Chem 1B Topics

Chemistry: Structure and Properties, *Nivaldo J. Tro; Pearson Education Inc. 2015, 2017*.

Week*	Chapter	Topic
1-2	*10 (11)*	*Gases*
3-4	*11 (12)*	*Liquids, Solids, Intermolecular Forces*
5	*12 (13)*	*Phase Diagrams & Crystalline Solids*
6-7	*13 (14)*	*Properties of Solutions*
8-9	*9 (10)*	*Thermochemistry*
10	*18 (19)*	*Free Energy & Thermodynamics*

Note: we will not discuss equilibrium reactions in Chem 1B
This is the last section in Chapters 18(19).

Entropy, Gibbs Free Energy. The 2nd and 3rd Laws of Thermodynamics.

Joseph Cugnot's steam powered car (1770s)

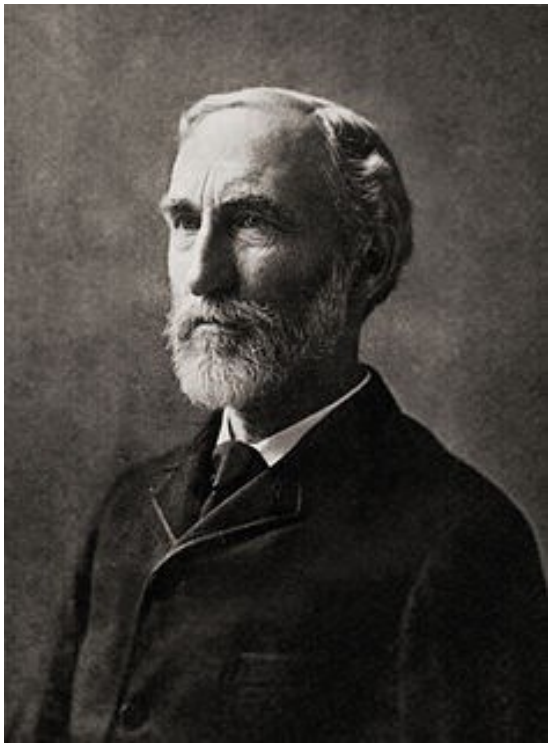
Saturn V rocket (7,500,000 pounds of thrust)

$$E = W + Q$$

$$H = E + PV$$

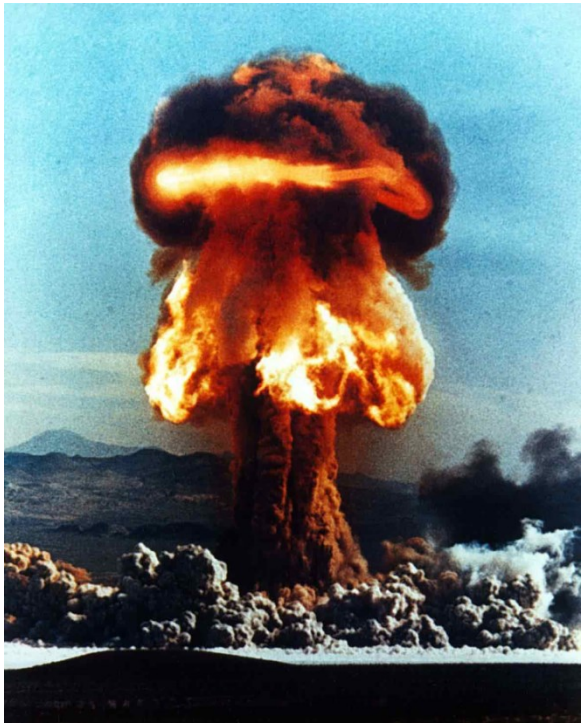
$$G = H - TS$$

$$dS = \frac{dQ}{T}$$



Josiah Willard Gibbs (1839-1903) – the founder of thermodynamics

Spontaneous Processes



These processes occur ***spontaneously*** & ***irreversibly*** reflecting the tendency of energy to "spread out"

Spontaneous process – does not need any input of energy from the surroundings to proceed

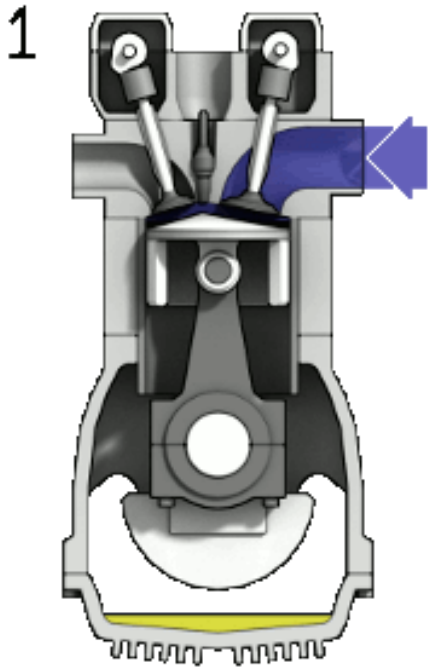
Irreversible process – permanently changes the surroundings and is EXCEEDINGLY unlikely to go in the reverse direction

Non-Spontaneous Processes

Changes can be *made to happen* in an "**unnatural**" (non-spontaneous) direction by applying ***work***.

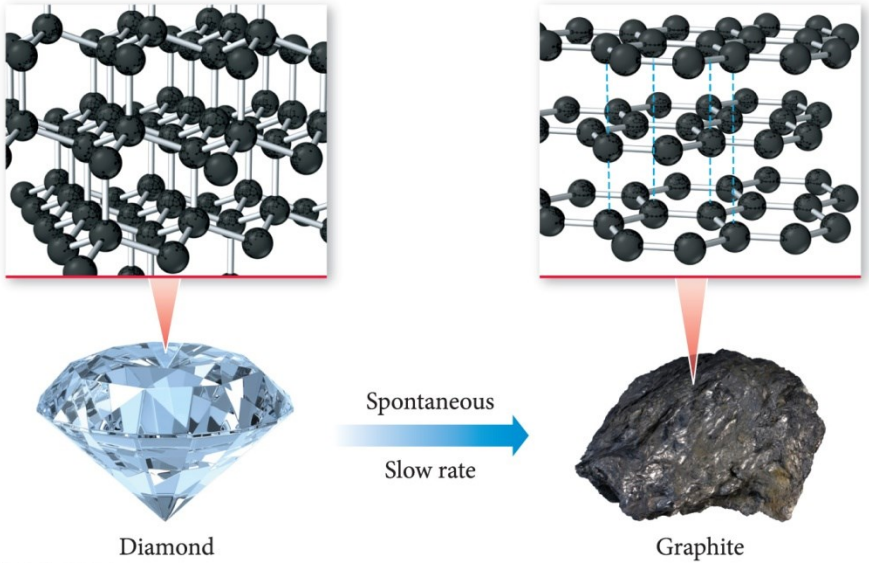
We can force an electric current through a block of metal to heat it to a higher temperature.

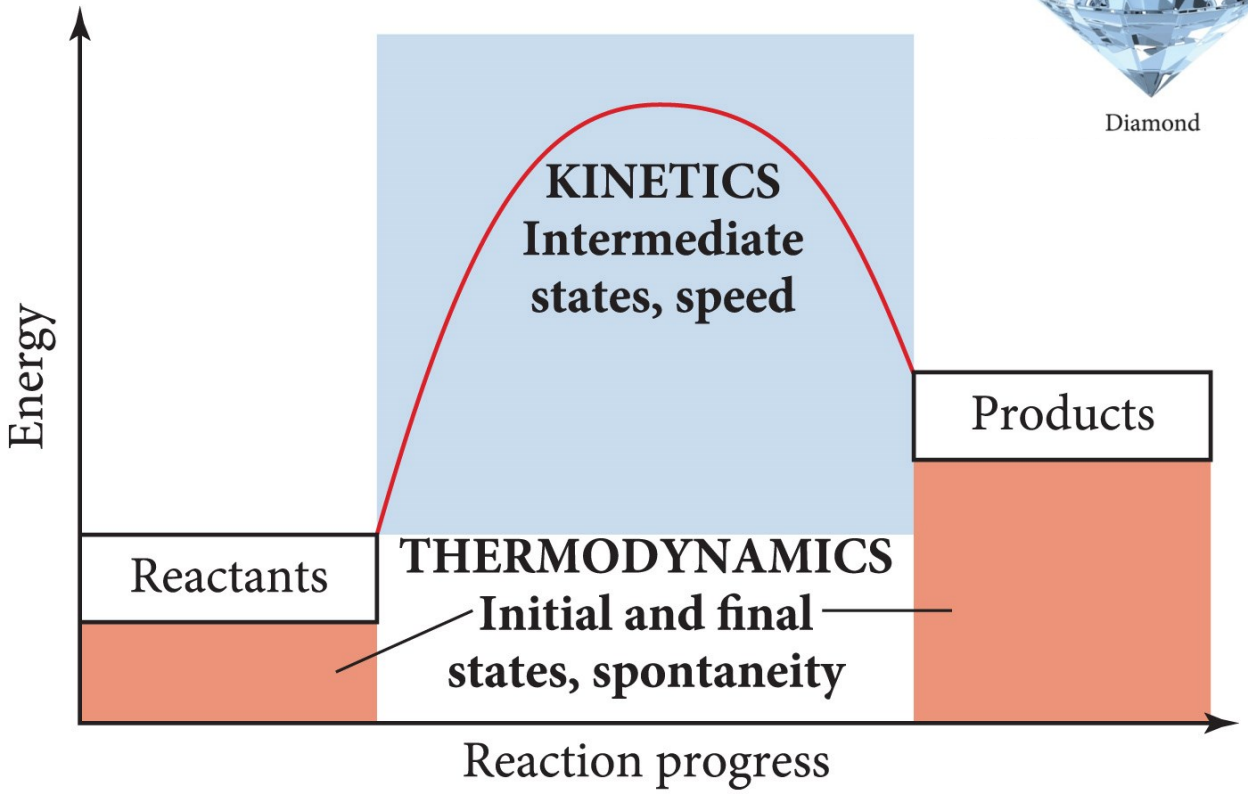
We can pressurize a gas into a smaller volume by pushing it with a piston.



Thermodynamics vs Kinetics

Spontaneity ≠ fast or slow!!!





- ***Thermodynamics*** tells you whether a process is spontaneous or not
- ***Kinetics*** tells you how fast the process is (Chem 1C)

Spontaneity and Enthalpy

The enthalpy of a reaction does contribute to its spontaneity

$$C_6H_{14}\,(l) + 9/2\ O_2(g) \rightarrow 6\ CO_2(g) + 7\ H_2O(l)$$

$$\Delta H^o = -4163\ \text{kJ / mol } C_6H_{14}$$

Fuel combustion is ***highly exothermic*** and ***definitively spontaneous*** as well as ***irreversible***

But … reaction enthalpy is not the only driving force that determines whether a reaction will proceed or not.

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

$$\Delta H^o = +6.01\ \text{kJ / mol } H_2O$$

Snow melting is ***endothermic*** but it is ***clearly spontaneous above 0° C***.

Entropy and Disorder

Dissolving NH_4NO_3 in water (solubility = 190 g/100 g H_2O at 20° C)

NH_4NO_3 cold-pack

Entropy is a thermodynamic state function that is related to the number of molecular arrangements (***microstates***) the system can take.

Why is it useful? The larger is the number of possible molecular arrangements the more ***probable*** is the system.

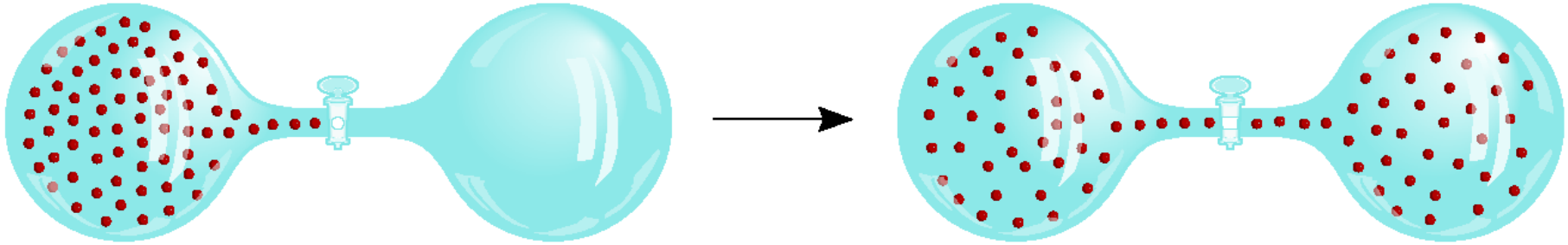
Driving forces in dissolution of this substance:

1). **Not enthalpy (*H*)** because $\Delta H_{soln}(NH_4NO_3)$ = + 26.7 kJ/mol!

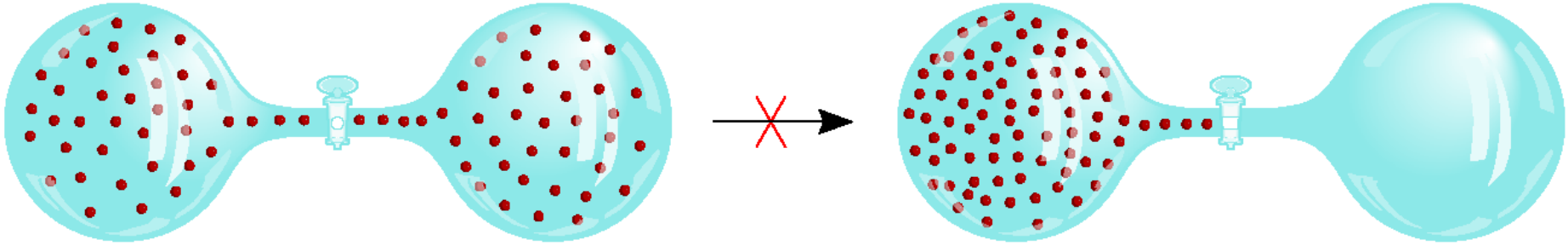
2). **Entropy (*S*)** – works to maximize the degree of disorder

Expansion of Gases

Spontaneous



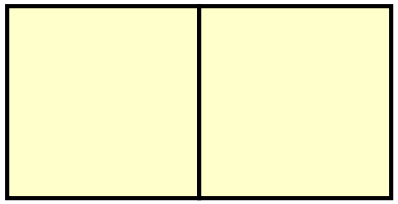
Non-spontaneous (requires a highly-skilled Maxwell's Demon)



The gases expand spontaneously and irreversibly to fill the entire volume available to them because they have more microstates accessible to them in an expanded state

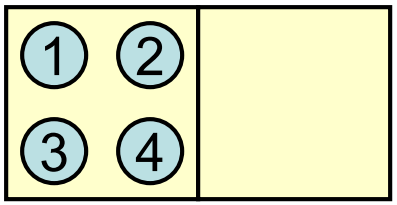
Statistical Nature of Microstates

Consider four distinguishable objects (molecules) and two distinguishable compartments (volumes in space).

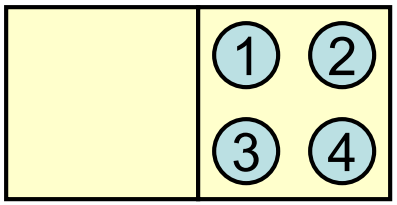


What are the possible arrangements of the four objects in the two compartments and how many microstates does each arrangement have?

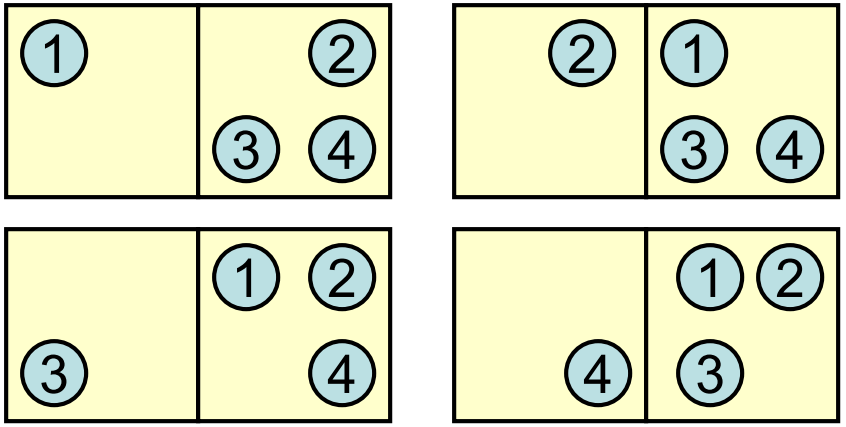
Arrangement A: all objects placed in the left compartment → ***1 microstate***



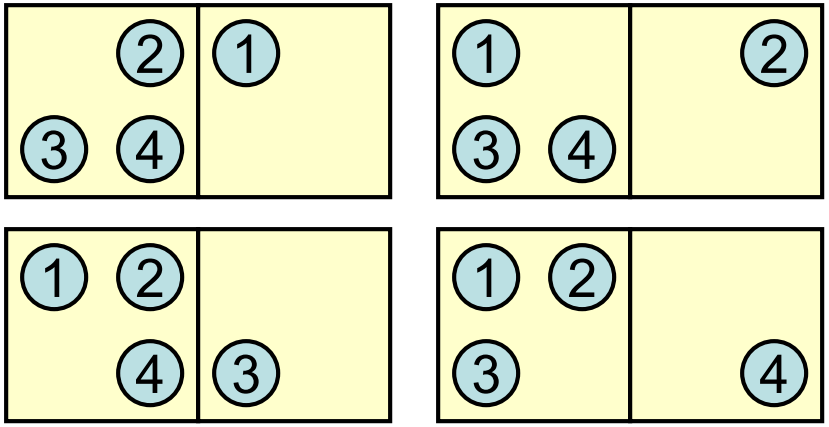
Arrangement B: all objects placed in the right compartment → ***1 microstate***



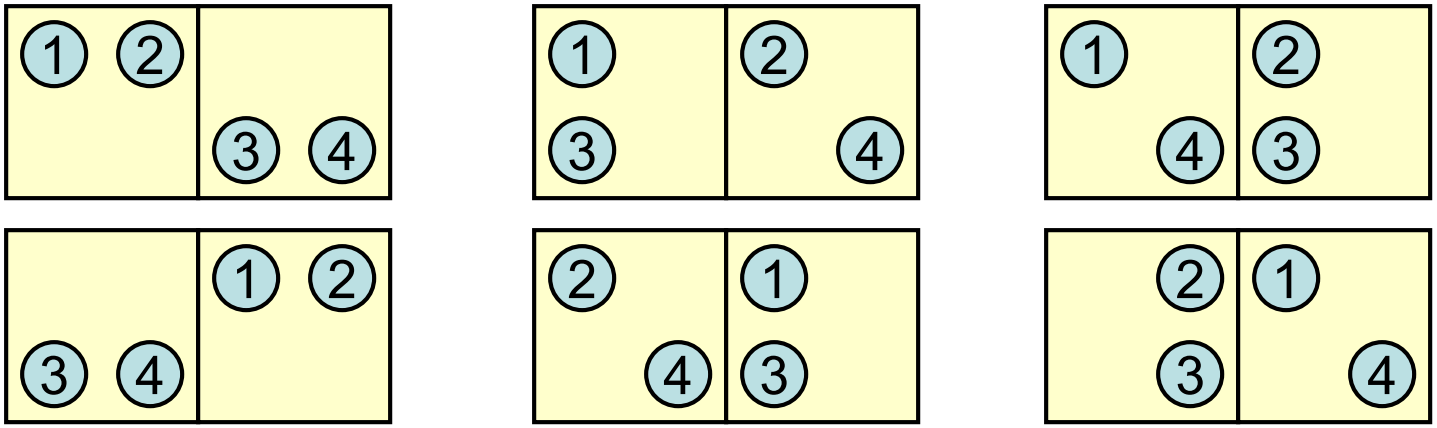
Arrangement C: one object is placed in the left compartment → ***4 microstates***



Arrangement D: one object is placed in the right compartment → ***4 microstates***



Arrangement E: equally distributed. This arrangement is **the most probable** because it corresponds to the largest number of possible microstates → ***6 microstates***



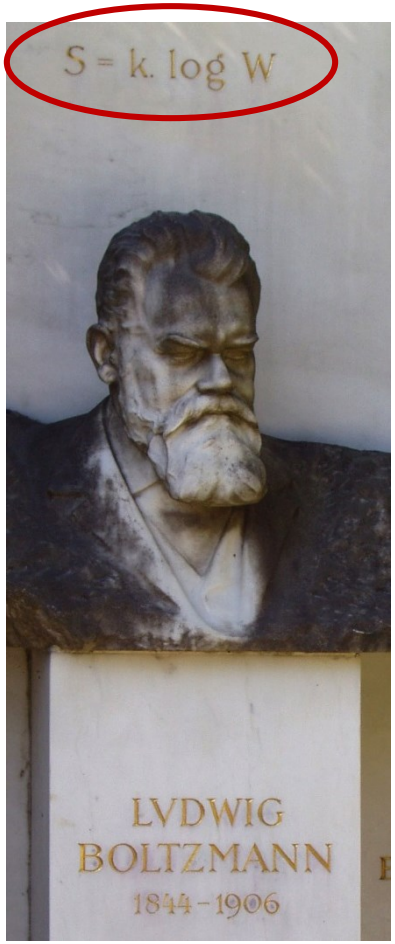
Molecular Definition of Entropy

The entropy ***S*** is defined to scale logarithmically with the total number of microstates (***W***). The higher is ***W*** the higher is ***S***.

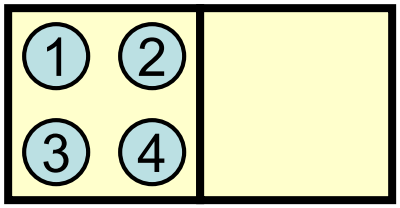
$$S = k \ln W$$

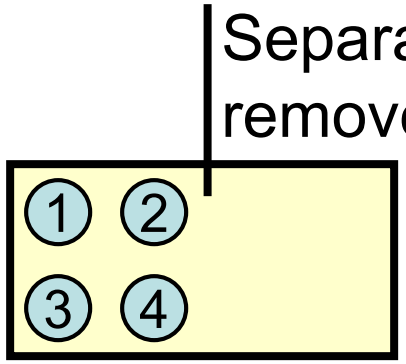
k = 1.3806503 × 10^{-23} J K^{-1}
(Boltzmann constant)

- Entropy cannot be negative (W ≥1)
- Unit of entropy is J/K



Entropy and Spontaneity





$W = 1$

$W = 16$ (sum of all the possible microstates shown in previous slides)

Which situation has higher entropy?

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

$S_{final} = k \ln(16) = 2.8\,k$

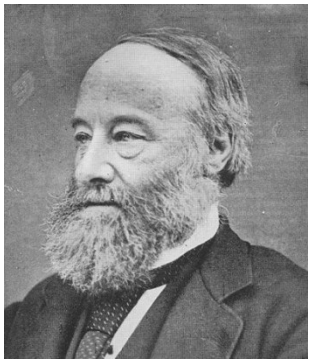
$\Delta S = S_f - S_i = 2.8\,k > 0$

A positive **change** in entropy corresponds to a spontaneous transition to a more probable state

First Law of Thermodynamics

Gottfried Wilhelm Leibniz (1646 – 1716) formally introduced the kinetic energy (he called it "vis viva" = living force) and the law of energy conservation for mechanical systems

James Prescott Joule (1818 -1889) experimentally confirmed conservation of energy in mechanical → heat transformations



Modern (more general) formulation:

"Energy can be converted from one form to another but it cannot be created or destroyed."

$$\Delta E_{universe} = \Delta E_{system} + \Delta E_{surroundings} = 0$$

Second Law of Thermodynamics

The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.

Rudolf Clausius (1822 - 1888)

A process will happen spontaneously if:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

The total change in entropy must be positive for a process to occur spontaneously.

For a **reversible process** (for example, a system at an equilibrium) the change in entropy of the universe is zero.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

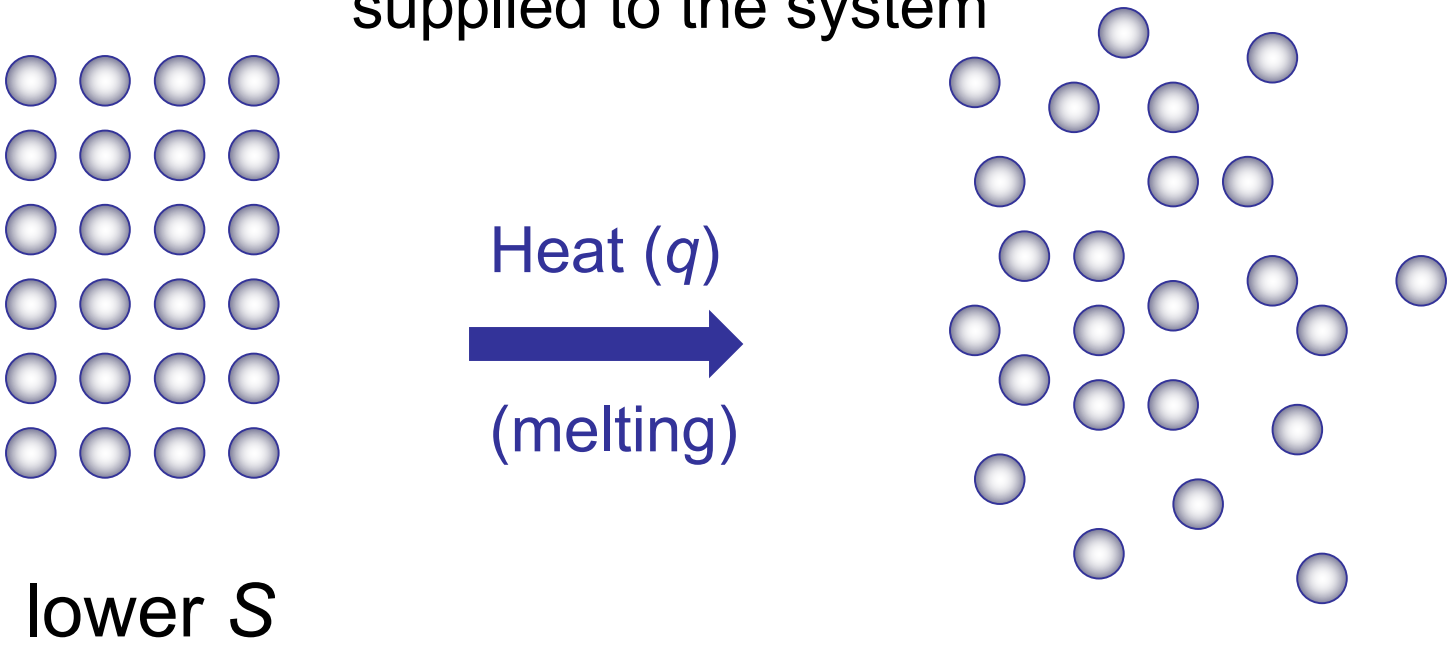
Perpetuum Mobile

A perpetuum mobile of the 1st kind produces work without the input of energy. Violates the 1st law of thermodynamics

A perpetuum mobile of the 2nd kind is a machine which converts thermal energy into mechanical work with 100% efficiency. Violates the 2nd law of thermodynamics (some of the heat will always be wasted on increasing the surroundings' entropy)

Macroscopic Definition of Entropy

Disorder and hence entropy increase when heat is supplied to the system

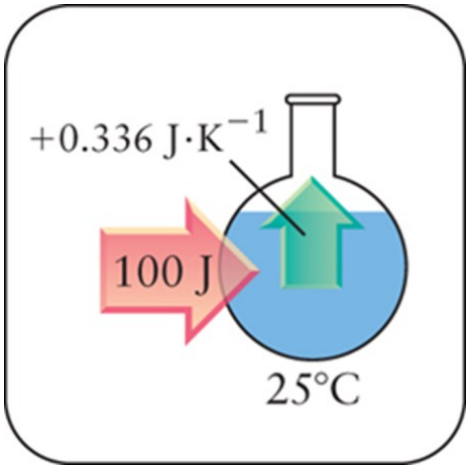


Reversible process – can reverse direction without dissipation of energy from an infinitesimal change in conditions. For such a process:

$$\Delta S_{system} = \frac{q_{reversible}}{T}$$

Sample Problem

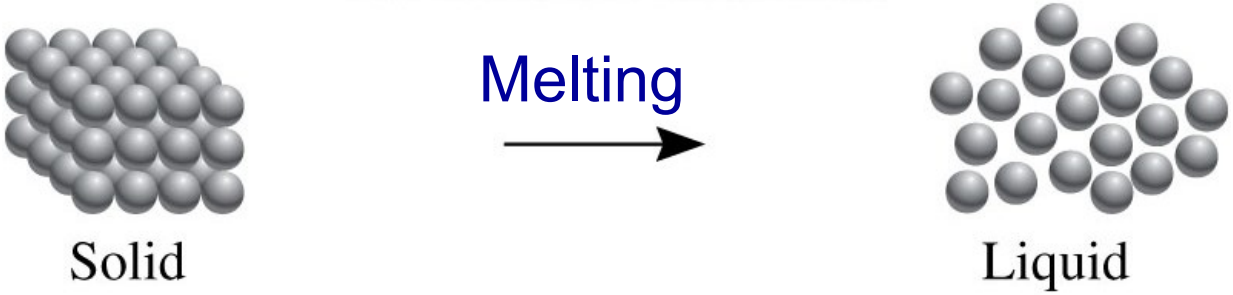
A large flask of water is placed on a heater and 100 J of energy is transferred reversibly to the water at 25° C. What is the change in entropy of the water?



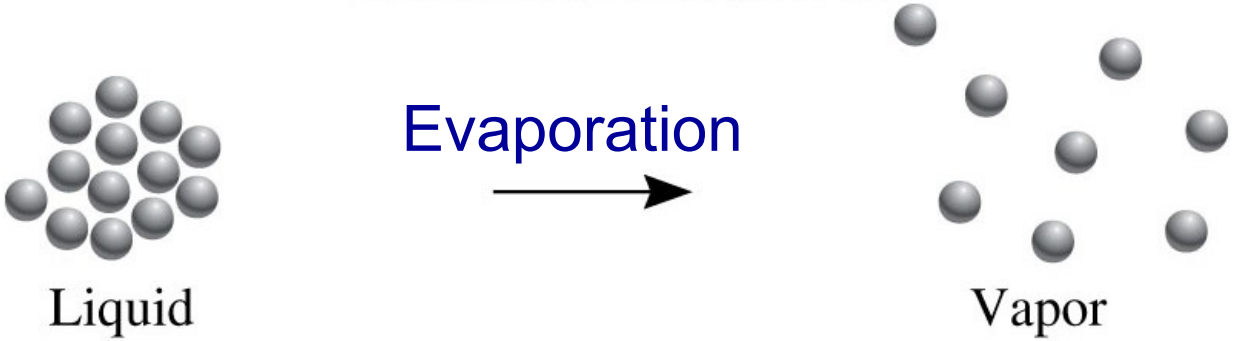
Favorable Entropy Changes

Lower entropy

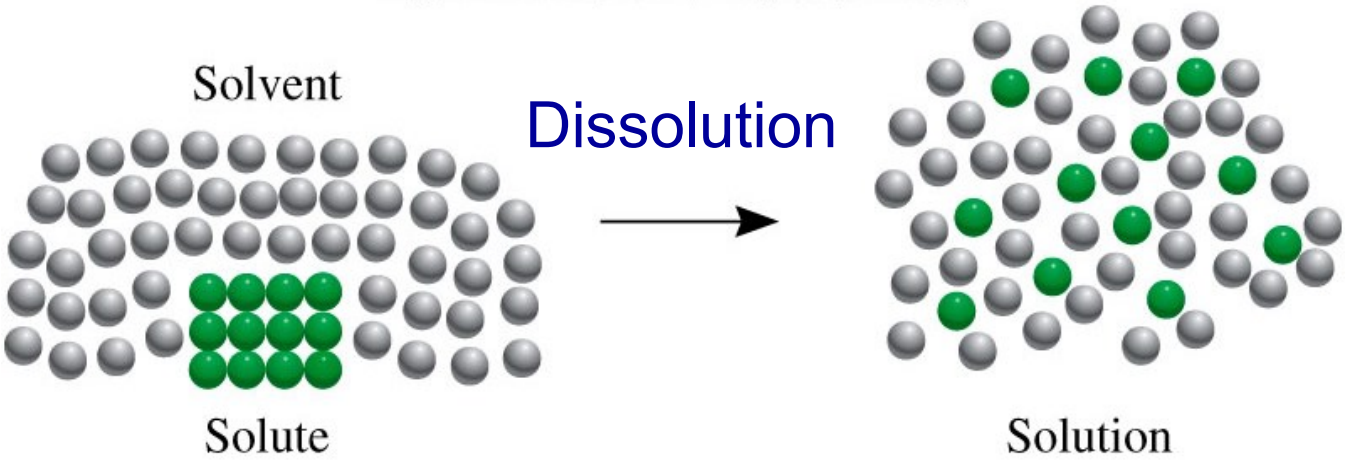
Higher entropy



$$\Delta S = \frac{\Delta H_{\text{fus}}}{T_m}$$



$$\Delta S = \frac{\Delta H_{\text{vap}}}{T_b}$$



$$\Delta S = \frac{\Delta H_{\text{soln}}}{T}$$

Standard Entropy

Unlike enthalpy, for which only the change is meaningful, entropy is an **absolute quantity**.

The entropy of one mole of a substance at standard conditions (1 atm, 25 °C) is called the standard entropy.

Substance	$S°$ (J/mol · K)	Substance	$S°$ (J/mol · K)	Substance	$S°$ (J/mol · K)
Gases		Liquids		Solids	
$H_2(g)$	130.7	$H_2O(l)$	70.0	$MgO(s)$	27.0
$Ar(g)$	154.8	$CH_3OH(l)$	126.8	$Fe(s)$	27.3
$CH_4(g)$	186.3	$Br_2(l)$	152.2	$Li(s)$	29.1
$H_2O(g)$	188.8	$C_6H_6(l)$	173.4	$Cu(s)$	33.2
$N_2(g)$	191.6			$Na(s)$	51.3
$NH_3(g)$	192.8			$K(s)$	64.7
$F_2(g)$	202.8			$NaCl(s)$	72.1
$O_2(g)$	205.2			$CaCO_3(s)$	91.7
$Cl_2(g)$	223.1			$FeCl_3(s)$	142.3
$C_2H_4(g)$	219.3				

Standard Entropy

Physical state – at a given temperature,
S(solid) < S (liquid) < S(gas)

State	S^o (J/mol K)
$H_2O(l)$	70.0
$H_2O(g)$	188.8

Dissolution – dissolved solids generally have larger entropy, distributing particles throughout the mixture.

Substance	S^o (J/mol · K)
$KClO_3(s)$	143.1
$KClO_3(aq)$	265.7

Standard Entropy

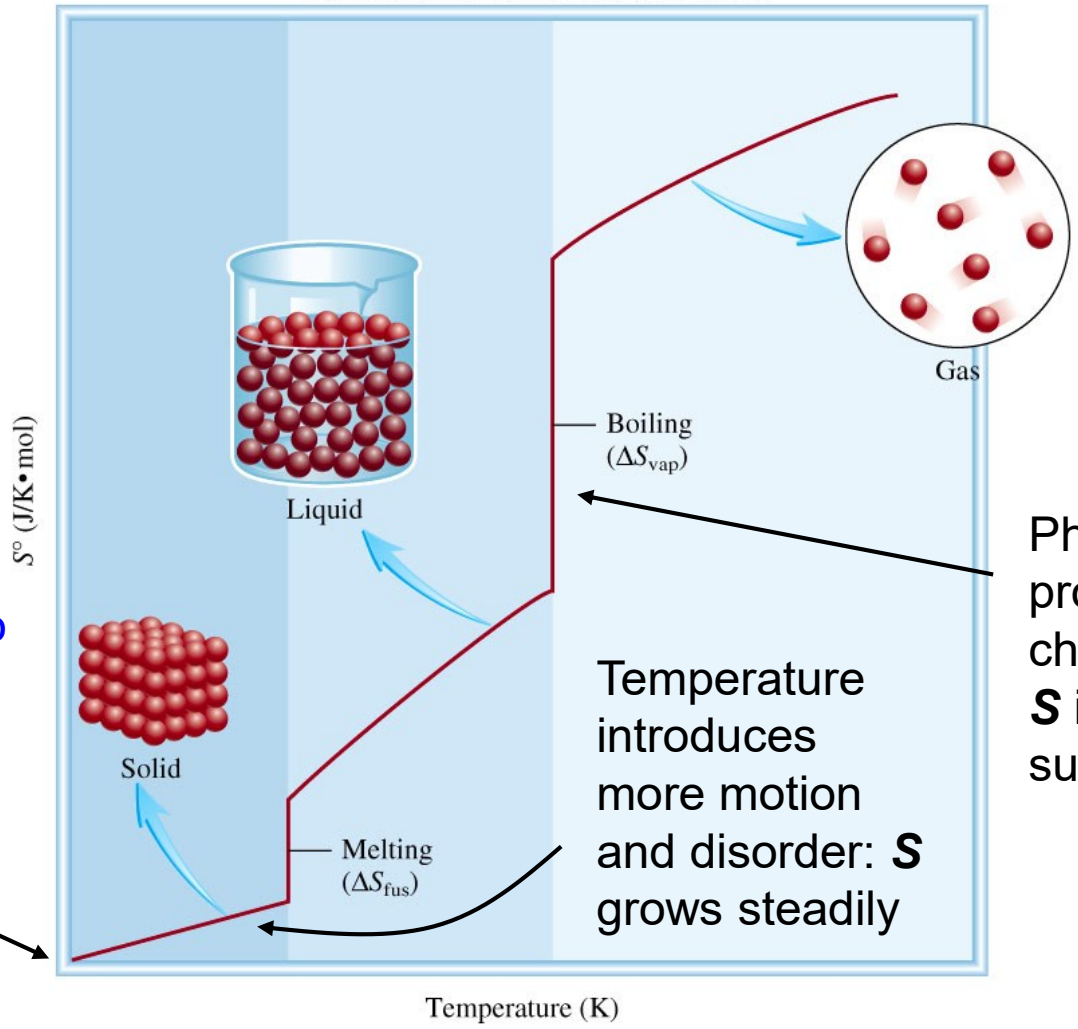
	$S°$ (J/mol·K)	
He(*g*)	126.2	
Ne(*g*)	146.1	
Ar(*g*)	154.8	
Kr(*g*)	163.8	
Xe(*g*)	169.4	

Molar mass – the larger is the molar mass, the larger is the standard entropy under given conditions

Molecular complexity – more complex molecules generally have larger entropy

Substance	Molar Mass (g/mol)	$S°$ (J/ mol · K)
CO(*g*)	28.01	197.7
C_2H_4(*g*)	28.05	219.3
NO(*g*)	30.006	154.8
Ar(*g*)	39.946	210.8

Standard Entropy vs Temperature



Perfect lattice, no rearrangements possible – only *W*=1 microstate exists:

S* = *k ln(W)

S = 0

Temperature introduces more motion and disorder: ***S*** grows steadily

Phase transitions produce major changes in order: ***S*** increases suddenly

The assumption that *S*=0 for a perfect crystal at T=0 K is the **Third Law of Thermodynamics**

Sample Problem

How does the entropy of a system change for each of the following processes?

(a) Condensing water vapor

(b) Forming sucrose crystals from a supersaturated solution

(c) Heating hydrogen gas from 60^0C to 80^0C

(d) Subliming dry ice

Standard Reaction Entropy

The entropy difference before and after a reaction can be determined from the standard entropies of the products and reactants:

$$\Delta S^{o}_{rxn} = \sum S^{o}(\text{products}) - \sum S^{o}(\text{reactants})$$

S^{o}(J/(K•mol))	
$NH_3(g)$	193
$N_2(g)$	192
$H_2(g)$	131

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

$$\Delta S^{o}_{rxn} = [2S^{o}(NH_3)] - [S^{o}(N_2) + 3S^{o}(H_2)]$$

$$= [2 \times 193] - [192 + 3 \times 131]$$

$$= -199 \text{ J/(K•mol)}$$

In this example $\Delta S_{rxn} < 0$: there is a decrease in entropy (there are fewer product molecules resulting in fewer possible microstates compared to the reactants)

Reactions Involving Gases

Because gases are inherently more disordered than liquids and solids the following simple rules apply:

- If a reaction produces more gas molecules than it consumes, $\Delta S^0 > 0$.
- If the total number of gas molecules diminishes, $\Delta S^0 < 0$.
- If there is no net change in the total number of gas molecules, then ΔS^0 may be positive or negative but the absolute value of ΔS^0 will be small.

What is the sign of the entropy change in Zn oxidation?

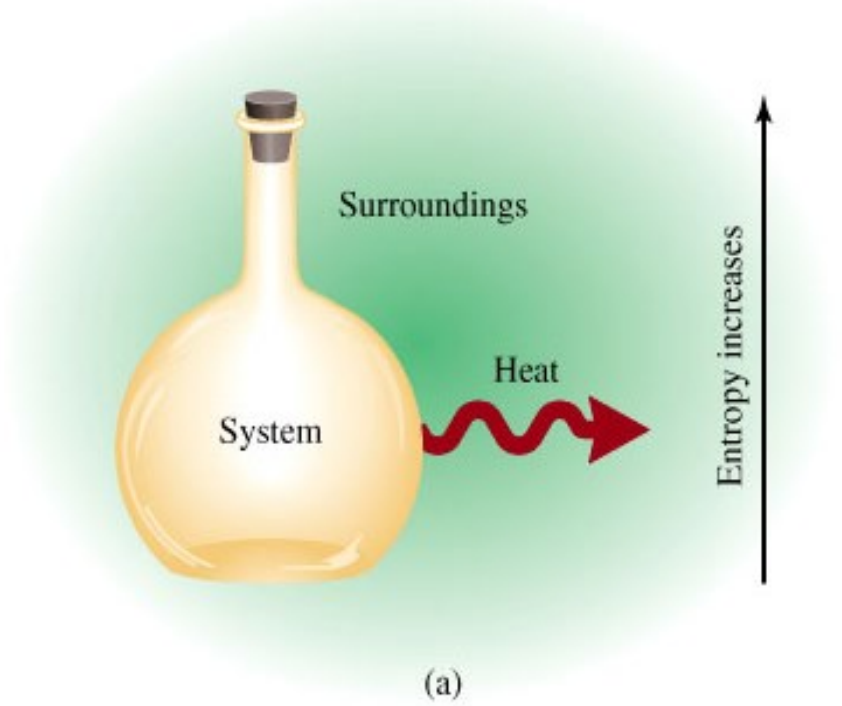
$$2\ Zn\ (s) + O_2\ (g) \rightarrow 2\ ZnO\ (s)$$

The total number of gas molecules goes down, ΔS is negative.

The Surroundings

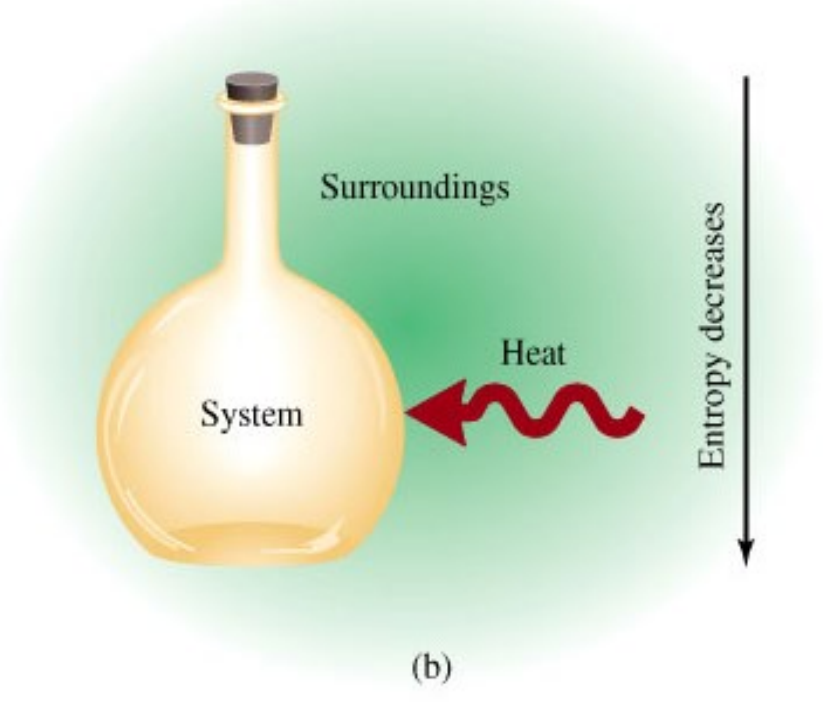
How the entropy of the surroundings changes is primarily determined by the heat flow to/from the system.

Surroundings gain heat and become more disordered in exothermic reactions



$\Delta S_{surr} > 0$

Surroundings lose heat and become more ordered in endothermic reactions



$\Delta S_{surr} < 0$

Entropy Changes in Surroundings

More precisely, the magnitude of ΔS_{surr} depends on both the heat flow and the temperature:

$$\Delta S_{surr} = -\frac{\Delta H_{rxn}}{T}$$

This is an alternative formulation of the 2nd law of thermodynamics.

For an exothermic reaction: $\Delta H_{rxn} < 0$ and $\Delta S_{surr} > 0$

The surroundings ***gain entropy*** in exothermic reactions

For an endothermic reaction: $\Delta H_{rxn} > 0$ and $\Delta S_{surr} < 0$

The surroundings ***lose entropy*** in endothermic reactions

Example of Determining ΔS_{surr}

Determine the entropy change of the surroundings at 25 °C for the following reactions:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\quad \Delta H = -572$ kJ

$2\,Sb_2O_3(s) + 6C(s) \rightarrow 4Sb(s) + 6CO(s)$ $\quad \Delta H = 778$ kJ

The first reaction:

$\Delta S_{surr} = -(-572\text{ kJ}) / 298\text{ K} = 1.92 \times 10^3$ J/K

Heat flows to surroundings, increasing the degree of randomness in the surrroundings.

The second reaction:

$\Delta S_{surr} = -788\text{ kJ} / 298\text{ K} = -2.61 \times 10^3$ J/K

Heat flows from surroundings to the system; thus the entropy of the surrounding decreases.

Which Reactions are Spontaneous?

Spontaneous:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

Signs of Entropy Changes

ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	*Process Spontaneous?*
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

Sample Problem

Will the following reaction be spontaneous under standard conditions: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

$\Delta H^\circ_{rxn} = -92.6$ kJ/mol

$\Delta S^\circ_{rxn} = -199$ J/K•mol

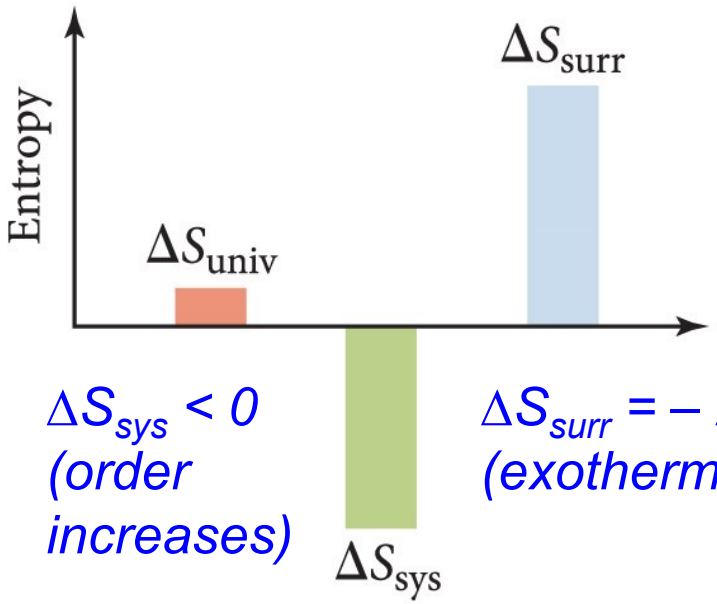
Role of Temperature

$$\Delta S_{surr} = -\frac{\Delta H_{rxn}}{T}$$

Because ΔS_{surr} changes with temperature, the balance between ΔS_{surr} and ΔS_{sys} can change at a different temperature

Water freezing: $H_2O(l) \rightarrow H_2O(s)$

Low Temperature: Spontaneous

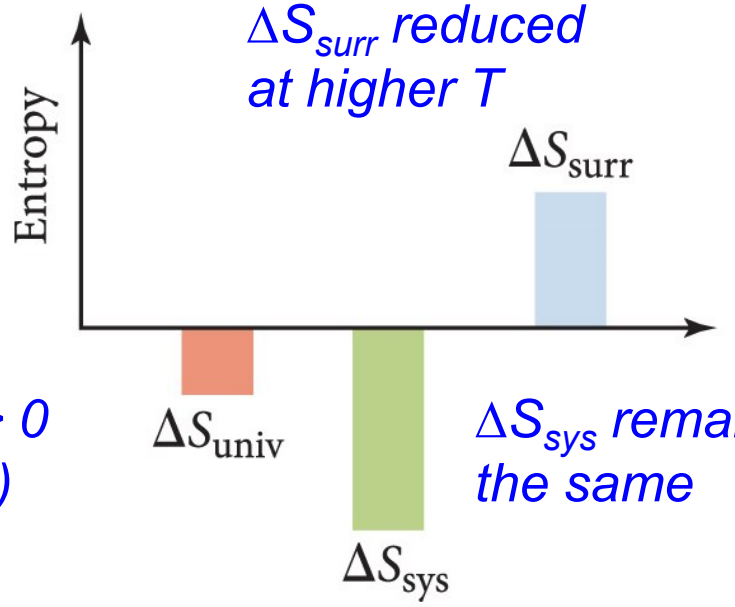


$\Delta S_{sys} < 0$ (order increases)

$\Delta S_{surr} = -\Delta H^{o}_{rxn} / T > 0$ (exothermic reaction)

High Temperature: Nonspontaneous

ΔS_{surr} reduced at higher T



ΔS_{sys} remains the same

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ = changes sign at higher T!

Thermodynamic State Functions

We have seen the following state functions:

$$E = \text{heat} + \text{work}$$

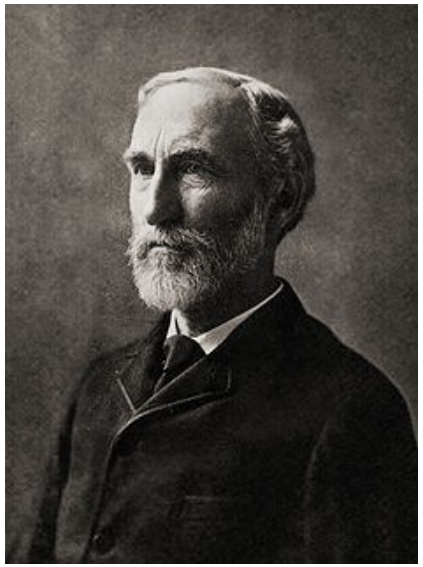
$\Delta E = q_V$ is useful for ***constant volume*** processes

$$H = E + PV$$

$\Delta H = q_P$ is useful for ***constant pressure*** processes

PROBLEM: Neither state function takes into account the entropy of the system and is suitable for processes at ***constant temperature***

Gibbs Free Energy



Josiah Willard Gibbs
(1839 –1903)

$$G = H_{sys} - T \cdot S_{sys}$$

ΔG is useful for processes that occur at ***constant pressure AND temperature***

$$\Delta G = \Delta H_{sys} - T \cdot \Delta S_{sys}$$

ΔG includes the effects of entropy and can be used to predict the spontaneity of a chemical reaction. Let us see how:

Free Energy and Spontaneity

Consider the change in free energy defined above:

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys} \xrightarrow{\text{divide by } (-T)} -\frac{\Delta G}{T} = -\frac{\Delta H_{sys}}{T} + \Delta S_{sys}$$

$$-\frac{\Delta G}{T} = \Delta S_{surr} + \Delta S_{sys}$$

$$-\frac{\Delta G}{T} = \Delta S_{univ}$$

A process is spontaneous if $\Delta S_{univ} > 0$, which means that a process is spontaneous if ΔG is ***negative***.

For a reaction to be spontaneous at constant T and P:

$$\Delta G < 0$$

Free Energy and Spontaneity

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

$\Delta G < 0$ The reaction is spontaneous in the forward direction.

$\Delta G > 0$ The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$\Delta G = 0$ The reaction is at equilibrium.

Free Energy of Formation

The standard free energy of formation (ΔG°_f) is the change in free energy associated with the formation of 1 mole of substance from its elements with all reactants and products in their ***standard states***.

ΔG°_f values have been **tabulated** for most compounds

Conventions for Standard States

State of Matter	Standard State
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure solid
Elements*	$\Delta G^\circ_f = 0$
Solution	1 molar concentration

*The most stable allotropic form at 25°C and 1 atm.

Free Energy of Reaction

The standard free energy of reaction ΔG^o is the change in free energy occurring when reactants in their standard states are converted to products in their standard states (1 atm, 25 °C). It can be calculated from the standard free energy of formation (ΔG^o_f) of the products and reactants:

$$\Delta G^o_{rxn} = \sum n_p \Delta G^o_f - \sum n_r \Delta G^o_f$$

$$2CH_3OH\,(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

	ΔG^o_f(kJ/mol)
$CH_3OH(g)$	-163
$O_2(g)$	0
$CO_2(g)$	-394
$H_2O(g)$	-229

Determine the ΔG^o of the reaction.
Is it spontaneous?

$$\Delta G^o_{rxn} = \sum n_p \Delta G^o_f - \sum n_r \Delta G^o_f$$

$$= 2 \times (-394\ \text{kJ/mol}) + 4 \times (-229\ \text{kJ/mol}) - 2 \times (-163\ \text{kJ/mol})$$

$$= -1378\ \text{kJ/mol}$$ yes, this reaction is spontaneous

Sample Problem

Consider the reaction of ethylene and water to form ethanol:

$C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$

Is this reaction spontaneous under standard conditions?

	ΔG^o_f (kJ/mol)
$C_2H_5OH(l)$	-175
$C_2H_4(g)$	68
$H_2O(l)$	-237

Sample Problem

What is the standard free-energy change for the following reaction at 25 ^{0}C? The free energies of formation are -394.4, -237.2, 0, and +124.5 kJ/mol for CO_2, H_2O, O_2, and C_6H_6, respectively.

Is the reaction spontaneous at 25 ^{0}C?

Free Energy and Hess's Law

Standard free energies cannot be measured directly, but are determined indirectly through measurements of ΔH^o and ΔS^o.

Once ΔG^o for a particular reaction is known, it becomes useful for predicting the free energy of other reactions because ΔG^o obeys Hess's law.

$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4\ H_2O\ (g)$ $\quad \Delta G^o = -1088$ kJ

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2\ H_2O\ (g)$ $\quad \Delta G^o = -801$ kJ

Determine ΔG^o for: $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

$2CO(g) + 4\ H_2O\ (g) \rightarrow 2CH_4(g) + 3O_2(g)$ $\quad \Delta G^o = -(-1088)$ kJ

$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4\ H_2O\ (g)$ $\quad \Delta G^o = 2(-801)$ kJ

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\quad \Delta G^o = -514$ kJ

The Effect of Temperature

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

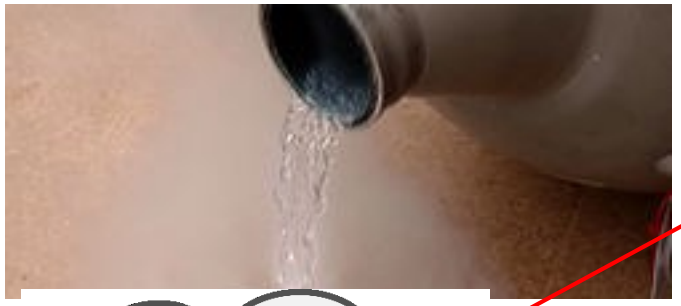
Dominates at low temperatures

Dominates at high temperatures

ΔH	ΔS	ΔG
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.
+	−	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.
−	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.

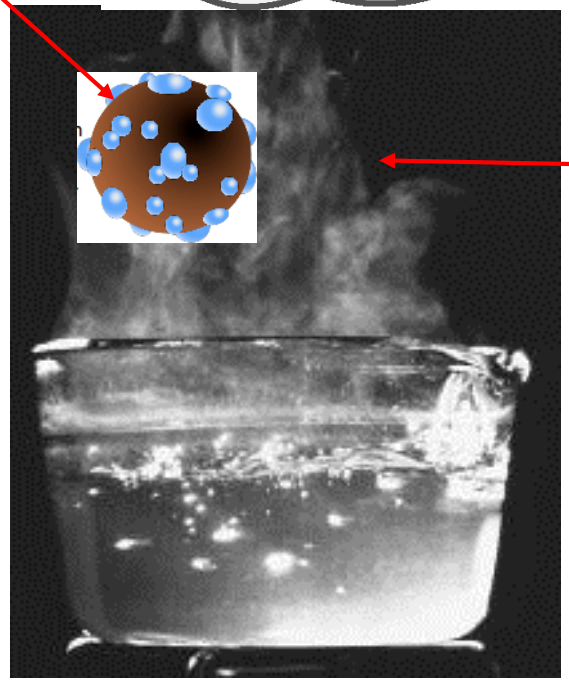
Cloud Formation Demo

Liquid Nitrogen
-196 ° C



Cool air
drives equilibrium
towards
condensation

Water vapor
collects on
room particles



Non-equilibrium
(high) concentration
water vapor causes
it to condense on
surfaces (particles).

Boiling water
100 ° C

Sample Problem

At what temperature is the following reaction spontaneous at 1 atm?

$Br_2\ (l) \rightarrow Br_2\ (g)$

$\Delta H^o = 31.0$ kJ/mol

$\Delta S^o = 93.0$ J/K•mol

The Effect of Temperature

In the last vaporization example, we can discriminate three regimes:

T > 333 K. The ΔS^o term dominates, the gain in entropy drives the process.

T = 333 K. The ΔS^o and ΔH^o contribution balance each other. The two phases co-exist (equilibrium).

T < 333 K. The ΔH^o contribution dominates. The process is spontaneous in the direction in which it is exothermic.

The free energy takes both enthalpy and entropy driving forces into consideration.

The balance between the enthalpic and the entropic driving forces determines the spontaneity of a reaction.

Sample Problem

Calculate the change in entropy (ΔS^o) of reaction (J/K) for the equation as written at T = 298 K. ΔG_f° = 18.33 kJ/mol and ΔH_f° = 62.44 kJ/mol for $I_2(g)$; $I_2(s)$ is the standard state for iodine.

$$I_2(g) \rightarrow I_2(s)$$

Ice Melting

What if we deviate from the normal phase transition temperature?
Consider the process of melting of ice:

$H_2O(s) \rightarrow H_2O(l)$ $\quad \Delta H^o = +6.03$ kJ/mol

$\Delta S^o = +22.1$ J/K•mol

Let us calculate the free energy change at -10 °C, 0 °C and 10 °C:

T(K)	ΔH^o (J/mol)	ΔS^o(J/K•mol)	$T\Delta S^o$	ΔG^o J/mol	ΔS_{surr}	ΔS_{univ}
263	6.03×10^3	22.1	5.81×10^3	2.2×10^2	22.9	-0.8
273	6.03×10^3	22.1	6.03×10^3	0	–22.1	0
283	6.03×10^3	22.1	6.25×10^3	-2.2×10^2	–21.3	+0.8

Melting of ice is spontaneous at temperatures > 0 °C

When T > 0 °C, $T\Delta S$ is larger than ΔH^o making $\Delta G^o < 0$ and $\Delta S_{univ} > 0$