial pressure, P :

$$a_A^{\text{gas}} = \frac{P}{1 \text{ bar}} = P$$

2. **For a solute in an ideal solution** (no electrostatic interactions between molecules and ions) the activity of a reaction component is equal to its molarity, C :

$$a_A^{\text{sol}} = \frac{C}{1 \text{ M}} = C$$

3. **For a pure solid or liquid** the activity is equal to unity:

$$a_A^{\text{pure solid}} = 1 \quad a_A^{\text{pure liquid}} = 1$$

Activities of Non-Ideal Gases and Solutions

All deviations from ideality are swept into an experimentally determined activity coefficient, γ

For a gas:

$$a^{\text{gas}} = \gamma P$$


For a solute:

$$a^{\text{liq}} = \gamma C$$

For a pure liquid or solid:

$$a^{\text{pure solid}} = a^{\text{pure liquid}} = 1$$

Note: that the correct definition of pH is

$$\text{pH} = -\log a_{\text{H}_3\text{O}^+} = -\log \left(\gamma \frac{[\text{H}_3\text{O}^+]\text{M}}{1 \text{ M}} \right) = -\log \left(\gamma [\text{H}_3\text{O}^+] \right)$$


Dimensionless because it is defined as a ratio

Example 20-6: Writing expressions for K_{eq} using activities

Q: Write K_{eq} for the following reactions and relate them to K_C or K_P , where appropriate:

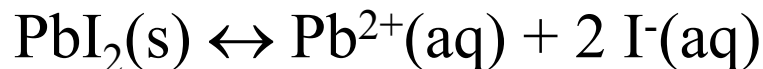
(a) The water gas reaction:



Solution:

$$K_{eq} = \frac{a_{\text{H}_2\text{(g)}} a_{\text{CO(g)}}}{a_{\text{C(s)}} a_{\text{H}_2\text{O(g)}}} = \frac{P_{\text{H}_2} P_{\text{CO}}}{P_{\text{H}_2\text{O}}} = K_P$$

(b) Formation of saturated aqueous solution of lead iodide, a very slightly soluble solute:



Solution:

$$K_{eq} = \frac{a_{\text{Pb}^{2+}\text{(aq)}} a_{\text{I}^-\text{(aq)}}^2}{a_{\text{PbI}_2\text{(s)}}} = \frac{[\text{Pb}^{2+}][\text{I}^-]^2}{1} = K_C = K_{sp}$$

(c) Oxidation of sulfide ion by oxygen gas (used in removing sulfides from wastewater, as in pulp and paper mills):



Solution:

$$\mathbf{K}_{\text{eq}} = \frac{\mathbf{a}_{\text{OH}^{-}(\text{aq})}^4 \mathbf{a}_{\text{S}(\text{s})}^2}{\mathbf{a}_{\text{O}_2(\text{g})} \mathbf{a}_{\text{S}^{2-}(\text{aq})}^2 \mathbf{a}_{\text{H}_2\text{O}(\text{l})}^2} = \frac{[\text{OH}^{-}]^4 \times \mathbf{1}^2}{P_{\text{O}_2(\text{g})} [\text{S}^{2-}]^2 \times \mathbf{1}^2} = \frac{[\text{OH}^{-}]^4}{P_{\text{O}_2(\text{g})} [\text{S}^{2-}]^2}$$

Note: K_{eq} does NOT correspond to either K_c or K_p



Solution:

$$\mathbf{K}_{\text{eq}} = \frac{\mathbf{a}_{\text{SiCl}_4(\text{g})}}{\mathbf{a}_{\text{Si}(\text{s})} \mathbf{a}_{\text{Cl}_2(\text{g})}^2} = \frac{P_{\text{SiCl}_4}}{\mathbf{1} \times P_{\text{Cl}_2}^2} = \mathbf{K}_P$$

ΔG° as Functions of Temperature

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

Even though ΔH° and ΔS° slightly depend on T, ΔG° depends on T mainly due to the T factor in the second term. Therefore, in our calculations of ΔG° we can assume that ΔH° and ΔS° do not depend on T.

Example 20-9:

Q: At which T will the K_{eq} for the formation of NOCl(g) be

$$K_{eq} = K_p = 1.000 \times 10^3?$$

Solution: Reaction of NOCl(g) formation is:



Using known formulas and data from Appendix D we get:

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ \text{NOCl(g)} - [2\Delta H_f^\circ \text{NO(g)} - \Delta H_f^\circ \text{Cl}_2\text{(g)}] = 2 \times 51.71 - 2 \times 90.25 - 0 \\ &= -77.08 \text{ kJmol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 2S_f^\circ \text{NOCl(g)} - 2S_f^\circ \text{NO(g)} - S_f^\circ \text{Cl}_2\text{(g)} = 2 \times 261.7 - 2 \times 210.8 - 223.1 \\ &= -121.3 \text{ Jmol}^{-1}\text{K}^{-1} = -0.1213 \text{ kJmol}^{-1}\text{K}^{-1}\end{aligned}$$

Note: We will not need data for ΔG°

Using the definition of ΔG° :

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

and the derived relationship between ΔG° and K_{eq} :

$$\Delta G^\circ = -RT \ln K_{eq}$$

we get

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq} \quad \text{or}$$

$$-T\Delta S^\circ + RT \ln K_{eq} = -\Delta H^\circ$$

If we assume that ΔH° and ΔS° do not depend on T, then:

$$T = \Delta H^\circ / (\Delta S^\circ - R \ln K_{eq}) =$$

$$= -77.08 \text{ kJmol}^{-1} / (-0.1213 \text{ kJmol}^{-1}\text{K}^{-1} - 8.314 \times 10^{-3} \text{ kJmol}^{-1}\text{K}^{-1} \times \ln(1 \times 10^3))$$

$$= 431.3 \text{ K}$$

Note: The assumption that ΔH° and ΔS° do not depend on T reduces the accuracy of our calculations, so that the number of significant figures is less than 4; however, we do not know how many.

K_{eq} as Functions of Temperature

From the expression:

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$$

we can also obtain the

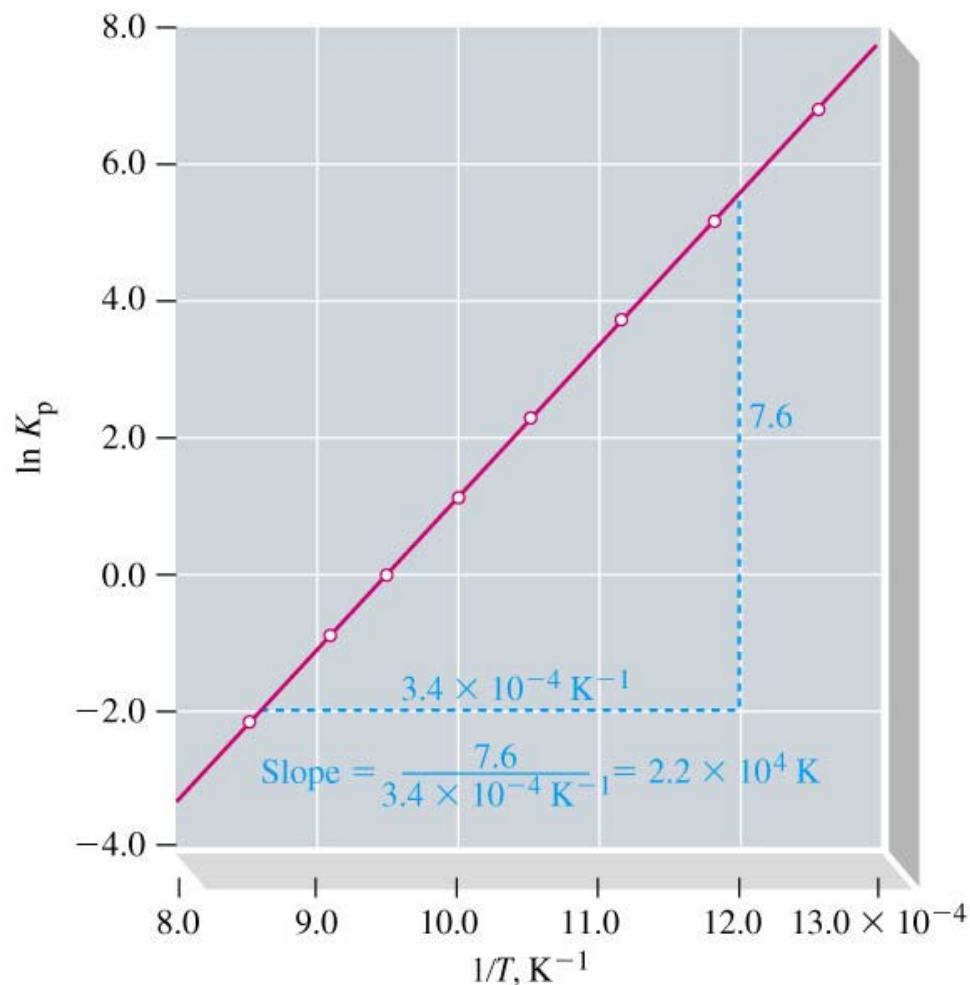
dependence of K_{eq} on T :

$$\begin{aligned}\ln K_{eq} &= -(\Delta H^\circ - T\Delta S^\circ)/RT \\ &= -\Delta H^\circ/RT + \Delta S^\circ/R\end{aligned}$$

Note: $\ln K_{eq}$ is a straight line in the $\ln K_{eq}$ vs. $1/T$ coordinates. Such a graph can be used to find ΔH° and ΔS° :

$$\Delta H^\circ = -\text{slope} \times R$$

$$\Delta S^\circ = \text{intercept} \times R$$



Dependence of K_p on T for:
 $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{SO}_3(\text{g})$

van't Hoff Equation

Using the equation:

$$\ln K_{eq} = - \Delta H^\circ / RT + \Delta S^\circ / R$$

For two different temperatures allows us to write two equations:

$$\ln K_1 = - \Delta H^\circ / RT_1 + \Delta S^\circ / R$$

$$\ln K_2 = - \Delta H^\circ / RT_2 + \Delta S^\circ / R$$

If we subtract the first equation from the second we will get the van't Hoff Equation:

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

Note: The structure of this formula is similar to that of the familiar formula that we used to connect rate constants, k_1 and k_2 with the energy of activation, E_a :

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Coupled Reactions

How to make a non-spontaneous reaction ($\Delta G > 0$) proceed?

1. Change the temperature (does not work for $\Delta H > 0$ and $\Delta S < 0$).
2. Carry out the reaction by electrolysis (will be discussed later in the course).
3. Combine the reaction with another process that is spontaneous ($\Delta G < 0$). Such combined processes are called Coupled Reactions.

Example: Extracting Cu from its oxide

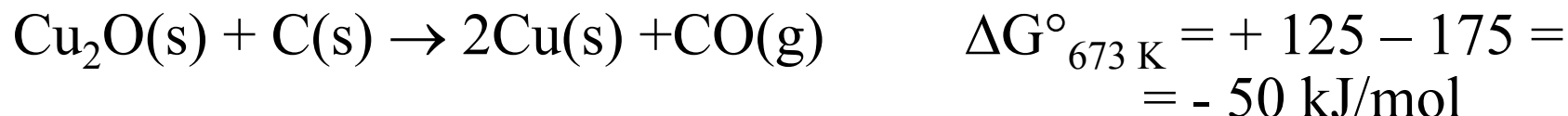


is non-spontaneous under standard conds. ($P_{\text{O}_2} = 1 \text{ bar}$) at $T = 673 \text{ K}$

Lets couple this reaction with the partial oxidation of carbon to carbon monoxide, which is spontaneous under these conditions:



The overall process will be spontaneous:



The Role of Coupled Processes in Biological Life

Life is possible only due to coupled processes

Many reactions involving biosynthesis of complex molecules are non-spontaneous under biological conditions.

They are carried out by coupling with spontaneous reactions

Example: Many biological processes are coupled with the ADP – ATP cycle (see “Focus On” section)

1. $\text{ATP} \rightarrow \text{ADP}$ reaction is spontaneous. Non-spontaneous processes can be carried out by coupling with the spontaneous $\text{ATP} \rightarrow \text{ADP}$ conversion ($\Delta G = -32.4 \text{ kJ/mol}$)
2. To maintain the pool of ATP the organism needs to effectively convert ADP back to ATP. This process is non-spontaneous.
3. Non-spontaneous $\text{ADP} \rightarrow \text{ATP}$ conversion is carried out by coupling with spontaneous oxidation of glucose:
$$\text{glucose} \rightarrow 2 \text{ lactate}^- + 2\text{H}^+ \quad (\Delta G = -218 \text{ kJ/mol})$$

The synthesis of glucose is non-spontaneous. What to couple it to?

Dispersal of Energy from the Sun is the Main Spontaneous Process

The synthesis of glucose (and other organic fuels) is non-spontaneous. It has to be coupled to a spontaneous process to proceed. The chain of coupled reactions is coupled with the **ultimate spontaneous process: dispersal of the Sun's energy**.

In the Sun: Thermonuclear reaction



On the Earth: Photosynthesis reaction



The Notion of Thermodynamic Death

The 2nd Law of Thermodynamics states that a universe (an isolated system) spontaneously proceeds to equilibrium as energy is dispersed from a higher concentrated state to a less concentrated one. No further spontaneous processes occur in the universe after that.

What is the future of our Universe? It is not an easy question since **we do not know the properties of the Universe in detail.**

1. We do not know whether or not the Universe is isolated.
 - a) If the Universe is not isolated (an open system), then its hypothetical surroundings have to be taken into account. We obviously know nothing about these surroundings.
 - b) If the Universe is isolated, then we still do not know enough about its properties. The Universe is currently expanding with acceleration. The scenarios would depend on whether or not this expansion is indefinite.

- If the Universe continues to expand indefinitely, then with dispersal of matter and energy the molecular/biological life (in its present quality) will become less possible.
- If the Universe stops to expand and starts to contract then it is possible that the Universe is oscillating. Then, every cycle in the Universe's periodic development will have a time span with conditions suitable for molecular life (in our usual understanding).
- Even if the Universe uses the script with the ultimate equilibrium at the end of its play, we have plenty of time, because of ... kinetics: Indeed, because of activation energies required, spontaneous processes are not instantaneous:

Example: $\text{C(diamond)} \rightarrow \text{C(graphite)}$ $\Delta G = -2.9 \text{ kJ/mol}$

... this is spontaneous, but an engagement ring is guaranteed to survive a few billion years.

The 2nd Law of Thermodynamics and Evolution:

The 2nd Law of Thermodynamics ($\Delta S_{\text{univ}} \geq 0$) is often paraphrased as “the Universe spontaneously moves from order to chaos”. This paraphrase is often used to state (naively or deliberately) that the 2nd Law of Thermodynamics precludes from natural origin of life and evolution since it seems that evolution goes from chaos to order when the 2nd Law requires that the Universe moves from order to chaos.

The misconception is obvious, but many science students who studied the 2nd Law and know how to use it to predict spontaneity of processes are still unable to find a flaw in this anti-evolutionists logic.

You know that: The 2nd Law does not prevent the decrease of entropy in an open system ($\Delta S_{\text{sys}} < 0$) if it is accompanied by the increase of entropy in the surroundings ($\Delta S_{\text{sur}} > 0$) so that the entropy of the Universe increases ($\Delta S_{\text{univ}} > 0$). Highly ordered life is possible due to coupled processes.

Note: In contrast to existing uneducated opinion, the formation of many complex organic molecules from their smaller precursors is thermodynamically favored ($\Delta G_f^\circ < 0$). See Appendix D on page A24.

Order in the Universe versus Complexity of the Components of the Universe

Life requires complexity in the Universe's components!

Complexity of the Universe's components increases by decreasing the order of the Universe!

1. Young Universe:

Highest order in the Universe was in the pre-big-bang Universe:

$$S_{t=0} = k \ln W = k \ln(1) = 0$$

At $t = 0$ the complexity of the Universe components was the lowest and life was impossible.

2. Mature Universe:

The order in the mature Universe is low:

$$S_{t \gg 0} \gg 0$$

The complexity of the mature Universe components is high and life is possible.

Essentials of the Two Last Lectures

The 2nd Law of Thermodynamics:

- In a spontaneous processes: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$
- In a reversible processes: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$

Macroscopic Definition of Entropy Change

- If surroundings are large, then T_{sur} does not change during the process. Entropy of surroundings is then defined as: $\Delta S_{\text{sur}} = q_{\text{sur}}/T_{\text{sur}}$
- For a reversible process: $\Delta S_{\text{sys}} = q_{\text{sys}}/T_{\text{sys}}$

The 3rd Law of Thermodynamics:

- Temperature of 0K is unattainable $\Rightarrow S \rightarrow 0$ when $T \rightarrow 0$

Standard molar entropy change

- The change of entropy for 1 mol of substance at 1 bar pressure

Standard molar entropy change in a chemical reaction:

$$\Delta S^\circ = \sum \nu_{\text{P}} S^\circ(\text{products}) - \sum \nu_{\text{R}} S^\circ(\text{reactants})$$