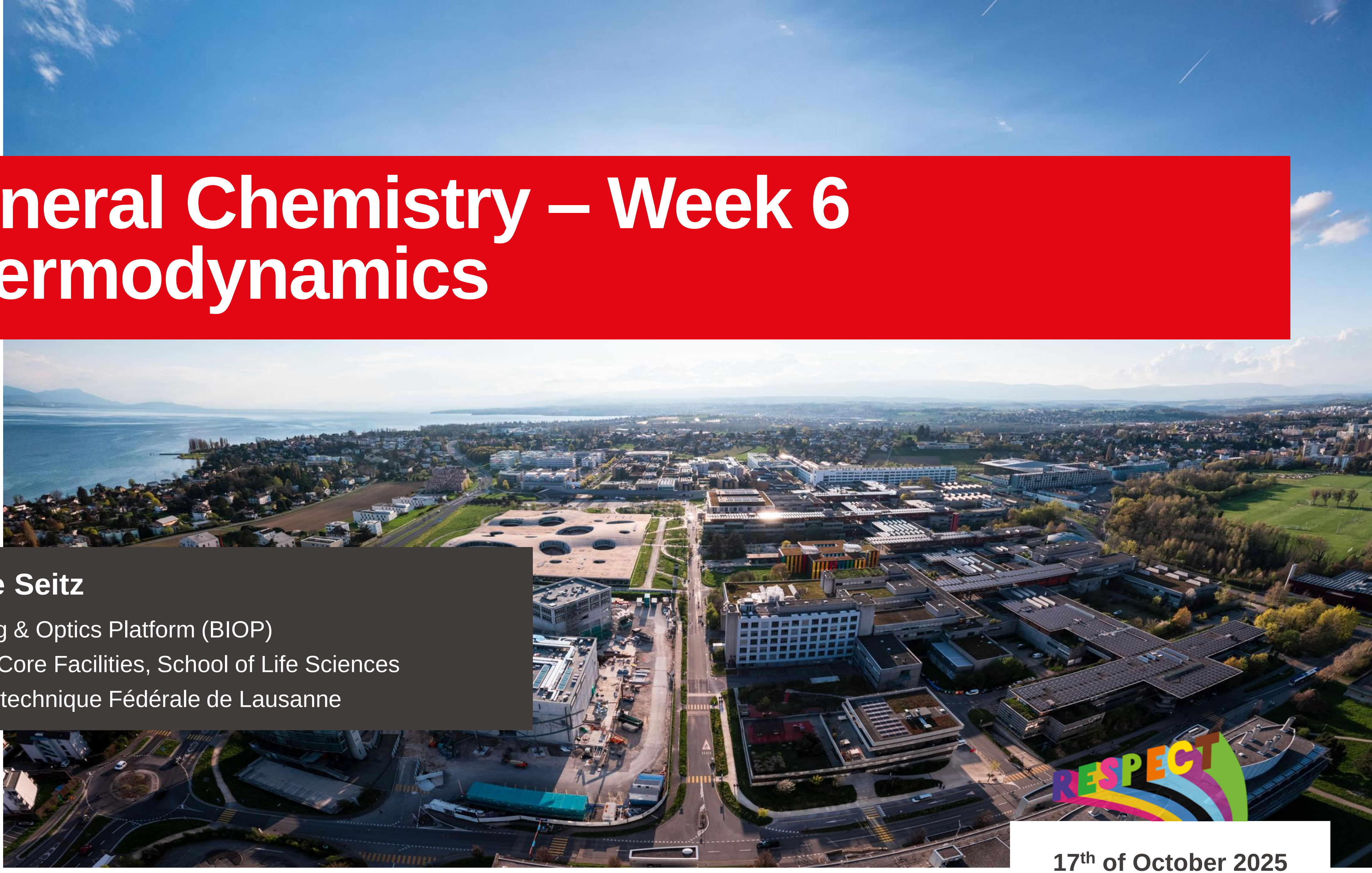

General Chemistry – Week 6
Thermodynamics

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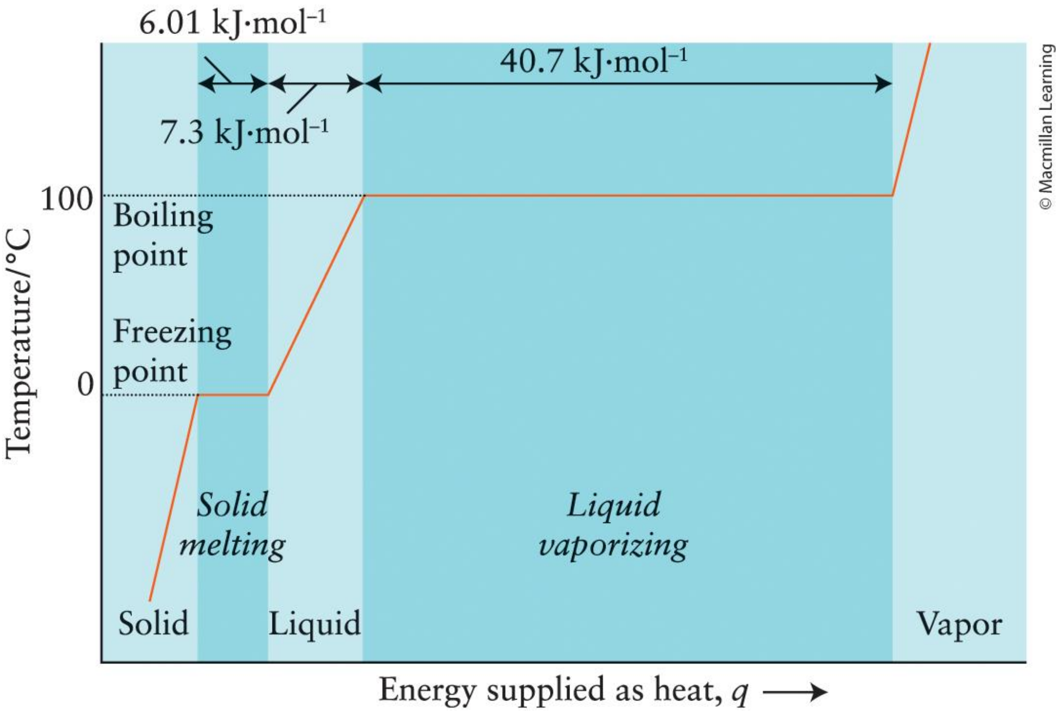
Recap last week

Heating Curves

- A heating curve shows the variation in the temperature of a heated sample.
- As a sample of ice is heated the temperature rises steadily.
- In a solid the molecules are still locked together as they oscillate vigorously around their mean positions.
- As the temperature rises, reaching the melting point, the molecules have enough energy to move past one another, overcoming the attractive forces between molecules.



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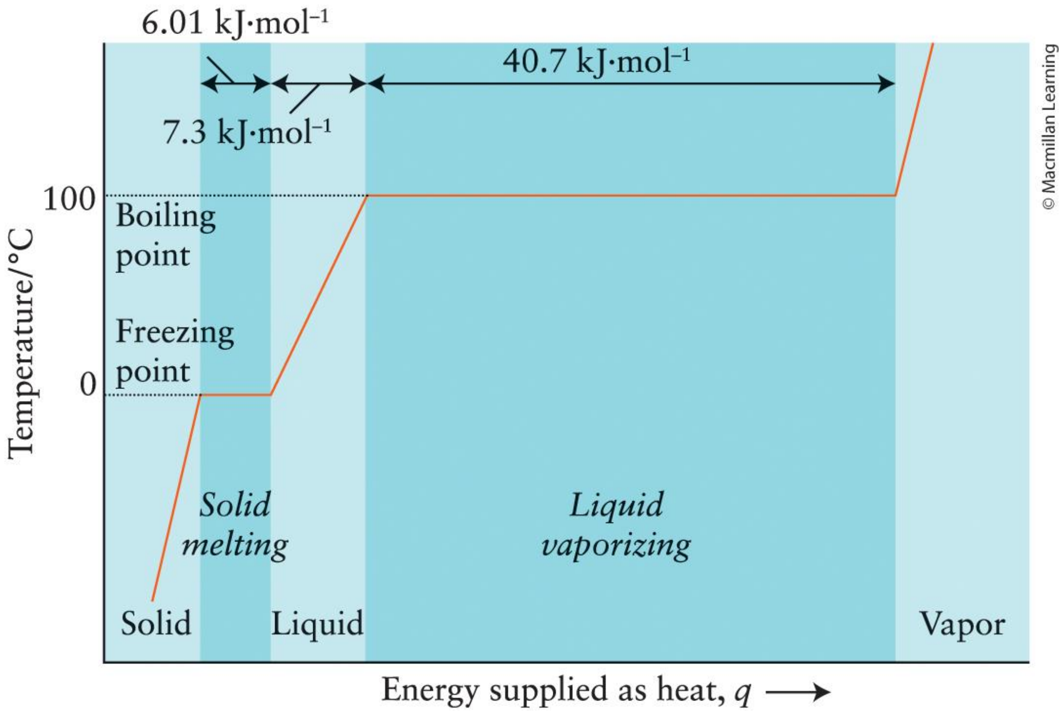
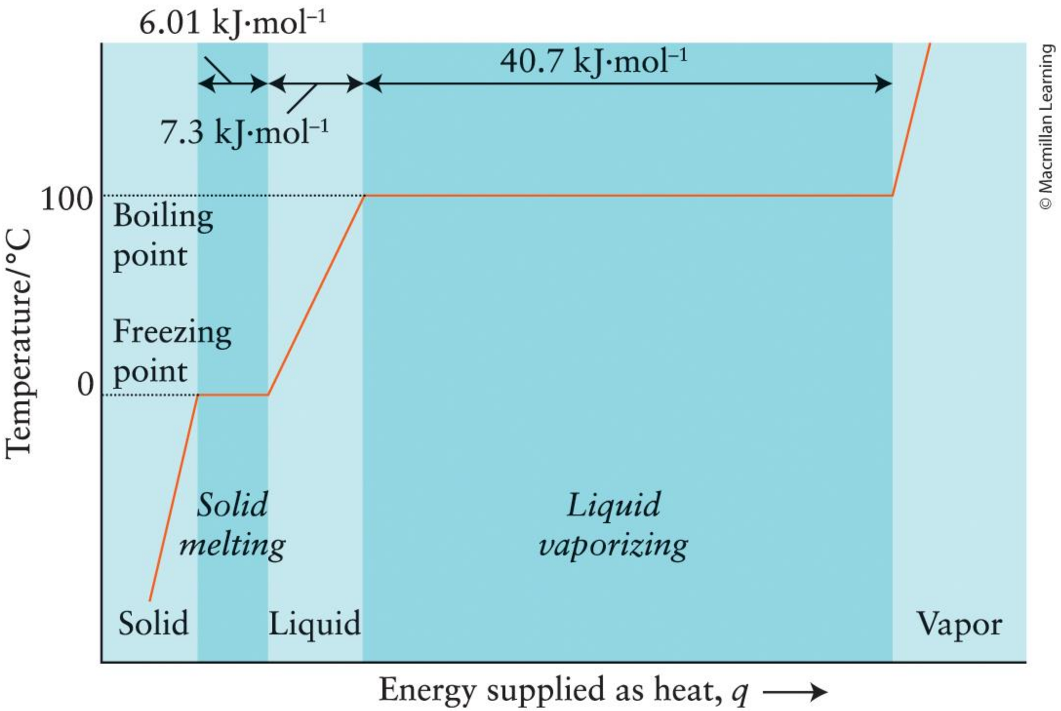
Heating Curves

- At this temperature, all the added energy is used to break all the attractive forces; the temperature remains constant at the melting point until all the ice has melted.
- Only then does the temperature rise again, and the rise continues right up to the boiling point.
- At the boiling point, the temperature rises again and comes to a halt.
- Now the water molecules have enough energy to escape into the vapor state, and all the heat supplied is used to form the vapor.



Heating Curves

- After the sample has evaporated and heating continues, the temperature of the vapor rises again.
- The steeper the slope, the lower the heat capacity. Both the solid and vapor phases have steeper slopes than liquid, so the liquid has a greater heat capacity.
- The liquid's high heat capacity is due largely to presence of intermolecular hydrogen bonds that can break and re-form as the molecules rotated. It requires more energy to break them.



Thermochemistry

- Enthalpy changes apply to chemical changes as well as physical processes.
- Thermochemistry is the branch of thermodynamics that deals with the heat absorbed or released during chemical reactions.

Reaction Enthalpy

- For example, the combustion (the complete reaction with oxygen) of methane releases 890. kJ of energy as heat.
- $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta H = -890.\ kJ$
- The equation for the combustion of methane is an example of a thermochemical equation, which consists of a chemical equation together with the state of the reaction enthalpy.
- The stoichiometric coefficients corresponding to an enthalpy change. For example, 1 mol CH_4 (g) and 890. kJ of heat.
- $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta H = -890.\ kJ$
- If the same reaction is multiplied by 2, then the change in enthalpy will be twice as great. $2\ CH_4(g) + 4\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(l)$ $\Delta H = -1780.\ kJ$
- For the reverse reaction, the change is enthalpy is the negative of the enthalpy of the forward process.
- $CO_2(g) + 2\ H_2O(l) \rightarrow CH_4(g) + 2\ O_2(g)$ $\Delta H = +890.\ kJ$

The Relation Between ΔH and ΔU

- We have measured heat with bomb calorimeter.
- At constant volume, the heat transfer is ΔU;

$$C_{V,\mathrm{m}} = \frac{\Delta U}{\Delta T}$$

- At constant pressure, it is ΔH; $C_{P,m} = C_{V,m} + R$
- However, it is sometimes necessary to convert the measured value of ΔU into ΔH.
- For example, it is easy to measure the heat released by the combustion of glucose in a bomb calorimeter, but to use that information in studying metabolism, which takes place at constant pressure, we need the enthalpy of reaction.

The Relation Between ΔH and ΔU

- For reactions in which no gas is generated or consumed, little expansion work is done—the difference between ΔH and ΔU is negligible, so we can set ΔH = ΔU.
- However, if a gas is formed in the reaction and expansion work is done, the difference can be significant.
- We can use the ideal gas law to relate the values of ΔH and ΔU for gases that behave ideally.

The Relation Between ΔH and ΔU

- The relation between ΔH and ΔU is $H = U + PV$, or $H = U + nRT$.

- We suppose initial amount of reactant gas is $n_{initial}$.
- $H_{initial} = U_{initial} + PV_{initial}$ or $= U_{initial} + n_{initial}RT$

- and after the reaction, the amount of ideal gas product molecules is nfinal.
- $H_{final} = U_{final} + PV_{final} = U_{final} + n_{final}RT$

- The difference is $\Delta H = H_{final} - H_{initial} = \Delta U + (n_{final} - n_{initial})RT$ or
- $\Delta H = \Delta U + \Delta n_{gas}RT$.

Standard Reaction Enthalpies

- Always specify the state of each substance: for methane,
  - $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g) \qquad \Delta H = -802.\ kJ$
  - $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \qquad \Delta H = -890.\ kJ$

- The difference between $H_2O(g)$ and $H_2O(l)$ is 88 kJ of energy so for transforming just one mole of $H_2O(g)$ to $H_2O(l)$, the ΔH_{vap} is 44.0 $kJ \cdot mol^{-1}$.

Standard Reaction Enthalpies

- Always specify the state of each substance: for methane,
  - $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$ $\Delta H = -802.$ kJ
  - $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta H = -890.$ kJ

- For the oxidation of methane to $H_2O(l)$ the $\Delta H° = -890.$ kJ. The heat output of 890. kJ indicates that 1 mol CH_4 (g) as pure methane gas at 1 bar is allowed to react with pure oxygen gas at 1 bar to produce 1 mol CO_2 (g) and 2 mol of H_2O (l) under standard state conditions.

- Standard state conditions exactly 1 bar at 298 K.

- The standard reaction enthalpy (also known as “standard enthalpy of reaction”), $\Delta H°$, is the reaction enthalpy when the reactants are in their standard states.

Enthalpy of Combustion

- The standard enthalpy of combustion, ΔHc°, is the change in enthalpy per mole of a substance that is burned in a combustion reaction under standard conditions.
- The specific enthalpy is the standard enthalpy of reaction divided by the mass of the sample and reported in kilojoules per gram.
- The enthalpy density is the enthalpy of reaction of a sample divided by the volume of the sample and is reported in kilojoules per liter.

The Heat Output of Reactions

Substance	Formula	$\Delta H_c°$/kJ·mol^{-1}	Specific enthalpy/kJ·g^{-1}
Hydrogen	$H_2(g)$	−286	142
Methane	$CH_4(g)$	−890	55
Ethanol	$CH_3CH_2OH(l)$	−1368	29.7
Propane	$CH_3CH_2CH_3(g)$	−2220	50.35
Glucose	$C_6H_{12}O_6(s)$	−2808	15.59
Benzene	$C_6H_6(l)$	−3268	41.8
Octane	$C_8H_8(l)$	−5471	48

- For example, the heat output from combusting 150. g of methane $CH_4 + 2\ O_2 \rightarrow 2\ H_2O + CO_2$: 1 mol CH_4 is chemically equivalent to 890. kJ.

$$\frac{890.\ \text{kJ}}{1\ \text{mol CH}_4} \times \frac{\text{mol CH}_4}{16.04\ \text{g CH}_4} \times \frac{150.\ \text{g}}{1} = 8.32\ \text{kJ}$$

Combining Reaction Enthalpies: Hess's Law

- Enthalpy is a state function; therefore, the value of ΔH is independent of the path between given initial and final states.

- When we calculated phase change, solid to a liquid or melting (fusion), we did it in two steps.
- $\Delta H_{fus} = H_m(\text{liquid}) - H_m(\text{solid})$

- The same rule applied to calculating heats of chemical reactions is known as Hess's law which states that the overall reaction enthalpy is the sum of the reaction enthalpies of each step.

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Combining Reaction Enthalpies: Hess's Law

- The oxidation of carbon as graphite, denoted C(gr), to carbon dioxide.
  $C(gr) + O_2(g) \rightarrow CO_2(g)$
- This can be thought of as two different steps.
- One step is the oxidation of carbon to carbon monoxide:
  $C(gr) + \frac{1}{2} O_2(g) \rightarrow CO(g) \qquad \Delta H^\circ = -110.5\ \text{kJ}$
- The second step is the oxidation of CO to CO_2.
  $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ = -283.0\ \text{kJ}$
- We can sum the previous two reactions to find our desired reaction.
  - $C(gr) + \frac{1}{2} O_2(g) \rightarrow CO(g) \qquad \Delta H^\circ = -110.5\ \text{kJ}$
  - $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ = -283.0\ \text{kJ}$
  - TOTAL: $C(gr) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ = -393.5\ \text{kJ}$

Combining Reaction Enthalpies: Hess's Law

- Hess’s law is a way to find unknown enthalpies.
  - Step 1: Select one of the reactants in the overall reaction and write down a chemical equation in which it also appears as a reactant.
  - Step 2: Select one of the products in the overall reaction and write down a chemical equation in which it also appears as a product. Add this equation to the equation from Step 1 and cancel species that appear on both sides of the equation.
  - Step 3: Cancel unwanted species in the sum obtained in Step 2 by adding an equation that has the same substance(s) on the opposite side of the arrow.
  - Step 4: Once the sequence is complete, combine the standard reaction enthalpies.
- Note: Reversing the equation, changes the sign of enthalpy.
- Note: If multiplying the stoichiometric coefficients by a factor, multiply the reaction enthalpy by the same factor.

Standard Enthalpies of Formation: $\Delta H_f°$

- It is impractical to list every standard reaction enthalpy.
- However, chemists have devised an ingenious alternative.
- First, they report the standard enthalpies of formation of substances per one mole.
- Then they combine these quantities to obtain the standard enthalpy of reaction needed.

Substance	**Formula**	**$\Delta H_f°/(\mathrm{kJ{\cdot}mol^{-1}})$**
Ammonia	$NH_3(g)$	−46.11
Nitrogen dioxide	$NO_2(g)$	+33.18
Water	$H_2O(l)$	−285.83
	$H_2O(g)$	−241.82

Standard state conditions C(gr), $H_2(g)$, $O_2(g)$ are all 0.

Standard Enthalpies of Formation: $\Delta H_f°$

- The standard enthalpy of formation, $\Delta H_f°$, is the change in enthalpy for forming the element or molecule in its standard state per one mole.

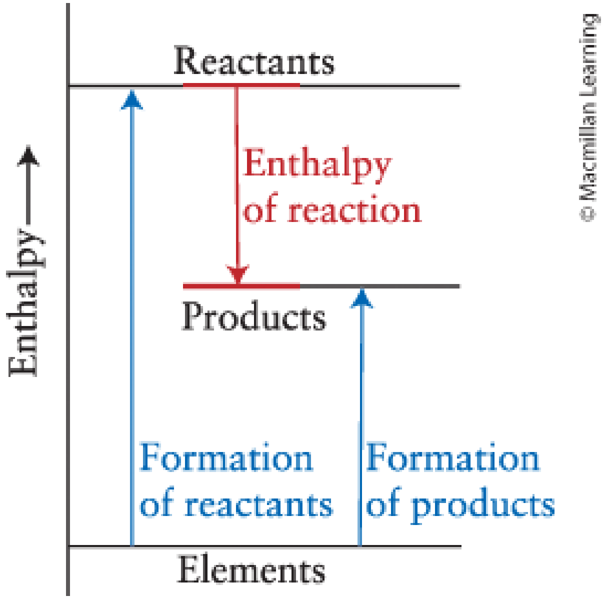
- “Standard state” means that the change occurred at exactly 1 bar at 298 K.

Standard Enthalpies of Formation: ΔHf°

- The standard enthalpy of formation, $\Delta H_f°$, of a substance is the standard reaction enthalpy per mole of formula units for the formation of a substance from its elements in their most stable form, as in the reaction.
- $2\ C(gr) + 3\ H_2(g) + ½\ O_2(g) \rightarrow C_2H_5OH(l) \qquad \Delta H° = -277.69\ kJ$
- Standard enthalpies of formation are expressed per one mole of molecules, as in $-277.69\ kJ\cdot mol^{-1}$, meaning that mole is unit.
- The standard enthalpy of forming 1 mol $C_2H_5OH(l)$ is −277.69 kJ, a ratio.

Combining Standard Enthalpies of Formation to Calculate a Standard Reaction Enthalpy

- First, calculate the reaction enthalpy for the formation of all products.
- Second, calculate the reaction enthalpy for all reactants.
- The difference between these two totals is the standard enthalpy of the reaction.



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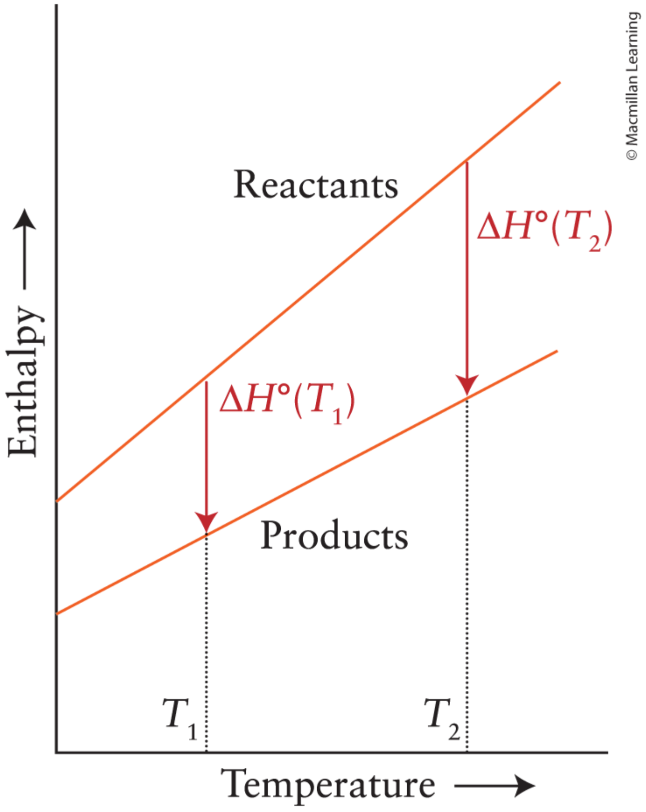
$$\Delta H° = \Sigma n\, \Delta H_f^{\circ}(\text{products}) - \Sigma n\, \Delta H_f^{\circ}(\text{reactants})$$

Reaction Enthalpy and Temperature

- Suppose we know the reaction enthalpy for one temperature but require it for another temperature.
- For instance, the temperature of the human body is about 37 °C, but the data givrn are for 25 °C.
- Does an increase of 12 °C make much difference to the reaction enthalpy of a metabolic process?

Reaction Enthalpy and Temperature



- The enthalpies of both reactants and products increase with temperature.
- The increase in enthalpy depends on its heat capacity at constant pressure, and it is easy to deduce using Kirchhoff's law.

$$\Delta C_P = \Sigma n \Delta C_{P,\mathrm{m}}(\text{products}) - \Sigma n \Delta C_{P,\mathrm{m}}(\text{reactants})$$

- $\Delta H°\ (T_2) = \Delta H°\ (T_1) + (T_2 - T_1)\ \Delta C_P$

Bond Enthalpies, ΔHB

- In chemical reactions, old bonds break and new ones form.
- Bond strengths are measured with bond enthalpies, ΔHB.
- Changes in standard molar enthalpies of a product and reactant for H_2: H_2 (g) → 2H (g) ΔH° = +436 kJ

- We write ΔHB (H-H) 436 kJ·mol^{-1} to report this value and conclude that 436 kJ of heat is needed to dissociate 1 mol H_2(g) into atoms.

- Positive enthalpies mean heat is supplied to break a bond; bond breaking is always endothermic and bond formation is always exothermic.

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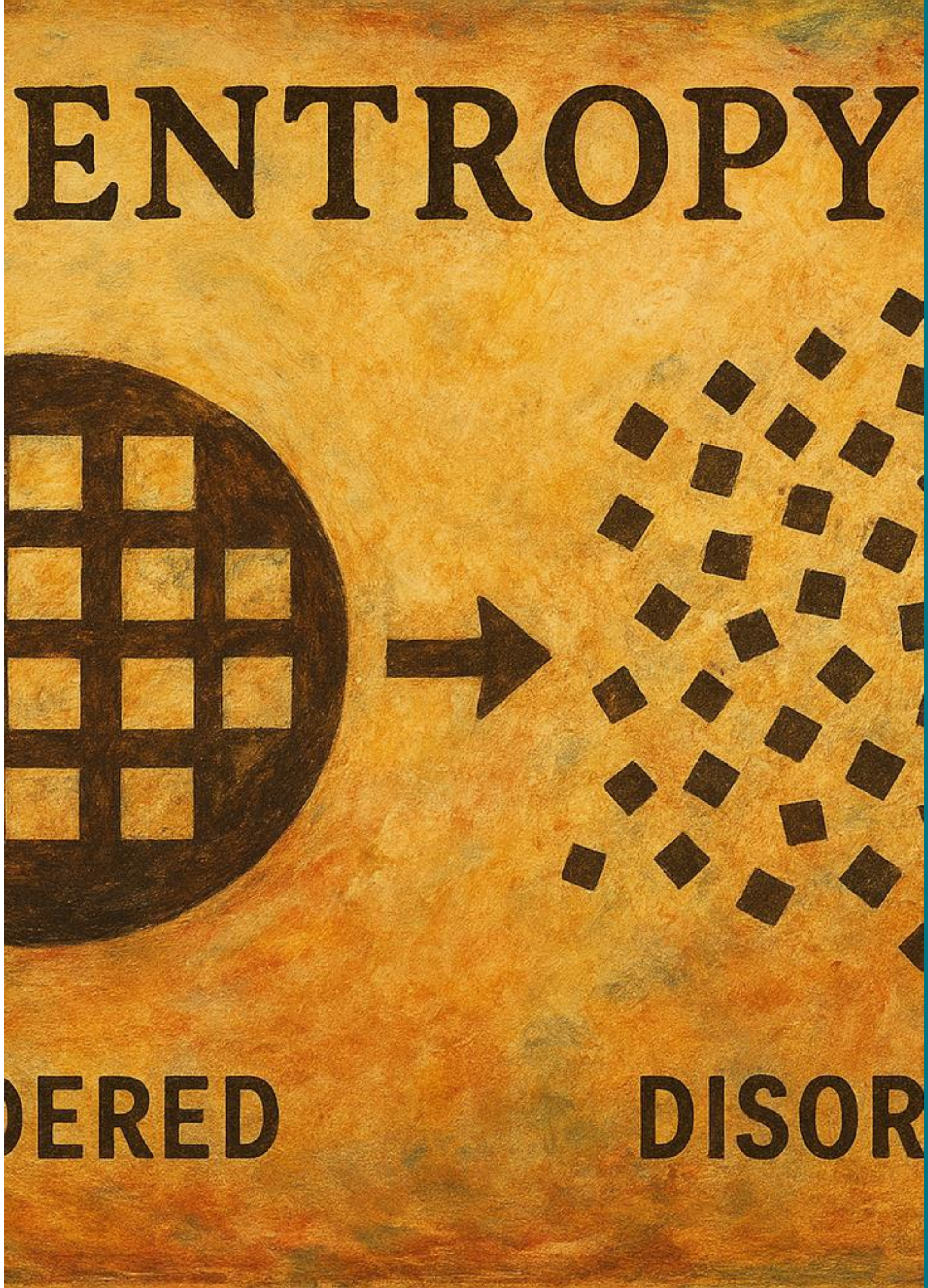

Beyond the First Law of Thermodynamics

- The first law of thermodynamics implies that if a reaction takes place, the total energy of the universe remains unchanged.

- But the first law does not address the questions that lie behind the "if."
- Why do some reactions have a tendency to occur?
- Why does a reaction even happen?

Spontaneous Change

- A spontaneous change is a change that has a tendency to occur without needing to be driven by doing work. A spontaneous change does not have to be fast.
- Molasses has a spontaneous tendency to flow, but at low temperatures, that flow may be very slow.
- A mixture of hydrogen and oxygen tends to react spontaneously but can be kept safely for centuries, provided it is not ignited with a spark.

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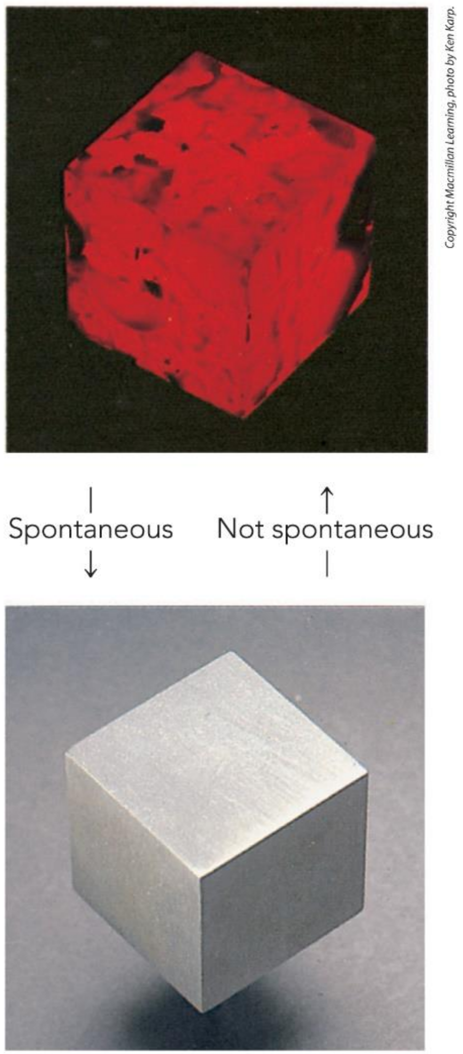
Spontaneous Change

- If no external influence drives a change (no work done on the system) the change is spontaneous.

- For example, the red hot block (top) cools spontaneously to the temperature of its surroundings, the cooler air around it (bottom). The reverse process, in which a cooler block becomes hotter spontaneously, does not occur.



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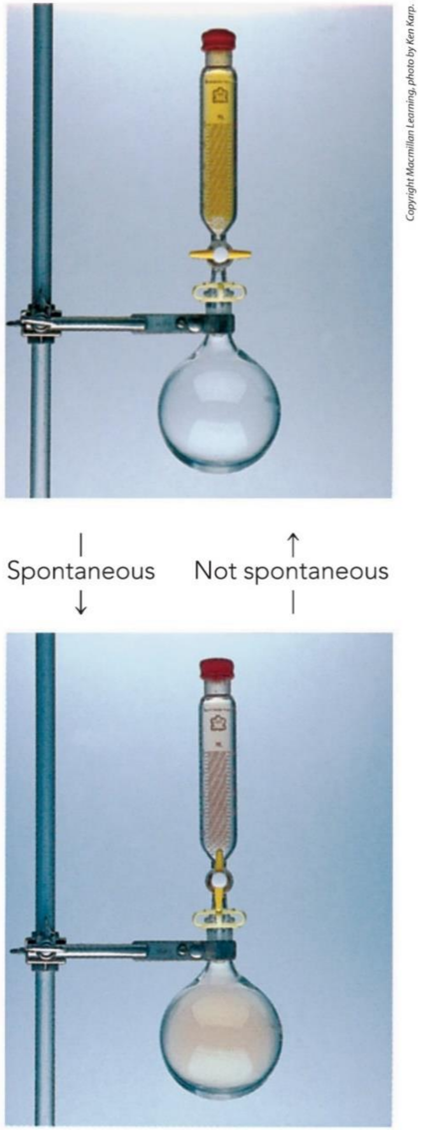
Spontaneous Change

- A spontaneous change occurs naturally without external influences.

- For example, the gas expands spontaneously into the lower evacuated flask. However, the reverse process does not occur spontaneously.



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Nonspontaneous Change

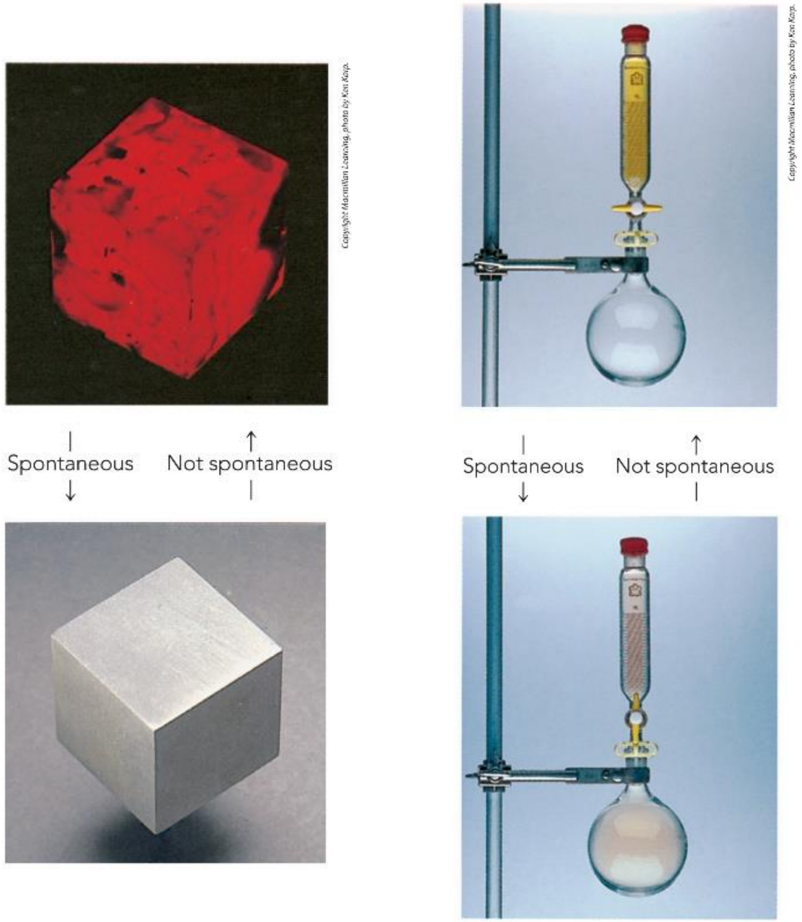
- Changes can be made to happen in an "unnatural" direction.
- We can force an electric current through a block of metal to heat it to a higher temperature.
- We can drive a gas into a smaller volume by pushing it with a piston.
- These are examples of a nonspontaneous change: we have to force them to happen; a nonspontaneous change is done with work.

The Second Law of Thermodynamics

- Entropy, S, is a measure of disorder. Low entropy means little disorder, whereas high entropy means great disorder.
- In an isolated system, the entropy increases in the course of any spontaneous change.
- The second law of thermodynamics states that the entropy of an isolated system increases in the course of any spontaneous change.
- The second law of thermodynamics is the tendency for chemical reactions to occur.

Entropy Examples

- As metal cools, entropy increases as energy spreads into the surroundings.
- As gases expand, entropy increases as the molecules spread through the container.
- Energy and matter disperse.



A Quantitative Picture of Entropy and Disorder

- The natural progression of a system and its surroundings is from order to disorder, from lower to higher entropy.
- To quantify entropy, we take a thermally insulated, sealed flask or a calorimeter to measure and make precise predictions about disorder.
- An entropy change in a system is calculated as

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

- where q is energy transferred, “rev” means energy must be transferred reversibly, infinitesimal change, T is the absolute temperature, and typical units for entropy are $\mathrm{J \cdot K^{-1}}$.

A Quantitative Picture of Entropy and Disorder

- Interpret $\Delta S = q_{rev}/T$:
- If a lot of energy is transferred as heat (large q_{rev}), there is a large increase in entropy.
- From the equation, the lower the temperature, T, the greater the change in ΔS. For example, sneezing in a quiet library will attract attention but sneezing in a noisy street may pass unnoticed.

Entropy is a State Function

- Changes in entropy of a system are independent of the path between its initial and final states so for a reversible process we use $\Delta S = qrev/T$.

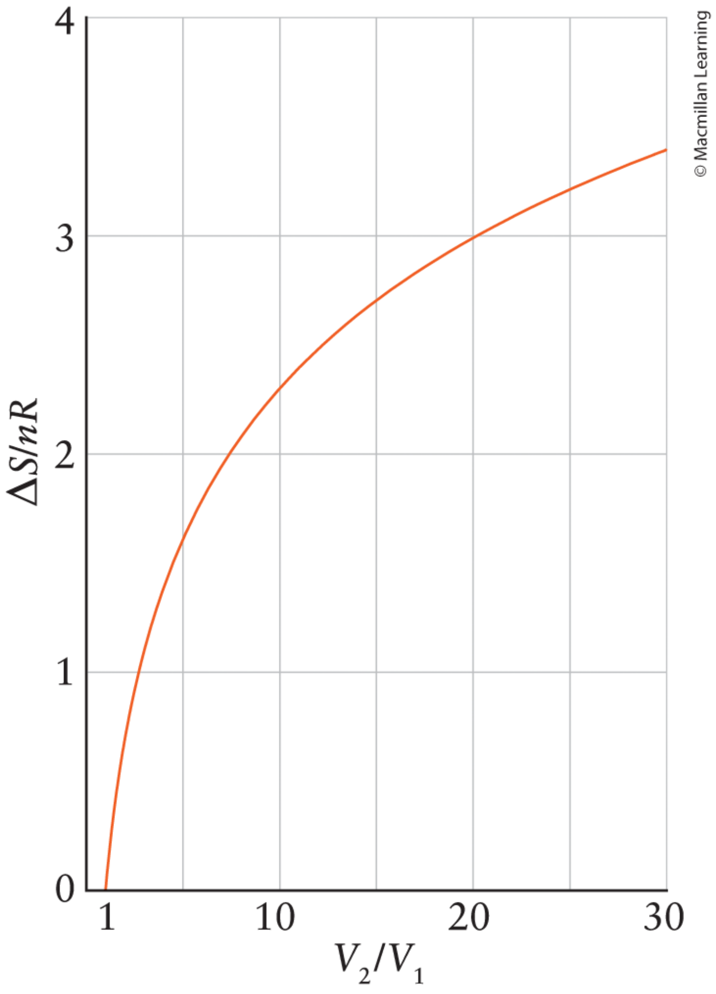
Other ***state functions*** (determined by knowing Final–Initial)

Mass (m)
Internal energy (U)
Helmholtz free energy (F)
Entropy (S)
Temperature (T)
Chemical composition
Density (ρ)

Enthalpy (H)
Gibbs free energy (G)
Exergy (B)
Pressure (P)
Volume (V)
Specific volume (v)
Altitude

Entropy with Changes in Volume

- The entropy of an ideal gas with changes in volume is an isothermal (temperature remains constant) expansion (reversible) at constant T. So, we begin with $\Delta S = q_{rev}/T$.



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Entropy with Changes in Volume

- For a reversible expansion with $q_{rev} = -w_{rev}$:

$$w_{rev} = -nRT \ln\frac{V_2}{V_1}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{-w_{rev}}{T} = \frac{nRT \ln\frac{V_2}{V_1}}{T} = nR \ln\frac{V_2}{V_1}$$

$$\Delta S = nR \ln\frac{V_2}{V_1}$$

Entropy and Physical State

- Phase changes occur at constant temperature.
- In order to use $\Delta S = q_{rev}T$ to calculate the entropy change for a substance going through a phase change at its transition temperature, note these three facts:
  - the temperature remains constant as heat is added;
  - the heat transfer is reversible;
  - all at constant pressure meaning that the heat supplied is equal to the change in enthalpy of the substance.
- Therefore, q_{rev} in $\Delta S = q_{rev}T$ can be replaced by ΔH for the phase change.

Entropy of Vaporization

- The entropy of vaporization, ΔS_{vap}, is the change in entropy per mole of molecules when a substance changes from a liquid to a vapor.

$$\Delta S_{\mathrm{vap}} = \frac{\Delta H_{\mathrm{vap}}}{T_{\mathrm{b}}}$$

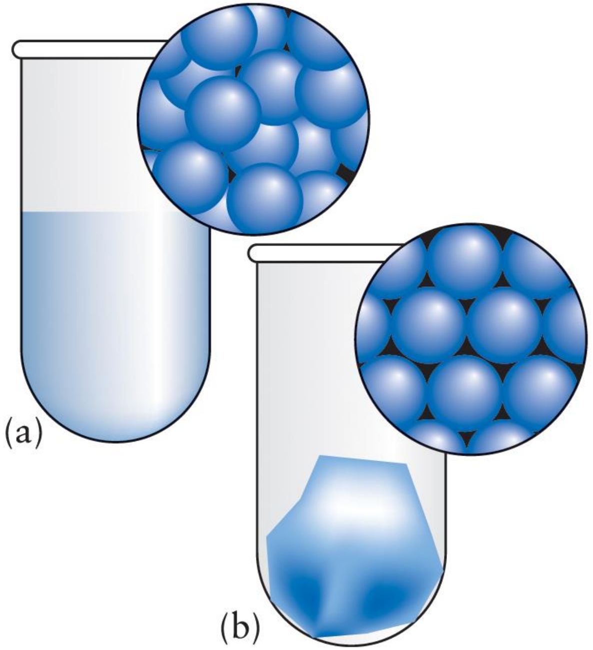
- where Tb is the boiling point

- The standard entropy of vaporization, ΔS°vap, is calculated similarly, but when the liquid and vapor are in their standard states (1 bar) and the boiling point is also at 1 bar.

Entropy of Fusion Change

- We can apply similar arguments used for vaporization and apply them to fusion (melting or freezing).

$$\Delta S_{\text{fus}}{}^{\circ} = \frac{\Delta H_{\text{fus}}{}^{\circ}}{T_{\text{f}}}$$



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The Boltzmann Formula

- Austrian physicist Ludwig Boltzmann (1877) proposed a molecular definition of entropy.

- The Boltzmann formula is $S = k \ln W$.

- where k is Boltzmann’s constant which is equal to 1.381 × 10−23 J·K−1, and W is the number of positions atoms or molecules can arrange into, known as microstates.

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The Boltzmann Formula

- W is the number of different microstates that correspond to the same energy.
- The entropy, S, calculated in Boltzmann’s formula is known as statistical entropy.
- Boltzmann was developing ideas based on atoms and molecules even before atoms were known to exist.

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A Molecular Interpretation of Entropy

- We’ve only calculated changes in entropy: $\Delta S = q_{rev}/T$.
- What exactly is entropy measuring the disorder of?
- Here we imagine entropy from an atomic view as a perfectly orderly state of matter with neither positional nor thermal disorder.
- This is a state where entropy is zero, a state of perfect order.
- This is the absolute scale of entropy, just as Kelvin is the absolute scale of temperature. This is the third law of thermodynamics.

The Third Law of Thermodynamics

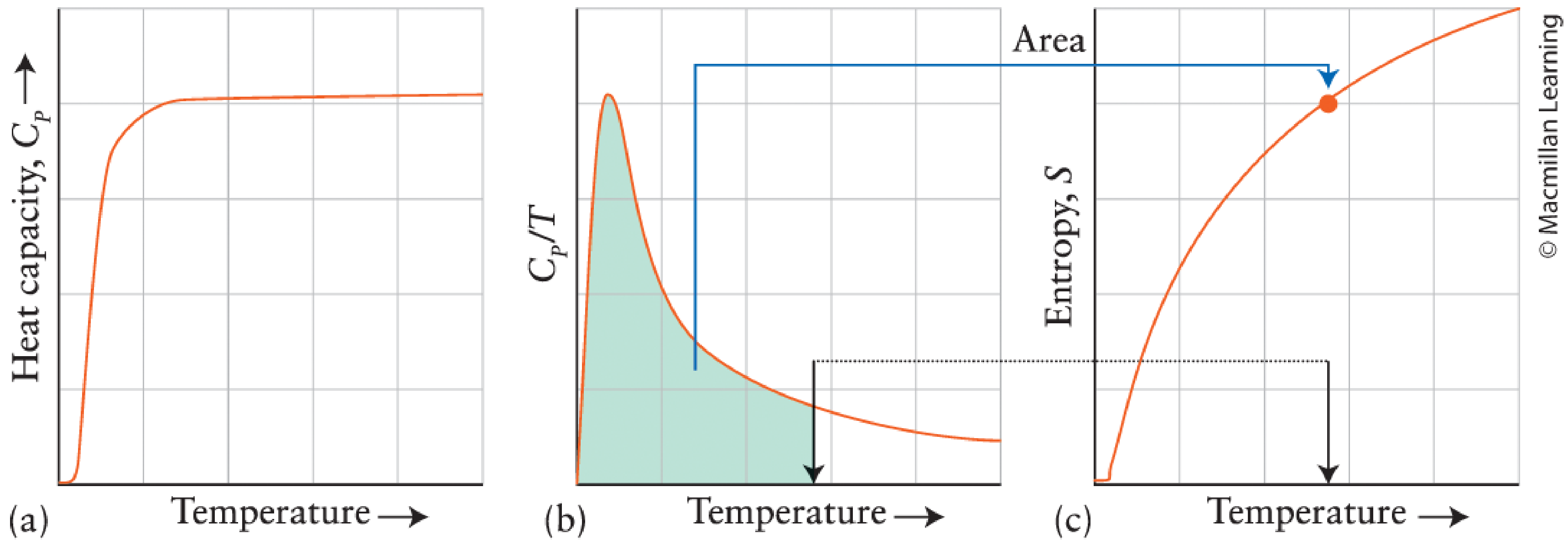
- The third law of thermodynamics states that the entropies of all perfect crystals approach zero as the absolute temperature approaches zero.
- In a perfect crystal, $S \rightarrow 0$ as $T \rightarrow 0$, implying a perfect orderly array, and so no positional disorder.
- We expect the entropy of any substance to be greater than zero above $T = 0$.

Standard Molar Entropies

- Boltzmann's formula is sometimes very difficult to implement (figuring out the different microstates) and requires a lot of manipulation.

- It's easier to combine our idea of the third law where S = 0 at 0 K and then compare S at a later temperature using heat capacities.

Finding Entropy Values for Calculations



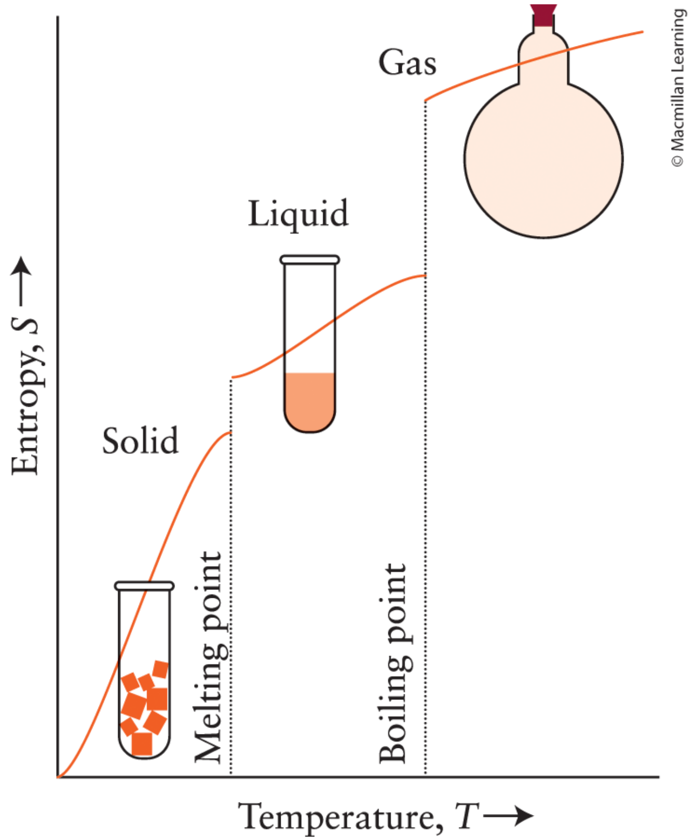
(a) The heat capacity is determined from close to absolute zero up to the temperature of interest.

(b) The area under the plot of CP/T against T is determined up to the temperature of interest.

(c) This area is the entropy of the substance at that temperature.

Finding Entropy Values for Calculations

- To measure the entropy of a substance at any temperature, we use the relationship
- S(T) = area under the plot of C_P/T against T from 0 to the temperature of interest
- If a phase transition takes place between T = 0 and the temperature of interest, then the corresponding entropy of transition must be added by using the equation $\Delta S_{fus} = \Delta H_{fus}/T_f$ with similar contributions from other transitions.



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Standard Molar Entropies: $S_m°$

Standard Molar Entropies at 25 °C

Gases	$S_m°/(J{\cdot}K^{-1}{\cdot}mol^{-1})$	**Liquids**	$S_m°/(J{\cdot}K^{-1}{\cdot}mol^{-1})$	**Solids**	$S_m°/(J{\cdot}K^{-1}{\cdot}mol^{-1})$
ammonia, NH_3	192.4	benzene, C_6H_6	173.3	calcium oxide, CaO	39.8
carbon dioxide, CO_2	213.7	ethanol, C_2H_5OH	160.7	calcium carbonate, $CaCO_3$	92.9
hydrogen, H_2	130.7	water, H_2O	69.9	diamond, C	2.4
nitrogen, N_2	191.6			graphite, C	5.7
oxygen, O_2	205.1			lead, Pb	64.8

- Gases have the most freedom (more W’s). Liquids have a greater freedom of movement than solids.
- More complex molecules have a greater freedom of movement.

Standard Molar Entropies: $S_m°$

Standard Molar Entropies at 25 °C

Gases	**$S_m°/(J·K^{-1}·mol^{-1})$**	**Liquids**	**$S_m°/(J·K^{-1}·mol^{-1})$**	**Solids**	**$S_m°/(J·K^{-1}·mol^{-1})$**
ammonia, NH_3	192.4	benzene, C_6H_6	173.3	calcium oxide, CaO	39.8
carbon dioxide, CO_2	213.7	ethanol, C_2H_5OH	160.7	calcium carbonate, $CaCO_3$	92.9
hydrogen, H_2	130.7	water, H_2O	69.9	diamond, C	2.4
nitrogen, N_2	191.6			graphite, C	5.7
oxygen, O_2	205.1			lead, Pb	64.8

- Polar molecules have lower entropy values.
- Heavier molecules have greater entropy values.

Standard Reaction Entropies: Changes to the System

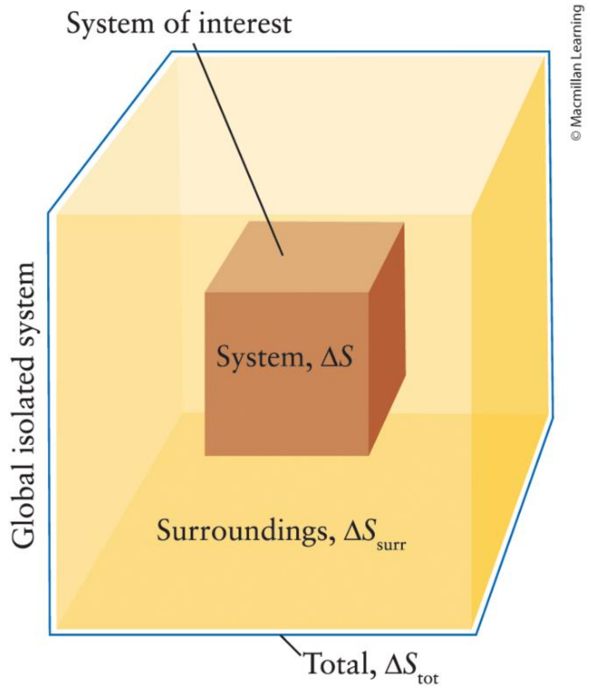
- It is possible to predict the sign of the entropy change of the system?
- We know a gas has a greater entropy value than either solids or liquids.
- A change in the amount of gas molecules normally dominates any other entropy change in a reaction.

Global Changes in Entropy

- Some processes seem to defy the second law.
- Cold packs spontaneously become ice cold.
- Highly organized, complex organisms form from slime, mud, or gas.
- The dilemma is resolved when we realize that the second law refers to an isolated system that includes the surroundings of the system.
- A process is spontaneous only if the total change in entropy, the sum of the changes in the system and the surroundings, is positive.

Global Changes in Entropy

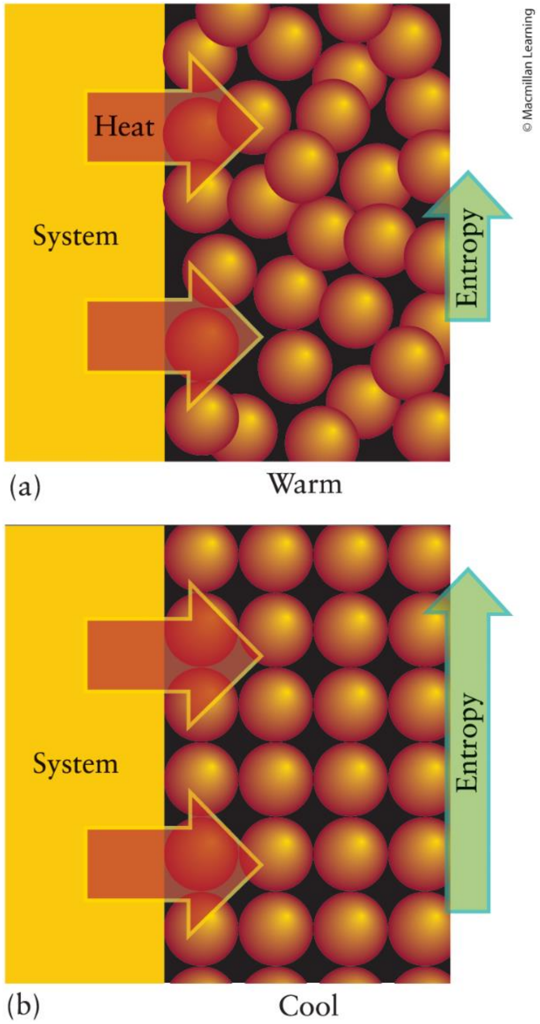
- The 2 parts to total entropy, ΔS_{tot}, are the system and the surroundings.
- $\Delta S_{tot} = \Delta S$ (system) + ΔS (surroundings)
- Missing from our previous discussion was the effect our system had on the surroundings.



Global Changes in Entropy: Effect of the Surroundings

- At low temperatures, T, there is a greater effect on ΔS.

- In (a) a more chaotic system, adding or removing heat has less of an effect than in (b) a less chaotic system.



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Global Changes in Entropy: Surroundings

- Freezing liquid water into a solid is not a favorable process.

- H2O (l) → H2O (s)
- 65.2 $J \cdot K^{-1} \cdot mol^{-1}$ 43.2 $J \cdot K^{-1} \cdot mol^{-1}$
- $\Delta S° = \Sigma n S_m° \text{ (products)} - \Sigma n S_m° \text{ (reactants)}$
  - $\Delta S° = -22.0\ J \cdot K^{-1} \cdot mol^{-1}$ (unfavorable)
- This is answered fully when we interpret ΔS_{tot} to include

$$\Delta S_{surr} = -\frac{q}{T} = -\frac{\Delta H}{T}$$

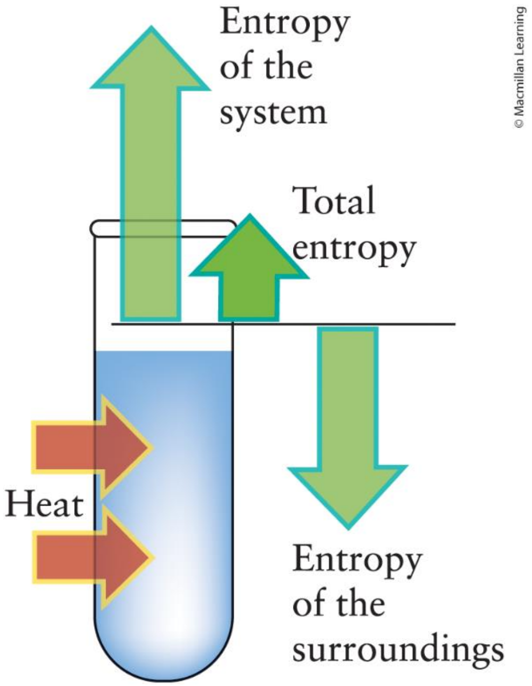
The Overall Change in Entropy

- ΔS_{tot} is a combination of both the system and surroundings: $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$
- If ΔS_{tot} is positive (an increase), the process is spontaneous.
- If ΔS_{tot} is negative (a decrease), the reverse process is spontaneous.
- If $\Delta S_{tot} = 0$, the process has no tendency to proceed in either direction (phase changes are the most common examples of when ΔStot = 0).

Spontaneous Endothermic Reactions

- Spontaneous endothermic reactions were a puzzle for nineteenth-century chemists, who believed reactions ran only if the energy of the system decreased; that is, if reactions were driven by heat leaving the system.
- As just seen, endothermic reactions are sometimes driven by the dominating increase in disorder of the system.

- $\Delta S_{tot} = \Delta S$ (system) $+ \Delta S$ (surroundings)
- $\Delta S_{surr} = -\Delta H/T$



The Clausius Inequality

- A process produces maximum work if it takes place reversibly. In other words, w_{rev} is more negative than w_{irrev}. However, since internal energy is a state function, ΔU is the same for any path between two states. Therefore, because $\Delta U = q + w$, it follows that $q_{rev} > q_{irrev}$. If q_{rev} in the definition of entropy $\Delta S = q_{rev}/T$ is replaced by the smaller quantity q_{irrev}, then $\Delta S > q_{irrev}/T$. This leads to the Clausius inequality:

$$\Delta S \geq \frac{q}{T}$$

- In an isolated system $q = 0$, so $\Delta S \geq 0$, meaning the entropy cannot decrease in an isolated system:
- $\Delta S \geq 0$ for any isolated system
- In other words, the total entropy of the universe is steadily increasing.

A Fundamental Difference Between ΔS_{sys} and ΔS_{surr}

- A reversible and irreversible path between two given states of the system leaves the surroundings in different states.
- ΔS_{sys} is a state function so it only depends on the difference between the final and initial states.
- ΔS_{surr} is not a state function. That is because work can be calculated as either w_{rev} or w_{irrev}, so

$$\Delta S \geq \frac{q}{T}$$

- is different for different processes.

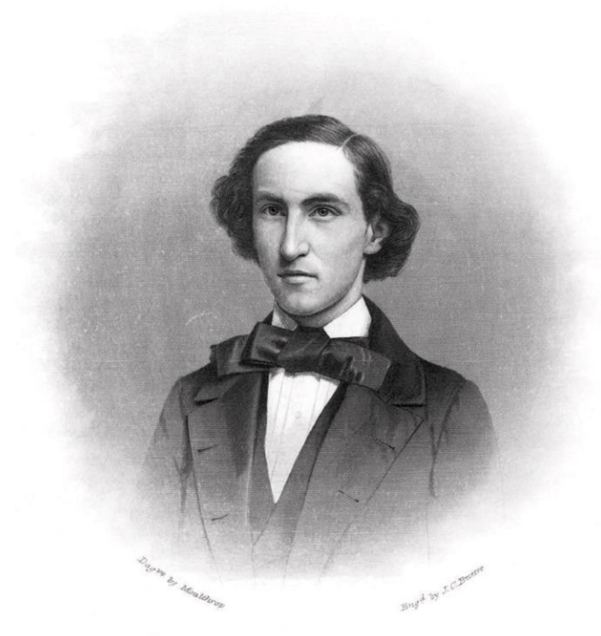
Gibbs Free Energy

- On challenge when using the second law of thermodynamics to indicate spontaneity of a reaction is that the entropies of the system and surroundings must be known.

- Gibbs free energy removes this challenge by expressing the combined entropy change of the system and surroundings as a single property of the system

Gibbs Free Energy

- The total entropy is equal to $\Delta S_{tot} = \Delta S + \Delta S_{surr}$. For a process at constant T and P, the change in entropy of the surroundings is equal to $\Delta S_{surr} = -\Delta H/T$. Therefore, combining these equations, we get $\Delta S_{tot} = \Delta S - \Delta H/T$. The total entropy change can then be calculated from information about only the system.
  - $\Delta S_{tot} = \Delta S - \Delta H/T$
  - $T\Delta S_{tot} = T\Delta S - \Delta H$
  - $-T\Delta S_{tot} = \Delta H - T\Delta S$
- $-T\Delta S_{tot} = \Delta G$ at constant temperature and pressure so the equation becomes
- $\Delta G = \Delta H – T\Delta S$



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Gibbs Free Energy

- Using Gibbs free energy formula, $\Delta G = \Delta H - T\Delta S$, to find spontaneity, we use the following criteria.

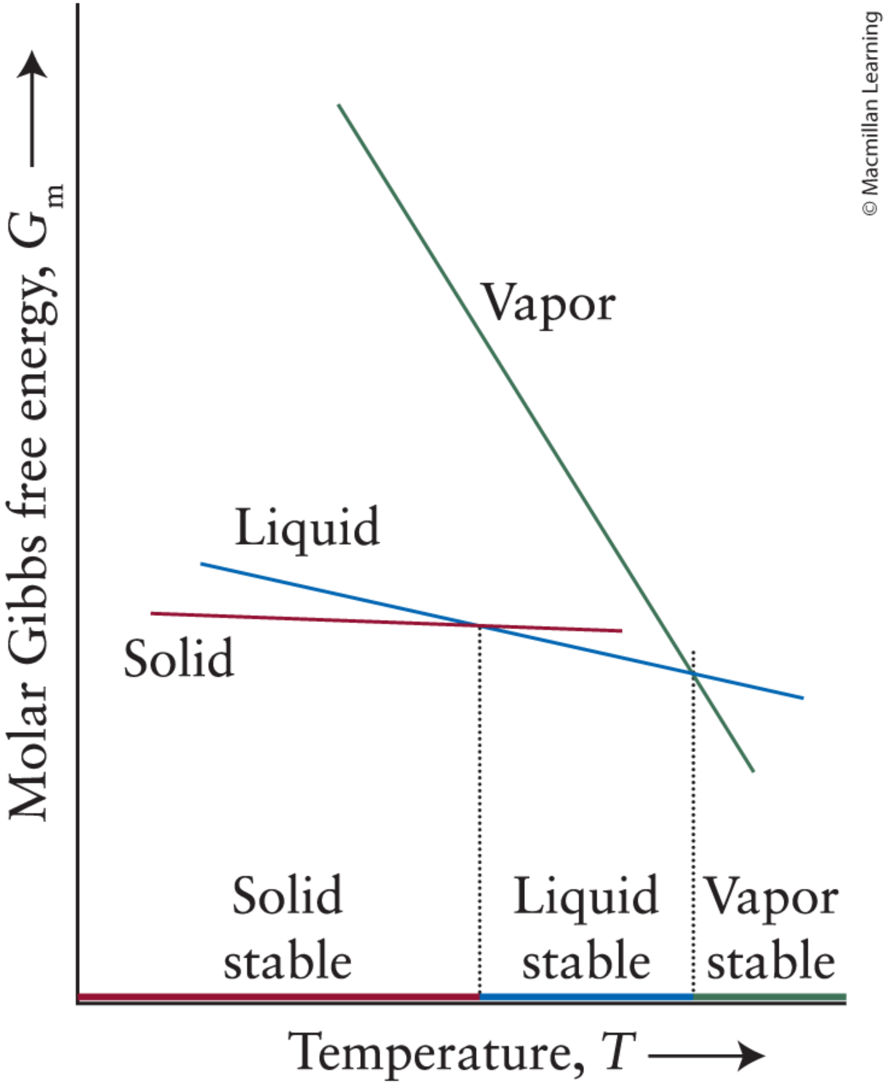
  Note when ΔG is large and negative, the process is spontaneous.

The Temperature Range of Spontaneity

ΔH	ΔS	**When spontaneous?**
−	−	at low T
+	+	at high T
+	−	not at any T
−	+	at all T

More Gibbs Free Energy

- Gibbs free energy decreases as the temperature is raised at constant pressure.
- As T increases, TS increases, too, and a larger quantity is subtracted from H, making unfavorably G positive.
- Gibbs free energy decreases more sharply with temperature for gases than for liquids.



Gibbs Free Energy of Reaction

- Our principal interest in chemistry is to calculate ΔG for a reaction.

- Gibbs free energy of reaction, ΔG, is commonly referred to as the “reaction free energy.”

- $\Delta G = \Sigma n G_m$ (products) − $\Sigma n G_m$ (reactants)

- Σ = sum of
- n = stoichiometric coefficients, moles
- Gm = molar Gibbs free energy

Gibbs Free Energy of Reaction

- For standard conditions of a chemical reaction, $\Delta G°$
- $\Delta G° = \Sigma nG_m°\text{ (products)} - \Sigma nG_m°\text{ (reactants)}$
- Standard Gibbs free energy of reaction, $\Delta G°$, is like the Gibbs free energy of a reaction, but it is in terms of the standard molar Gibbs energies of the reactants and products.
- The standard Gibbs free energy of formation, $\Delta G_f°$, is the standard free energy of reaction per mole for the formation of a compound from its elements in their most stable form at 1 bar, 298 K (25 °C) per mol.

Gibbs Free Energy: Constants

Standard Gibbs Free Energies of Formation at 25 °C

Gases	**$\Delta G_f°/(\text{kJ·mol}^{-1})$**	**Liquids**	**$\Delta G_f°/(\text{kJ·mol}^{-1})$**	**Solids**	**$\Delta G_f°/(\text{kJ·mol}^{-1})$**
NH_3	–16.45	benzene, C_6H_6	+124.3	$CaCO_3$	–1128.8
CO_2	–394.4	ethanol, C_2H_5OH	–174.8	AgCl	–109.8
NO_2	+51.3	H_2O	–237.1		
H_2O	–228.6				

- The standard Gibbs free energy of formation of hydrogen iodide gas at 25°C is $\Delta G_f°(\text{HI, g}) = +\ 1.70\ \text{kJ·mol}^{-1}$. It is the standard Gibbs free energy of reaction for $\frac{1}{2}\ H_2(g) + \frac{1}{2}\ I_2(s) \rightarrow HI(g)$.

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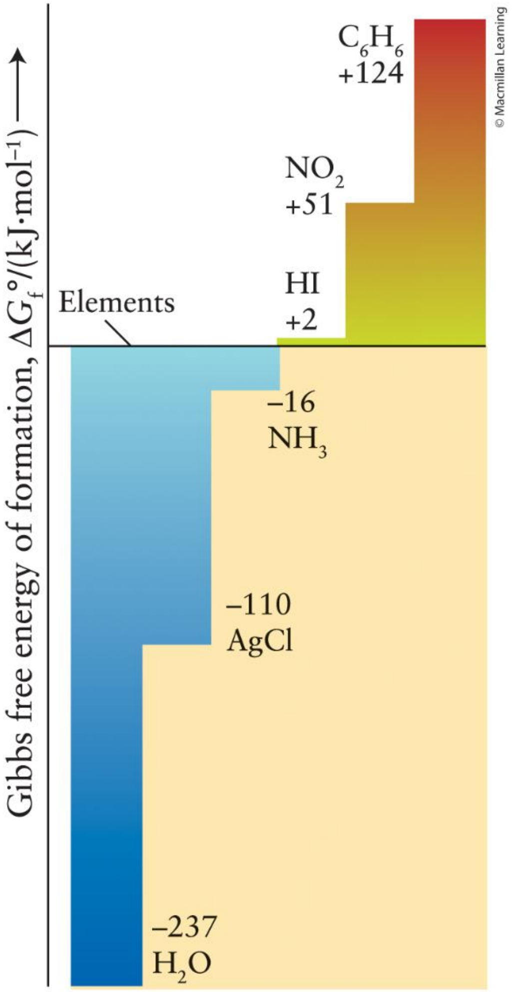
Thermodynamically Stable vs. Unstable Compounds

- Standard Gibbs free energy of formation is an indication of a compound's stability.
- If $\Delta G_f°$ < 0, then elements are poised to change spontaneously into the compound. They are thermodynamically stable compounds.
- If $\Delta G_f°$ > 0, then the reverse is true; the compound is poised to change spontaneously into the pure elements. They are thermodynamically unstable compounds.
- The $\Delta G_f°$ for benzene is +124 kJ·mol^{-1} at 25 °C, so benzene is unstable and is poised to decompose spontaneously into its elements.



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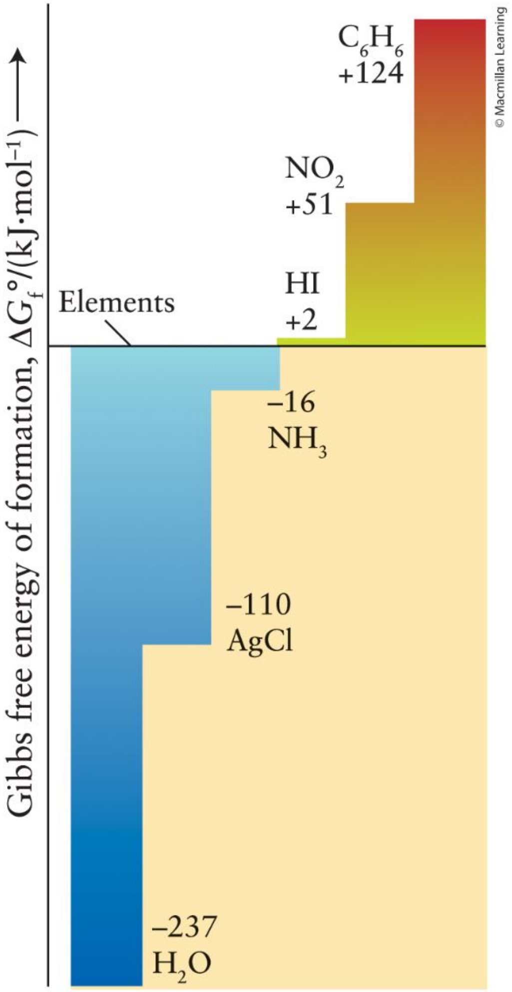
Labile, Nonlabile, and Inert Compounds

- That tendency may not be realized because the decomposition may be very slow. Benzene can, in fact, be kept indefinitely without decomposing at all.
- Substances that are thermodynamically unstable but survive for long periods are called nonlabile. So benzene is thermodynamically unstable but nonlabile.
- Substances that decompose or react rapidly are called labile. Most radicals are labile.



Gibbs Free Energy and Nonexpansion Work

- We are now ready to see why the Gibbs free energy is called free energy.
- Gibbs free energy is a measure of the energy free to do nonexpansion work.
- Nonexpansion work is any kind of work other than expansion against an opposing pressure.

Gibbs Free Energy and Nonexpansion Work

- Nonexpansion work includes electrical work and mechanical work (like stretching a spring or carrying a weight up a slope).
- Electrical work—the work of pushing electrons through an electrical circuit—is the basis of generating chemical electrical power.
- Nonexpansion work also includes the work of muscular activity, the work of linking amino acids together to form protein molecules, and the work of sending nerve signals through neurons, key ideas in bioenergetics.

Gibbs Free Energy and Nonexpansion Work

- To find the relationship between the Gibbs free energy and the maximum nonexpansion work, begin with the equation $\Delta G = \Delta H - T\Delta S$ for an infinitesimal change (denoted "d") in G at constant temperature:

- $dG = dH - TdS$ at constant temperature

- Then, take the equation $H = U + PV$ to express the infinitesimal change in enthalpy at constant pressure:

- $dH = dU + PdV$ at constant pressure

- Combine the two equations:

- $dG = dU + PdV - TdS$ at constant temperature and pressure

Gibbs Free Energy and Nonexpansion Work

- Then, take the equation $\Delta U = w + q$ to express the infinitesimal change in internal energy: $dU = dw + dq$
  Add $dU = dw + dq$ to the equation $dG = dU + PdV - TdS$:
- $dG = dw + dq + PdV - TdS$ at constant temperature and pressure

- For the maximum work that a process can do, we want a reversible process:

- $dG = dw_{rev} + dq_{rev} + PdV - TdS$ at constant temperature and pressure

- We can use $dS = dq_{rev}/T$ to replace dq_{rev} by TdS and cancel the two TdS:

- $dG = dw_{rev} + TdS + PdV - TdS$
- $dG = dw_{rev} + PdV$ at constant temperature and pressure

Gibbs Free Energy and Nonexpansion Work

- Previous: $dG = dw_{rev} + PdV$

- At this point, we recognize that the system may do both expansion work and nonexpansion work:
- $dw_{rev} = dw_{rev,\ e} + dw_{rev,\ expansion}$

- Reversible expansion work (matching the external to the internal pressure):
- $dw_{rev,\ expansion} = -PdV$

- Combine the previous two equations
- $dw_{rev} = dw_{rev,\ e} - PdV$

Gibbs Free Energy and Nonexpansion Work

- Previous: $dw_{rev} = dw_{rev,e} - PdV$ and $dG = dw_{rev} + PdV$

- Substitute $dw_{rev} = dw_{rev,e} - PdV$ into our expression for dG, the PdV cancel leaving $dG = dw_{rev,\ e}$ since the conditions are at constant temperature and pressure.

- Because $dw_{rev,\ e}$ is the maximum nonexpansion work that the system can do (because it is achieved reversibly), we obtain

- $dG = dw_{e,\ max}$ or $\Delta G = dw_{e,\ max}$ at constant P and T for any G we calculate.

Gibbs Free Energy and Nonexpansion Work: Applied

- How much nonexpansion work is done in our body in the oxidation of glucose, $C_6H_{12}O_6$(s, glucose) + 6 O_2(g) → 6 CO_2(g) + 6 H_2O(l) to make peptide links (a link between amino acids) in a protein?
- We calculated Gibbs free energy of reaction is −2879 kJ per mol or 180.0 g of glucose.
- It takes 17 kJ of work to build 1 mol of peptide links in a protein.
- So 1 mole of glucose or 180. g of glucose can build about (2879 kJ)/(17 kJ) = 170 moles of peptide links.
- A typical protein has several hundred peptide links, and so several glucose molecules must be sacrificed to build one protein molecule.

Free Energy and Life

- Many biological reactions, such as the construction of a protein from amino acids or the construction of a DNA molecule, are not spontaneous and are driven by an external source of energy.

- That energy comes from sunlight and the chemicals in food that have stored solar energy.

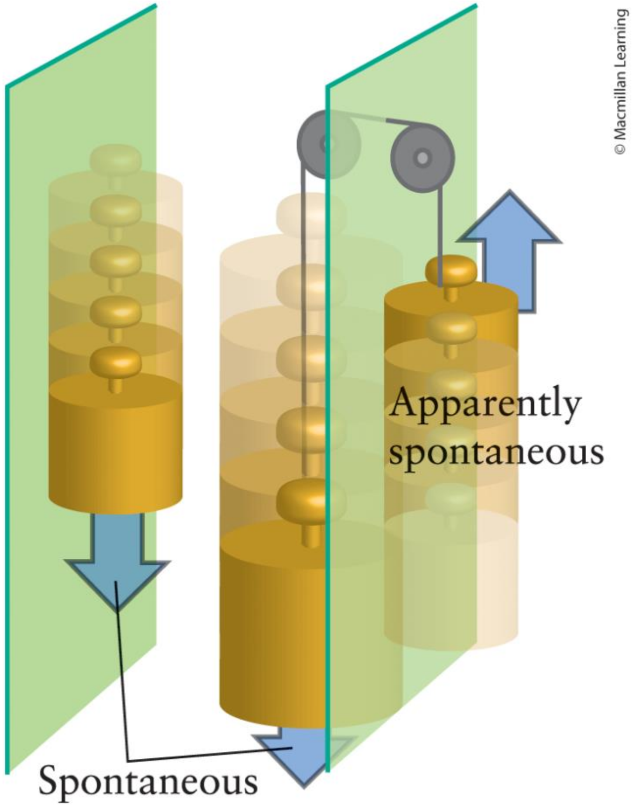
- Many biological chemical reactions are nonspontaneous reactions. To make these reactions work, we must use entropy to drive a reaction forward.

Free Energy and Life

- Staying alive is very much like using weights tied to each other over a pulley.

- The lighter weight can not move on its own.

- However, by connecting a lighter weight to a heavier weight falling, then dropping the heavy weight, the light weight can soar upward.



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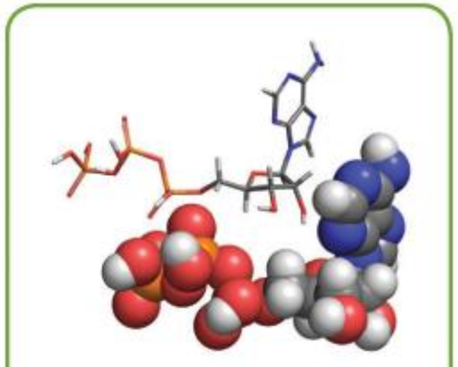
Free Energy and Life

- The hydrolysis of adenosine triphosphate, ATP, to adenosine diphosphate, ADP, is frequently how biological organisms couple and drive nonspontaneous reactions.
- To restore ADP with 2 phosphates to ATP with 3 takes +30 kJ of energy.
- We eat food in a combustion reaction that releases 2500 kJ per mole of energy per mole of glucose. Eating glucose is our heavy weight, enough to “recharge” 80 moles of ADP.
- Once we stop eating, decay begins; entropy continues forward.



1 Adenosine triphosphate, ATP

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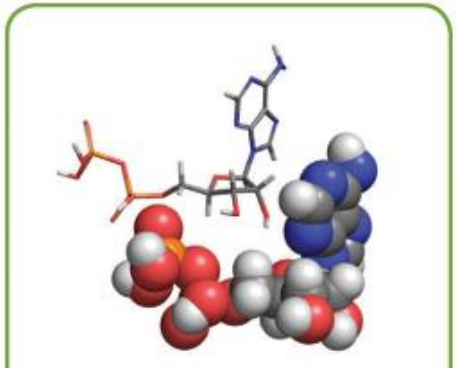

2 Adenosine diphosphate, ADP

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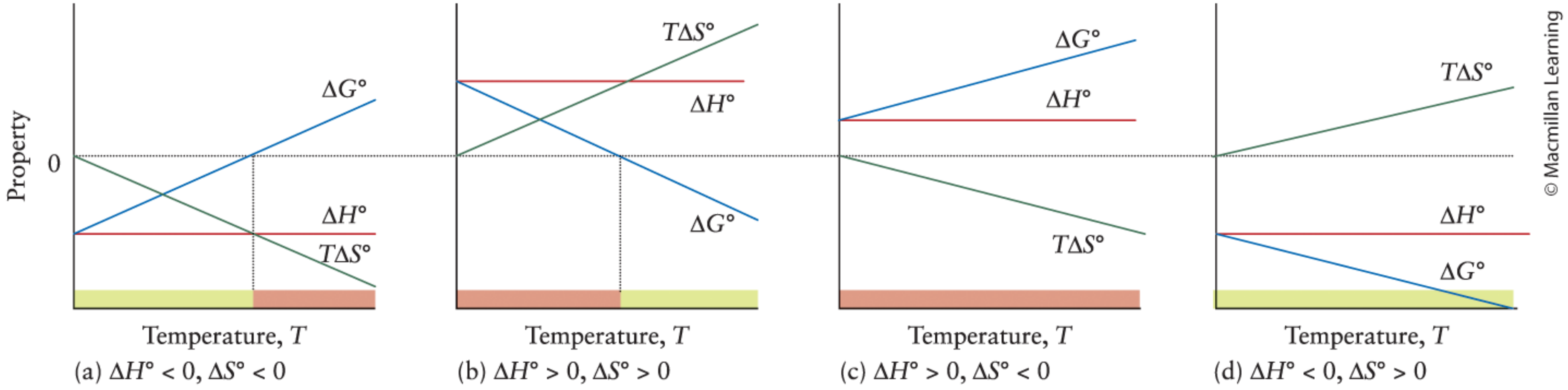
Free Energy and Life

Leroy Laverman.

The source of our heavy weight is the sun.

The Effect of Temperature

- ΔG° does depend on temperature: ΔG° = ΔH° – TΔS°



Spontaneous if:

- (a) T is low (b) T is high (c) never (d) always

- Exothermic, ΔH° < 0 and ΔS° < 0, as long as T remains low, ΔG° is “–”
- Endothermic, ΔH° > 0 and ΔS° > 0, if T is high enough, ΔG° will be “–”
- Endothermic, ΔH° > 0 and ΔS° < 0, this is never spontaneous at any T
- Exothermic, ΔH° < 0 and ΔS° > 0, spontaneous at any T

The Pressure-Dependence of Gibbs Free Energy

- The Gibbs free energy of a solid or a liquid changes very little with pressure.

- However, the pressure dependence of the Gibbs free energy of a gas is significant.