Thermodynamics & Thermochemistry (Thermodynamic Fundamentals)

What is Thermodynamics?

Thermodynamics is the field of physics that studies how heat, work, energy, and entropy interrelate for a specific chemical or physical process. ***Thermochemistry*** is the specific application of ***thermodynamics*** to chemical processes.

In the world of ***thermodynamics***, important terms like ***heat, work, energy,*** and ***entropy*** have specific meanings, which we will discuss later.

By studying ***thermodynamics,*** we can determine if a reaction or process will happen, but NOT *how fast* a reaction or process will occur. To measure the *speed* of a reaction or process, we use ***kinetics***, which we covered in an earlier chapter.

Before going on, I must now teach you about things called ***state functions***.

What are State Functions?

State functions are chemical or physical properties that only depend on the *initial and final states of the system*, NOT on *how the system got there*.

For example, let's imagine that Mike and Ari are both on the 40th floor of a building. you ask the question, "On which floor of the building are Mike and Ari located?", answer is, "the 40th."

Does it matter how they got to that floor? No, it doesn't, because the answer to the question only depends on their current location; not on how they got there.

For example, if Mike got to the 40th floor by taking the elevator, but Ari got there by scaling the building *Mission Impossible* style, it still does not change the answer to the original question. "On which floor of the building are Mike and Ari located?" 40th." Thus, their final *state* (being on the 40th floor) *has nothing to do with how they got there*.

What are State Functions?

State functions are similar. Again, they are properties that only depend on the *initial and final states of the system*, NOT on *how the system got there*.

For example, at 25 °C and 1.0 atm of pressure, the ***entropy*** (level of disorder) of 1 mole of water is 70.0 J/K.

But, if I have 1 mole of water *vapor* at high temperature and 1.0 atm of pressure, and I *lower* its temperature down to 25 °C, then guess what? Its final entropy will still be 70.0 J/K.

Do you see what I'm saying? For a property like ***entropy***, it doesn't matter that my first sample started at low-temp and got warmed up to 25 °C, and that my second sample started at high-temp and got cooled down to 25 °C. Their final state (25 °C and 1 atm) is the same, even though they took different paths to get there.

Why Do We Care?

This stuff is important because in ***thermodynamics***, we often talk about things like ***energy*** (***E***), ***entropy*** (***S***), ***enthalpy*** (***H***), ***work*** (***w***), and ***heat*** (***q***).

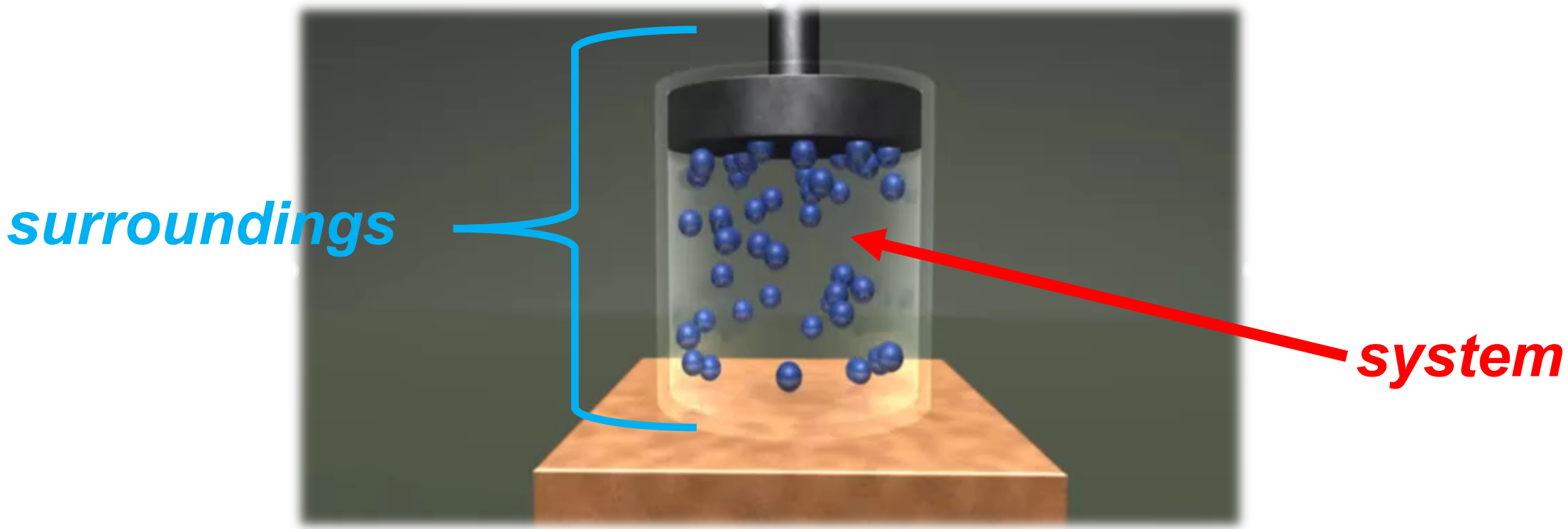
As it turns out, ***work*** and ***heat*** are NOT state functions, but pretty much all the other properties we'll cover in this chapter are. Just so you know:

$$\Delta E = w + q$$

If you're only given the ***ΔE***, you cannot determine the values of ***w*** and ***q***, because ***w*** and ***q*** are NOT state functions and *do* depend on the *pathway*, not just the final and initial states.

System and Surroundings

In ***thermodynamics***, we often use the words ***system*** and ***surroundings***. To explain, when studying a chemical reaction, the reactants and products are the ***system***. The container around the reaction, as well as everything beyond it, are the ***surroundings***. The ***system*** and ***surroundings*** together are called the ***universe***.



Thermodynamic Laws

For the EXAM, there are three laws of ***thermodynamics*** that you should know:

Law #1 (conservation of energy): Energy cannot be created or destroyed. It can only be converted from one form to another.

Law #2: The ***entropy*** (disorder) of the universe is always increasing. If one system becomes more ordered, it does so by making another system (or surroundings) more disordered. In other words, the combined change in ***entropy*** of a system and its surroundings (the "universe") must be positive:

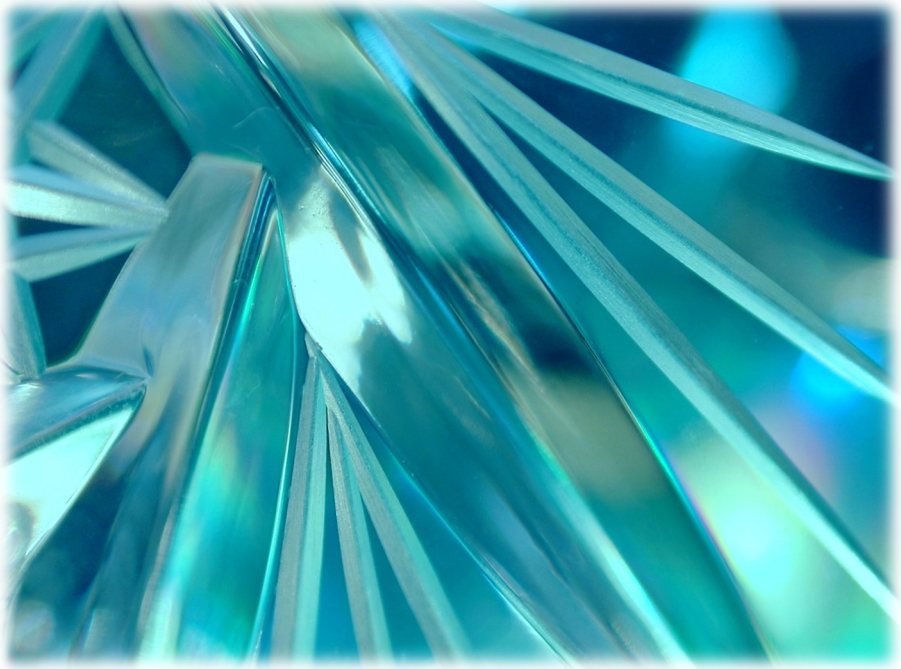
$$\Delta S_{universe} > 0$$

$$\Delta S_{system} + \Delta S_{surroundings} > 0$$

Thermodynamic Laws

For the EXAM, there are three laws of ***thermodynamics*** that you should know:

Law #3: For a perfect crystal that's been cooled to 0 K (–273 °C, called ***absolute zero***), its entropy is *close to (or approaches) zero*.



Thermodynamics & Thermochemistry (Enthalpy)

What is Enthalpy?

Simply defined, ***enthalpy*** (***H***) is the amount of heat-energy a substance contains. For any chemical reaction or physical change, we can determine the difference in ***enthalpy*** (or ***change in enthalpy***, ***ΔH***) between the products and reactants, as follows:

$$\Delta H = \text{total } H_{products} - \text{total } H_{reactants} = H_{final} - H_{initial}$$

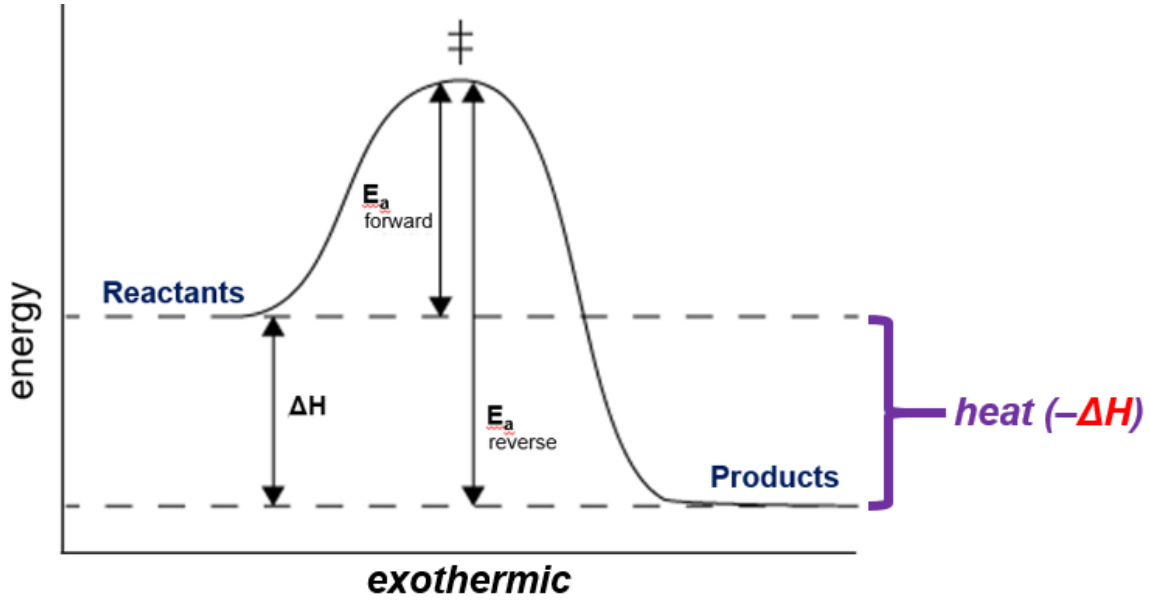
For example, for the following generic reaction:

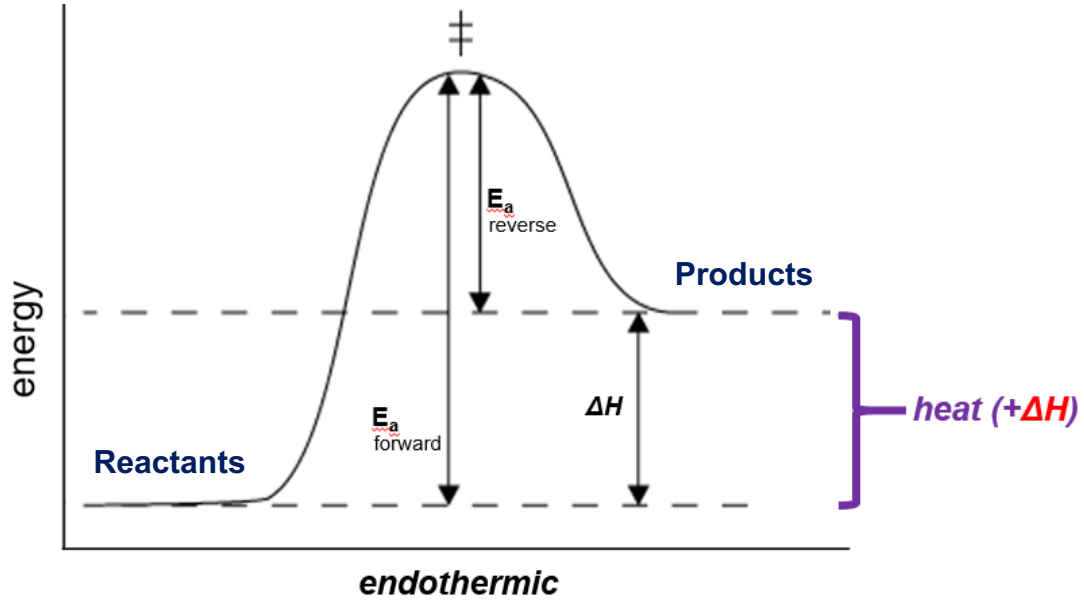
$$A \rightarrow B \qquad \Delta H = -100 \text{ kJ}$$

. . . Its negative ***ΔH*** means that product **B** is more stable than reactant **A**. A reaction with a negative ***ΔH*** is an ***exothermic reaction***, which means that it gives off heat.

What is Enthalpy?

In contrast, a reactant or process with a *positive* ***ΔH*** is an ***endothermic reaction***, which means that it *consumes* heat. You might remember this subject discussed in our earlier chapter on ***kinetics***, with ***reaction coordinate diagrams*** like these:





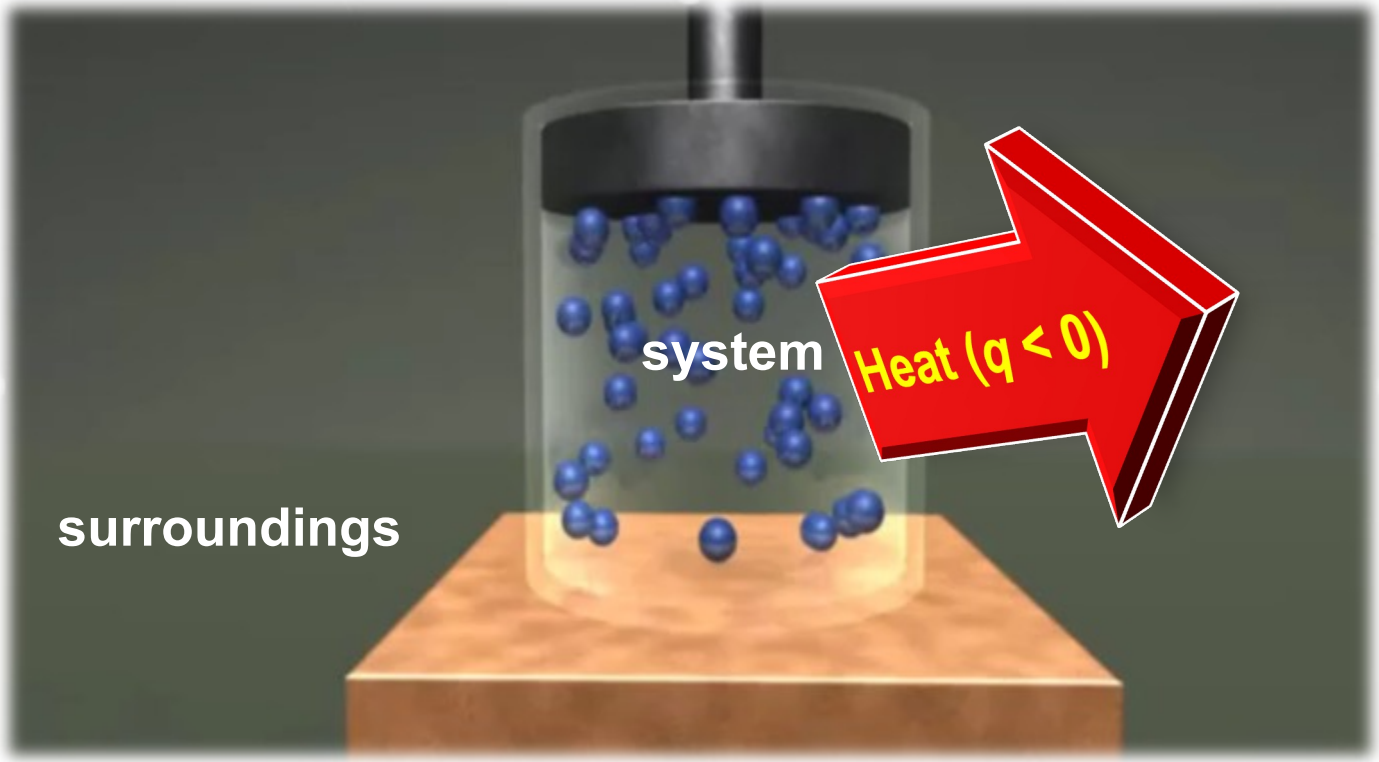
What is Enthalpy?

Enthalpy (***H***) is a ***state function***. This means that ***ΔH*** for any transformation depends only on the final and initial states in its calculation and NOT on the path taken to get there.

$$\Delta H = \text{total } H_{products} - \text{total } H_{reactants} = H_{final} - H_{initial}$$

Endo vs. Exothermic

Again, an ***exothermic*** process is one that gives off heat to its surroundings. ***Exothermic*** processes have negative ***ΔH*** values (***ΔH*** or $q < 0$). Just like money being withdrawn from your bank account (which is a negative thing), ***exothermic*** processes lose heat to their surroundings (a negative ***ΔH***).



Endo vs. Exothermic

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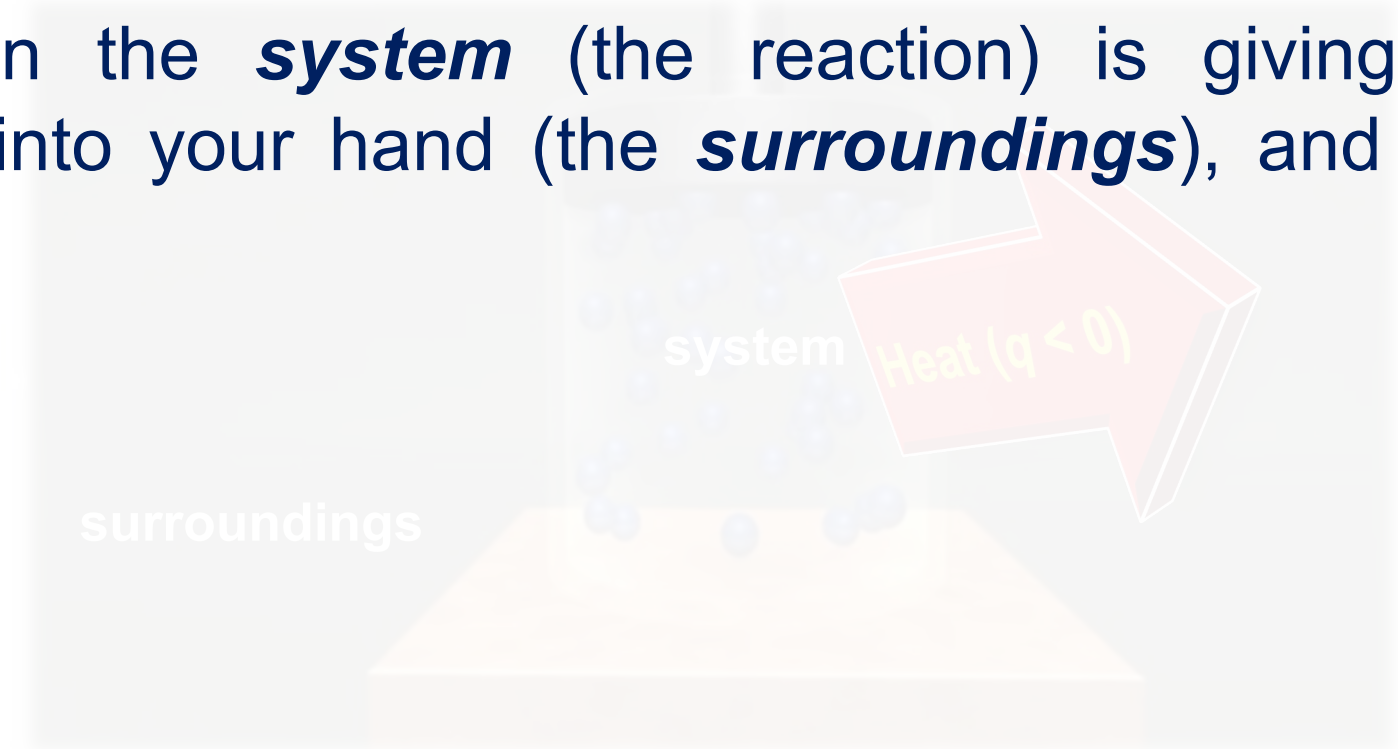
This means that ***exothermic*** processes feel hot.

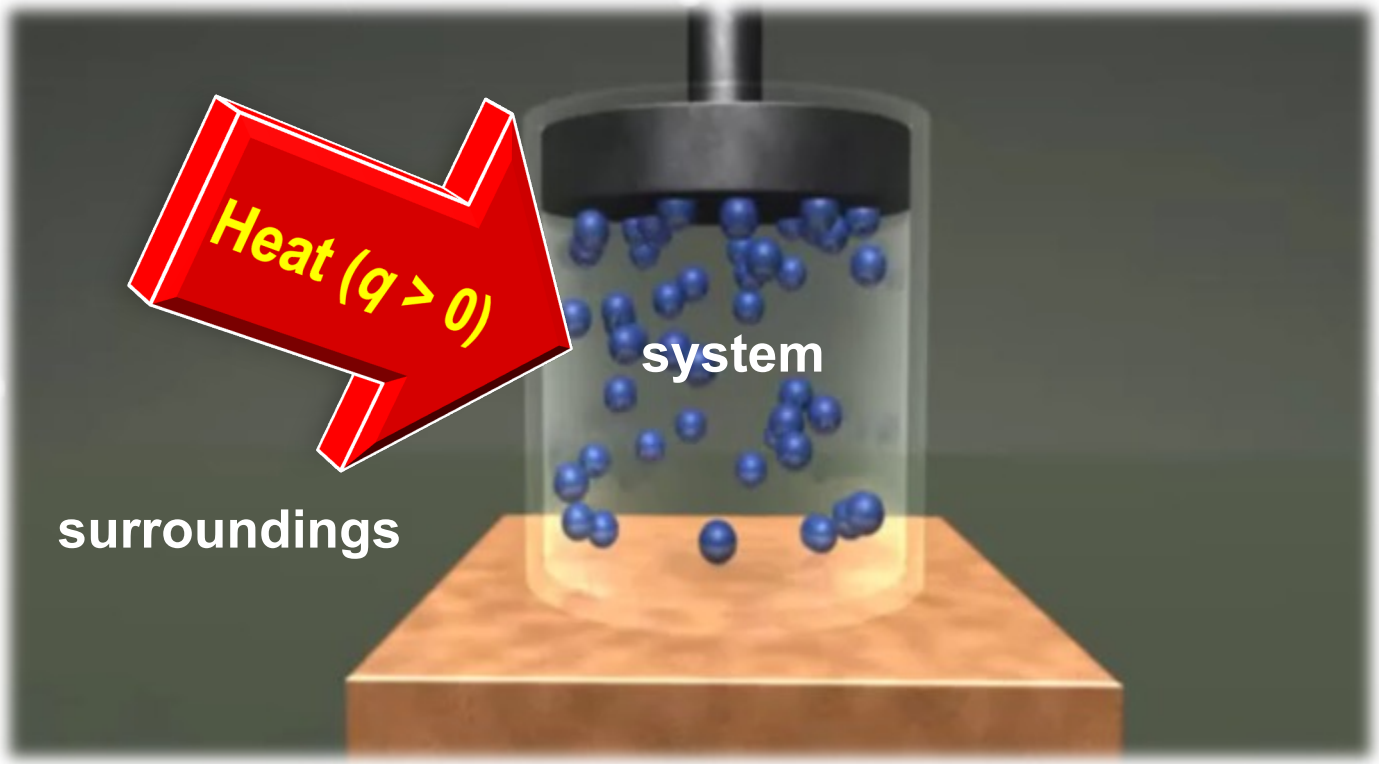
Thus, if you feel the side of a flask in which a reaction is going, and it feels hot, then the ***system*** (the reaction) is giving off heat and transferring it into your hand (the ***surroundings***), and the reaction is ***exothermic***.



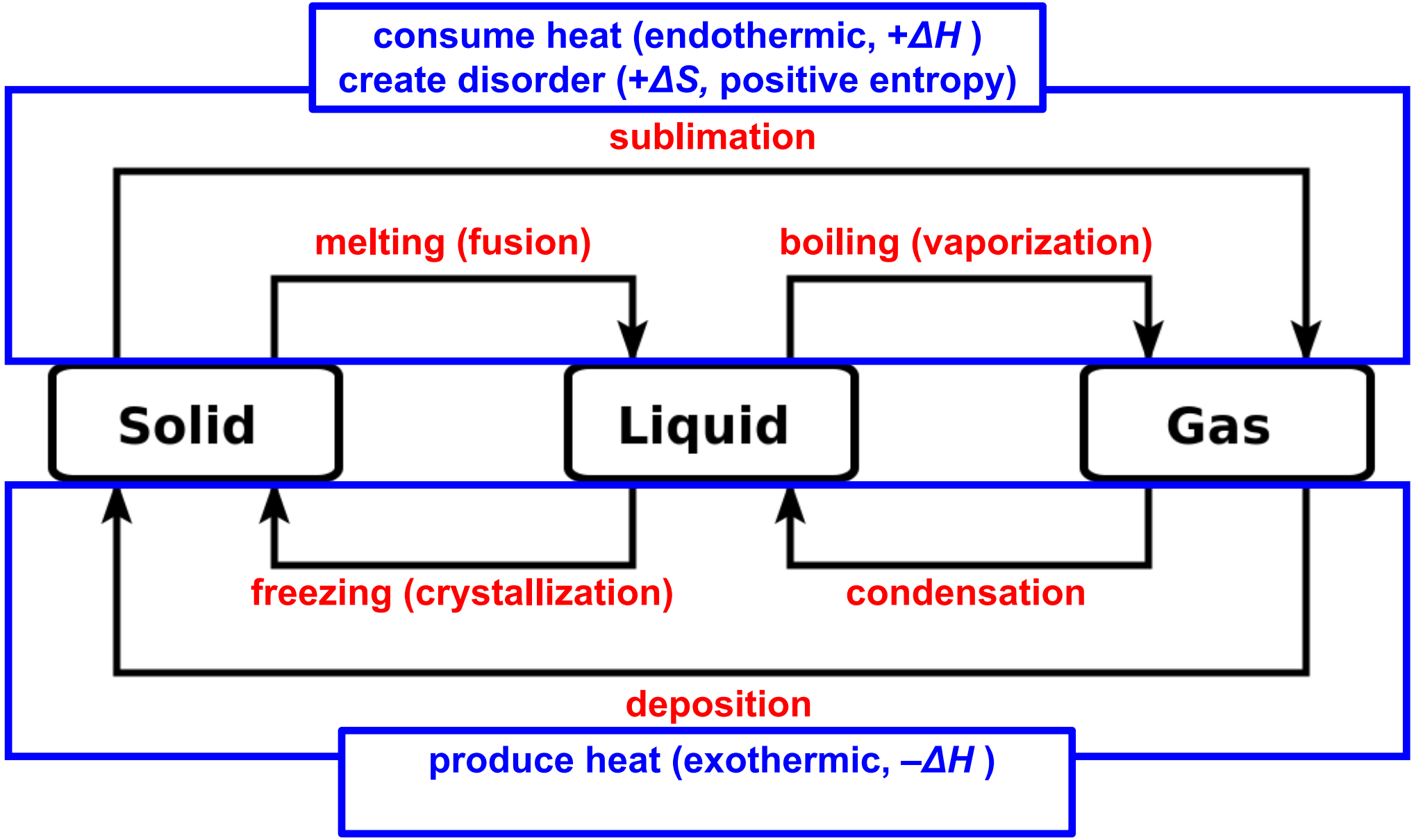
Endo vs. Exothermic

By comparison, an ***endothermic*** process is one that consumes heat from its surroundings. ***Endothermic*** processes have positive ***ΔH*** values (***ΔH*** or ***q*** **> 0**).
like money being deposited into your bank account (which is a positive tr
endothermic processes consume heat from their surroundings (a positive ***ΔH***).

Endothermic processes and reactions feel cold.



Phase Changes



Phase Changes

Converting from a . . .	to a . . .	is called:	ΔH
solid	liquid	fusion	
liquid	gas	vaporization	+ (endothermic)
solid	gas	sublimation	
gas	solid	deposition	
gas	liquid	condensation	– (exothermic)
liquid	solid	crystallization	

Thermodynamics & Thermochemistry (Enthalpies of Formation)

To Review

As I taught in a previous video, ***enthalpy*** (***H***) is the amount of heat-energy a substance contains. For any chemical reaction or physical change, we can determine the difference in ***enthalpy*** (or ***change in enthalpy***, ***ΔH***) between the products and reactants, as follows:

$$\Delta H = H_{products} - H_{reactants} = H_{final} - H_{initial}$$

I also taught you that reactions with negative ***ΔH*** values are ***exothermic*** (give off heat and feel hot to the touch), while reactions with positive ***ΔH*** values are ***endothermic*** (absorb heat and feel cold to the touch).

What Are Enthalpies of Formation?

An ***enthalpy of formation*** is the ***ΔH*** of the chemical reaction of forming *one mole of a single substance from its parent elements*, at 298 K (25 °C) and 1 atm.

Don't confuse with ***STP!***

For example, H_2O is made from two ***parent elements***: hydrogen and oxygen. Because these two elements are ***diatomic***, in their elemental forms, hydrogen's formula is H_2, and oxygen's is O_2. Thus, the chemical reaction of forming 1 mole of H_2O from its ***parent elements*** looks like this:

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \rightarrow H_2O_{\,(l)}$$

To make this reaction completely correct, we have to add the physical states of each substance at 25 °C and 1 atm. Under these conditions, H_2 and O_2 are gases, and H_2O is a liquid. To balance this equation while keeping a 1 (1 mole) in front of the H_2O, we have to add a ½ coefficient to the O_2.

What Are Enthalpies of Formation?

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \rightarrow H_2O_{\,(l)} \qquad \Delta H^\circ_f = -286\ \text{kJ/mol}$$

Because this equation represents the chemical reaction of forming *one mole of H_2O from its parent elements* at 25 °C and 1 atm, the ***ΔH*** of this reaction is the ***enthalpy of formation*** for liquid H_2O.

As I also taught you in a prior video, the ***ΔH*** for any transformation or reaction (ΔH_{rxn}) can be calculated as follows:

$$\Delta H_{rxn} = \text{total } H_{products} - \text{total } H_{reactants} = H_{final} - H_{initial}$$

What Are Enthalpies of Formation?

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \rightarrow H_2O_{\,(l)} \qquad \Delta H^\circ_f = -286\ \text{kJ/mol}$$

Because this equation represents the chemical reaction of forming *one mole of H_2O from its parent elements* at 25 °C and 1 atm, the ***ΔH*** of this reaction is the ***enthalpy of formation*** for liquid H_2O.

This can be written in a more-technically correct way, as follows:

$$\Delta H_{rxn} = \Sigma n H_{products} - \Sigma n H_{reactants}$$

ΔH°_f of Elements in Standard States

There's something else that you need to know about ***enthalpy of formation*** (***ΔH°_f***): the ***enthalpy of formation*** (***ΔH°_f***) of any element in its ***standard state*** is 0 kJ/mol.

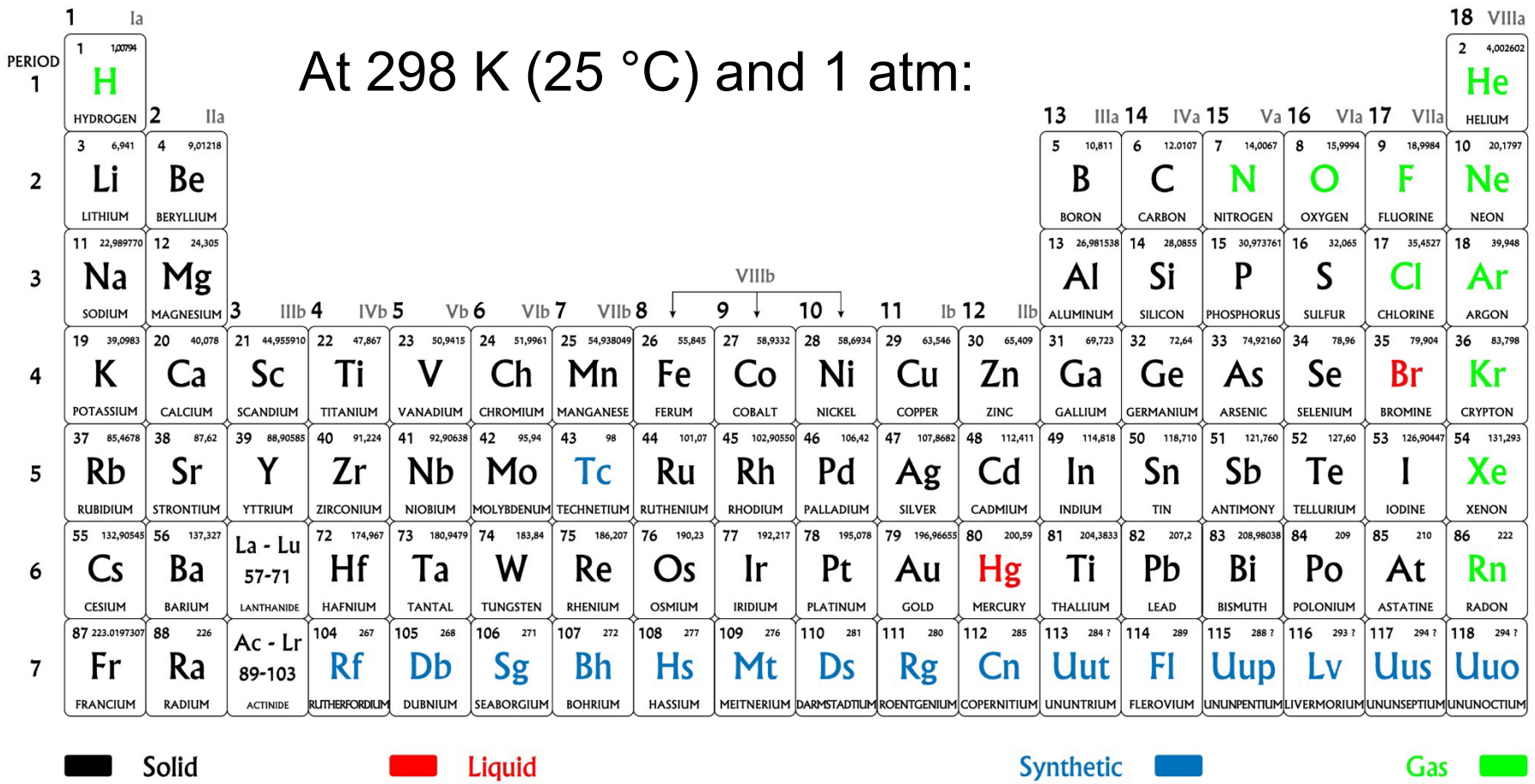
What does that mean? At 298 K (25 °C) and 1 atm, in what state (solid, liquid, or gas) is H_2? A gas, of course. Thus, the ***ΔH°_f*** of H_2 *gas* is zero. The ***ΔH°_f*** of H_2 *liquid* or H_2 *solid*, in contrast, is NOT zero. Just of H_2 *gas*, because *gas* is the ***standard state*** of H_2 at 298 K and 1 atm.

The same is true of any other element: the ***enthalpy of formation*** (***ΔH°_f***) of any element in its ***standard state*** (solid, liquid, or gas) is 0 kJ/mol.

Again, do NOT confuse ***standard state*** (298 K and 1 atm) with ***standard temperature pressure***, or ***STP*** (0 °C and 1 atm).

ΔH°_f of Elements in Standard States

At 298 K (25 °C) and 1 atm:



ΔH°_f of Elements in Standard States

For example, what is the ***enthalpy of formation*** (ΔH°_f) of the following?

- $He_{(g)}$
- $N_{2\,(g)}$
- $F_{2\,(g)}$
- $Br_{2\,(l)}$
- $C_{(graphite)}$
- $H_{2\,(g)}$
- $O_{2\,(g)}$
- $Cl_{2\,(g)}$
- $Hg_{(l)}$
- $S_{8\,(s)}$

Zero!

Question

Using the information in the table below, calculate the ΔH_{rxn} for the following reaction:

$$C_2H_5OH_{(g)} + 3\,O_{2\,(g)} \rightarrow 2\,CO_{2\,(g)} + 3\,H_2O_{(g)}$$

	ΔH_f° (kJ/mol)
$C_2H_5OH_{(g)}$	-200
$CO_{2\,(g)}$	-400
$H_2O_{(g)}$	-250

Thermodynamics & Thermochemistry (Thermodynamic Equations)

Energy, Heat, and Work

As with everything in science, the field of ***thermodynamics*** includes a variety of equations we can use to calculate . . . Things. For example, for any ***system*** undergoing a chemical or physical change:

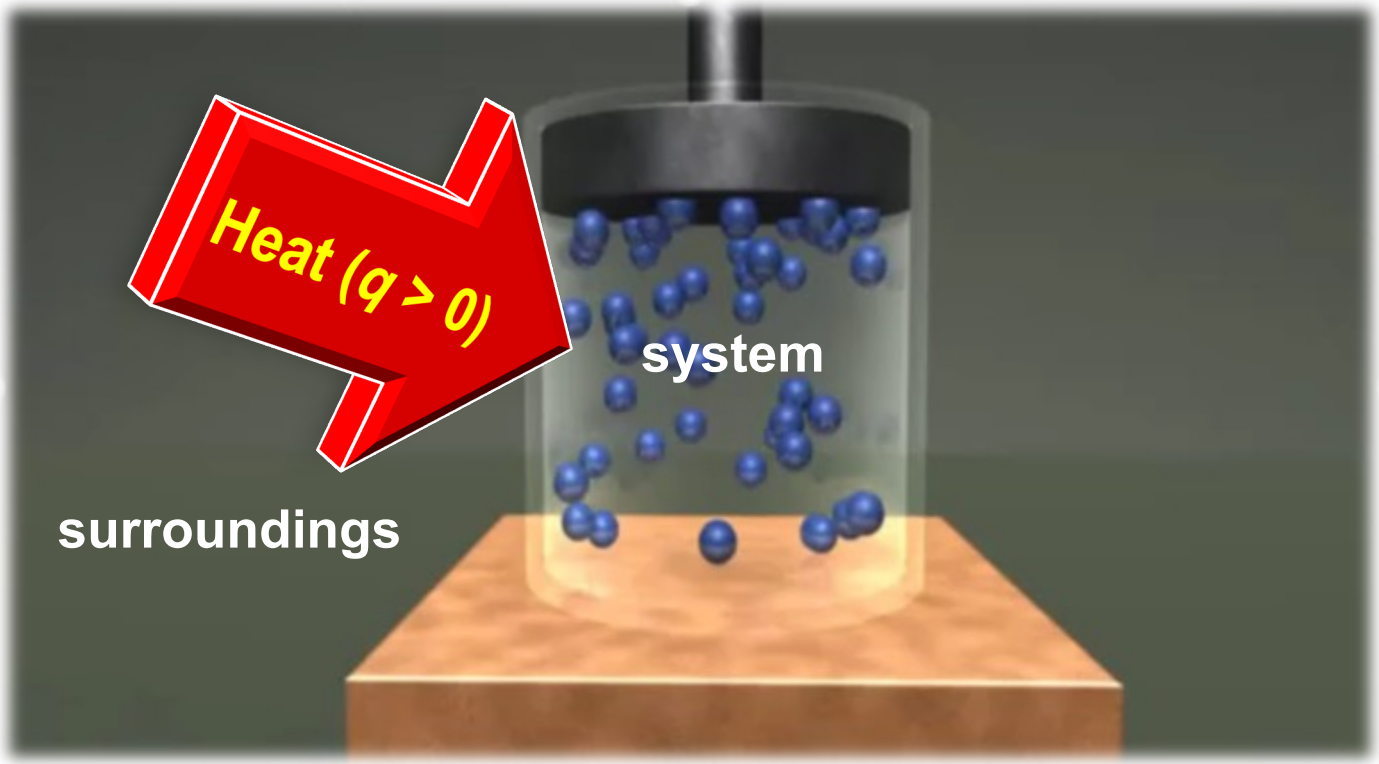
$$\Delta E = q + w$$

Where:

- ΔE = the system's internal change in ***energy***
- w = the amount of work done *by* the system or *to* the system
- q = the system's change in heat

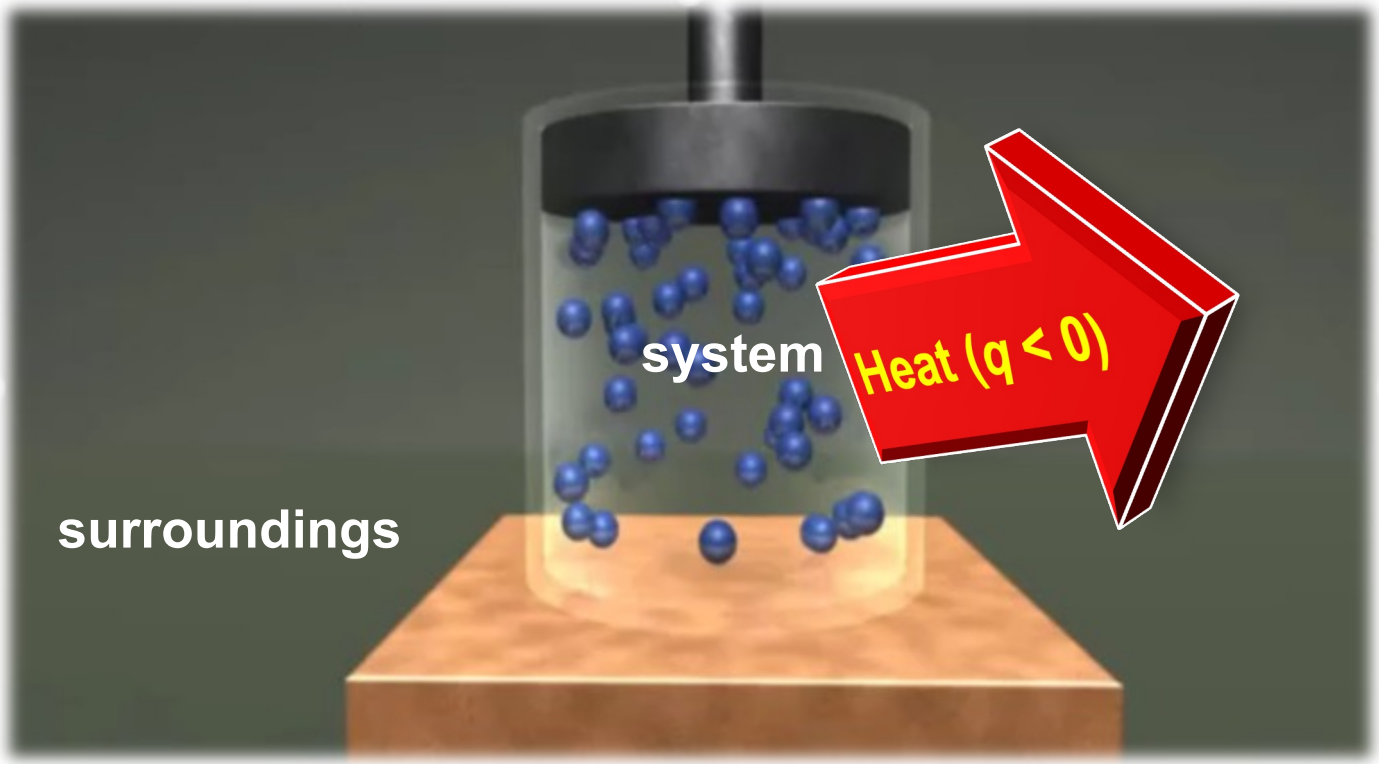
Energy, Heat, and Work

If ***q*** is positive (***q* > 0**), then the surroundings are transferring heat *into* the system, much like making a positive deposit into a bank account. Physical processes with positive ***q*** values are ***endothermic*** (feel cold) because they suck heat from their surroundings.



Energy, Heat, and Work

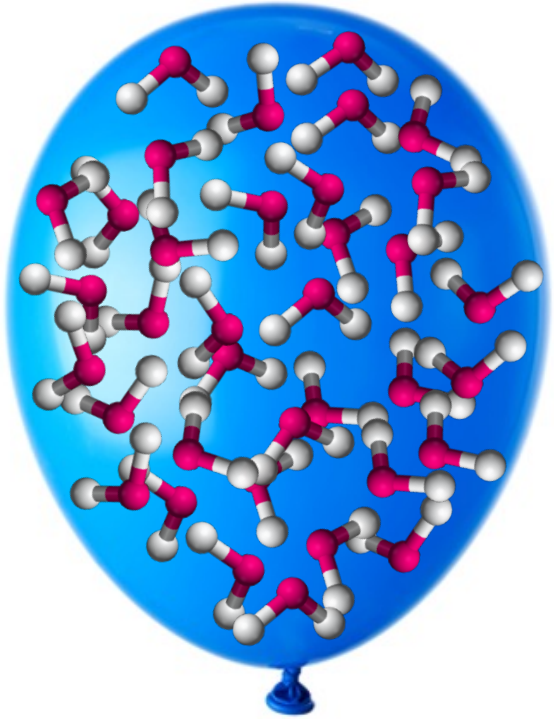
If ***q*** is negative (***q* < 0**), then the system is transferring heat *into* the surroundings, much like making a *withdrawal* from a bank account (which is negative). Physical processes with negative ***q*** values are ***exothermic*** (feel hot) because they give off heat to their surroundings.



A Work/Pressure Equation

Another important equation relates ***work*** to ***pressure*** and ***volume:***

$$w = -P\Delta V$$



Where:

- ***P*** = the system's internal ***pressure***
- ***ΔV*** = the system's internal change in ***volume***

For example, if you take a balloon and squeeze it, then you (the surroundings) have just compressed the gas ***system*** by reducing its volume.

A Work/Pressure Equation

Another important equation relates ***work*** to ***pressure*** and ***volume:***

$$w = -P\Delta V$$

(ΔV: ⊖)

So in this situation, is ΔV positive or negative? Negative. So will w be positive or negative? Positive.

Similar to ***q***, a positive ***w*** means that the surroundings are doing work *on* the system. From this example, we can see that if ΔV is negative (the system is being ***compressed***), then ***w*** is positive. This means that the surroundings are doing ***compression-work*** on the system.

A Work/Pressure Equation

Another important equation relates ***work*** to ***pressure*** and ***volume:***

$$w = -P\Delta V$$

ΔV is positive

In contrast, if you increase the volume, then ΔV is positive. In this case, the gas has expanded (positive ΔV), which means that the system has done work *on the surroundings*.

In this situation (positive ΔV), you get a negative w. Thus, a negative w means a positive ΔV, which means (once again) that the system (in this case, the gas) has done work on the surroundings.

Why Do We Care?

The reason this is important is because it is a source of easy definition questions that the EXAM may ask.

$$\Delta E = q + w$$

$$w = -P\Delta V$$

$q > 0$ **(endothermic)**	Heat is transferred to the system (from the surroundings)
$q < 0$ **(exothermic)**	Heat is transferred to the surroundings (from the system)
$w > 0$	The surroundings do work on the system (compression)
$w < 0$	The system does work on the surroundings

Thermodynamics & Thermochemistry (Calorimetry)

Heat Transfer

Heat transfer occurs by three means:

Conduction: heat transfer due to direct contact, via molecular agitation within a material • *Example:* if you bite into hot pizza and burn your mouth, it's because the heat gets transferred by direct contact from the pizza to your mouth.

Convection: heat transfer due to the motion of a liquid or gas, such circulating hot air • *Example:* a convection oven circulates hot air to cook food.

Radiation: heat transfer via electromagnetic radiation • *Examples*: transferring heat with no medium in-between, through forms of radiation like ***infrared light***, ***microwave radiation***, ***visible light***, ***gamma radiation***, etc.

Important Terms

- **<u>calorie (cal)</u>:** The amount of heat required to raise 1.0 g of liquid water by 1.0 °C. This is also called water's ***specific heat*** and is equal to 4.19 J.

In general, a substance's ***specific heat*** (**C**) is the amount of energy required to increase the temperature of 1.0 gram of it by 1.0 °C or 1.0 K.

Specific heat varies from one substance to another, and for the same substance, from one physical state to another. For example:

- $C_{\text{liquid water}} = 4.19\ J/g\times C$
- $C_{\text{ice}} = 2.05\ J/g\times C$
- $C_{\text{steam}} = 2.0\ J/g\times C$
- $C_{\text{aluminum}} = 0.90\ J/g\times C$

These values tell us that it takes a lot more energy to heat up 1.0 gram of liquid water than 1.0 gram of aluminum. If you had an aluminum block sitting next to a tub of water of the same mass on a hot day, and you left them both out for the same amount of time, the aluminum block would be warmer at the end of the day than the water.

Important Terms

- **calorie (cal):** The amount of heat required to raise 1.0 g of liquid water by 1.0 °C. This is also called water's ***specific heat*** and is equal to 4.19 J.

- **Calorie (Cal):** This is the "calorie" used on nutrition labels and is equal to 1,000 calories, or 1 kilocalorie.

As an example, if a banana contains 100 Calories, then it contains 100,000 calories. We determine this experimentally by using something called a ***bomb calorimeter:*** a device that doesn't let heat in or out and burns (combusts) the banana to see how much heat it releases.

Calorimetry

Calorimetry is a technique used to measure how much heat is produced by a chemical reaction –in other words, that chemical reaction's ***heat transfer***. Devices used to measure this are called ***bomb calorimeters***. Under a ***constant-pressure system:***

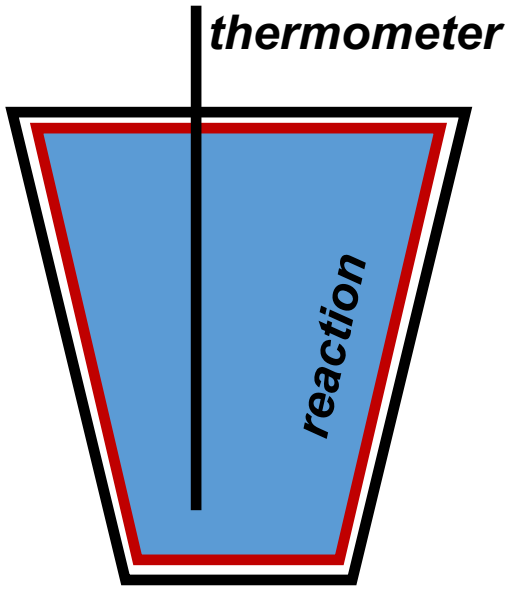
$$\Delta H = q$$

As I stated in a prior video, a negative ***q*** means an ***exothermic*** reaction. Because $\Delta H = q$ in a ***constant-pressure system***, a negative ΔH also means an ***exothermic*** reaction.

Calorimeters allow scientists to measure ΔH for chemical reactions, by measuring the heat (***q***) they produce or transfer to their surroundings.

Calorimetry

Here's how a ***bomb calorimeter*** works:



This takes us to the following equation:

$$q = -C_{calorimeter}\Delta T$$

- q = the amount of heat the reaction produces
- $C_{calorimeter}$ = the calorimeter's ***specific heat***
- ΔT = the temperature change caused by the reaction

Question

For example, let's suppose that you used a ***bomb calorimeter***, whose ***heat capacity*** is 2000 cal/°C, to measure a banana's heat content (***calories***). During the banana's combustion, the temperature changed from 15 °C to 20 °C. What is this banana's ***q***?

$$q = -C_{calorimeter} \Delta T$$

$$q = -(2000 \text{ cal/°C})(20°C - 15°C) = -10{,}000 \text{ cal}$$

Thermodynamics & Thermochemistry (Heat Curves)

To Review

As I taught you in a prior video, a substance's ***specific heat*** (**C**) is the amount of energy required to increase the temperature of 1.0 gram of that substance by 1.0 °C or 1.0 K.

I also taught you that ***specific heat*** varies from one substance to another, *and* for the same substance, from one physical state to another. For example:

- $C_{\text{solid water (ice)}} = 2.05\ J/g\times C$
- $C_{\text{liquid water}} = 4.18\ J/g\times C$
- $C_{\text{gaseous water (steam)}} = 2.0\ J/g\times C$

To Review

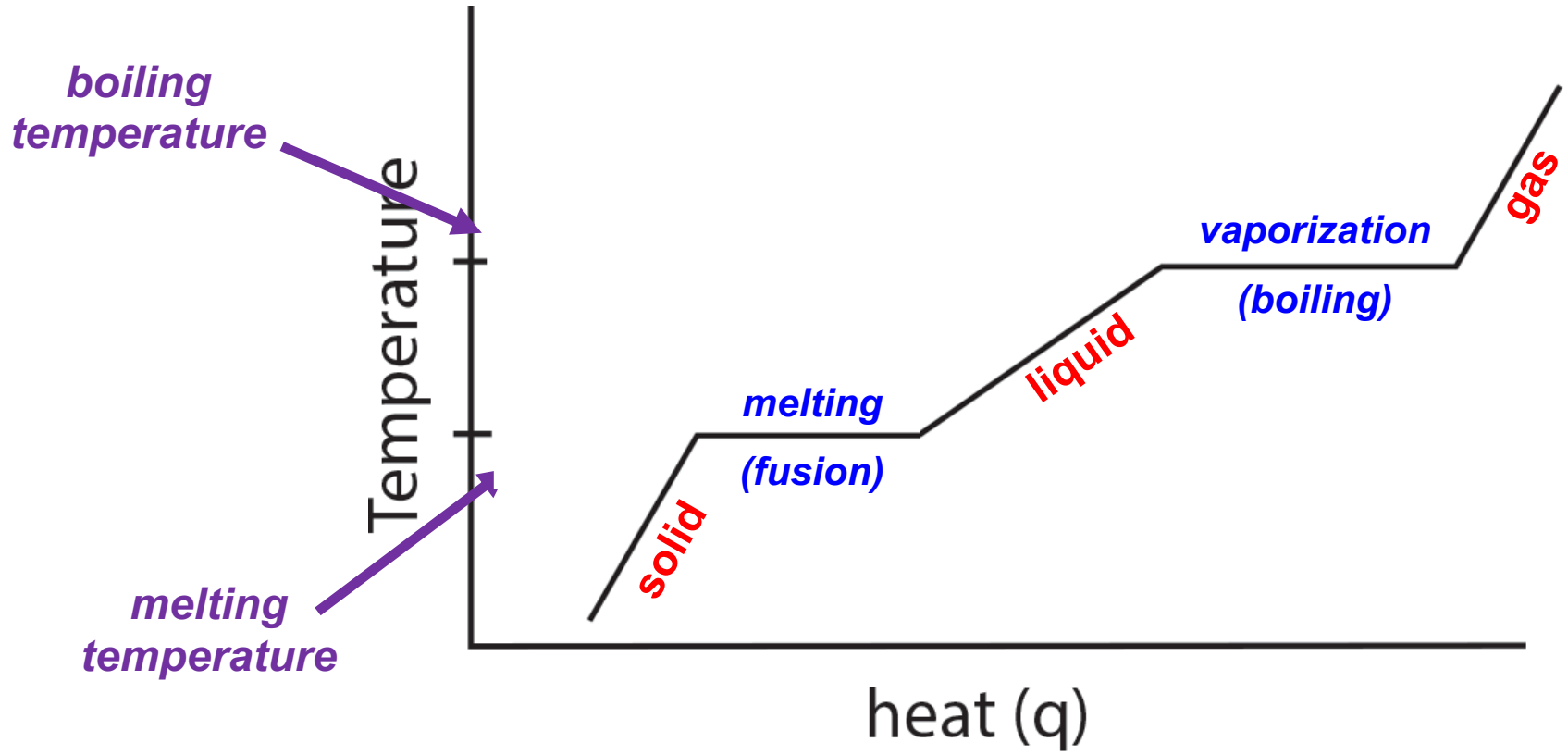
I also explained that ***bomb calorimetry*** can be used to determine the amount of energy (heat content, or calories) in a substance, by using the equation: $q = C\Delta T$.

. . . Where ***q*** is the amount of heat the substance or reaction produces, ***C*** is the calorimeter's ***specific heat***, and ΔT is the temperature change caused when the reaction is run or the substance is burned. When measuring the ***q*** for a specific *amount* of a substance, we add ***m*** (the substance's mass) to the equation, as follows:

$$q = mC\Delta T$$

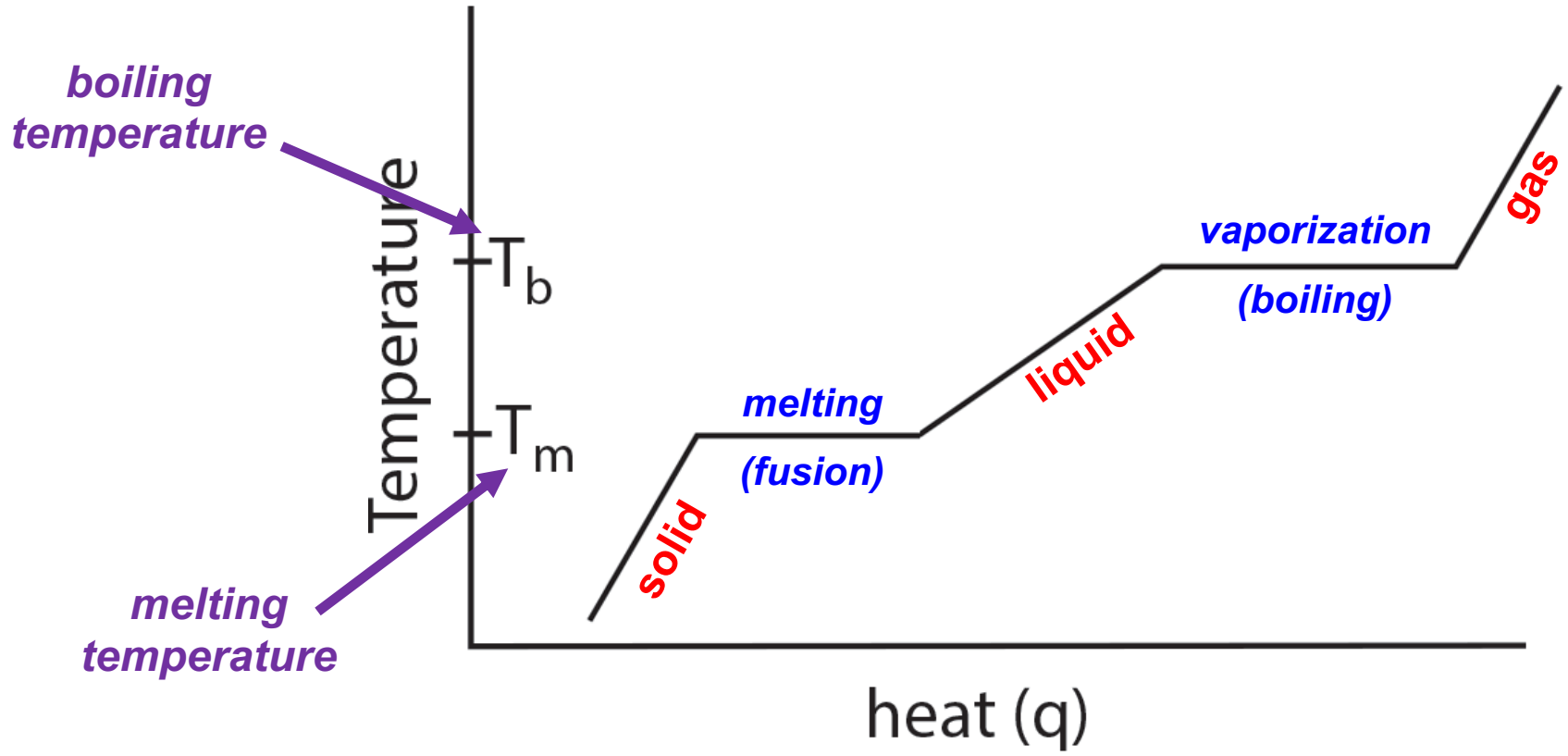
Heat Curves

Heat curves are diagrams that show how a substance changes from a solid to a liquid to a gas, as temperature is raised.



Heat Curves

We can use our equations to calculate the amount of heat required for a *specific amount* of a specific substance to traverse this journey:



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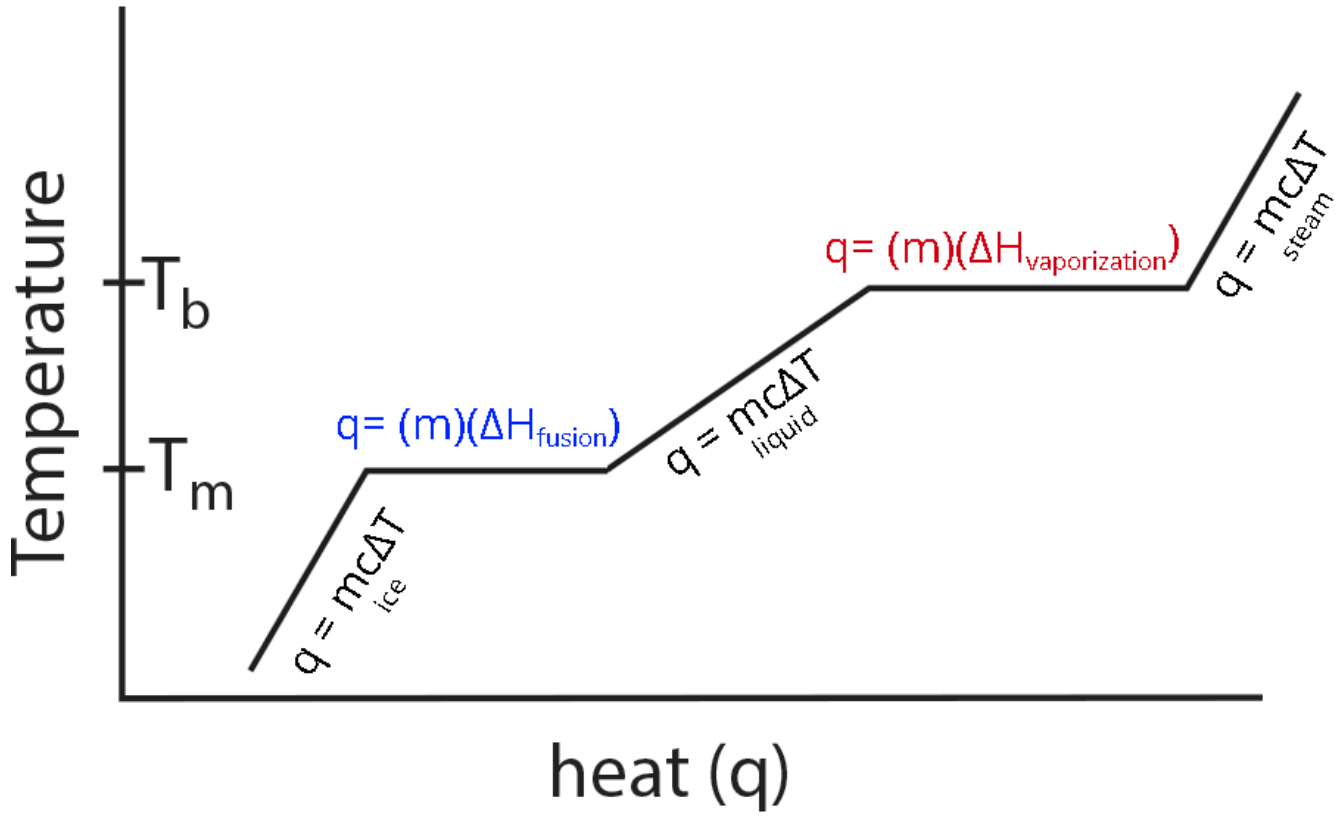


Questions

How much energy is required to increase the temperature of 36.0 g of H_2O from –20 °C to 50 °C, keeping in mind the following:

- $C_{ice} \approx 2.00$ J/g×C
- $C_{liquid\ water} \approx 4.00$ J/g×C
- $\Delta H_{fusion} \approx 6000$ J/mol

Questions

What is the final temperature (T_{Final}) of a 10.0 g ingot of silver that starts at 120 °C and is placed in 20.0 g of liquid H_2O at 40 °C, keeping in mind the following:

- $C_{solid\ silver} \approx 0.25$ J/g×C
- $C_{liquid\ water} \approx 4.00$ J/g×C

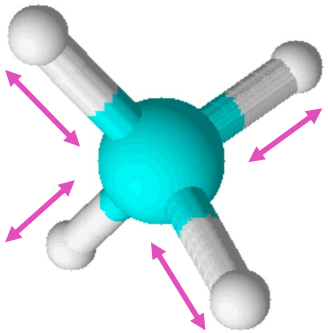
Thermodynamics & Thermochemistry (Entropy)

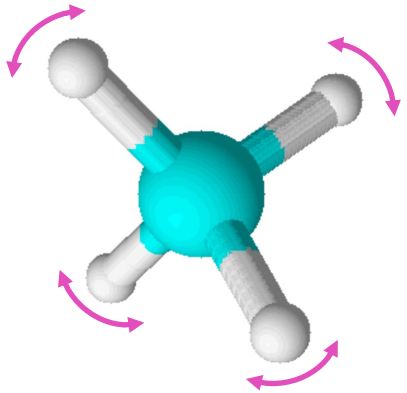
What is Entropy?

Simply defined, ***entropy*** (***S***) is a number we use to convey how disordered a substance is.

↑ ***S*** = ↑ **disorder**

The fact is, *all* substances have *some* amount of disorder, which is more-or-less directly related to how much that substance moves. In fact, even individual molecules move around, which means that they also have some amount of disorder. There is ***entropy*** in everything. Also, as molecules' structures get more complex, their ***entropy*** goes up.





What is Entropy?

Keeping that in mind, it should make sense that:

↑ ***S*** = ↑ **disorder** = ↑ **movement**

Having said that, I ask: which of the following would have the highest entropy? Which would have the lowest?

- a gas? ***most disordered = highest entropy***
- a liquid
- a solid? ***least disordered = lowest entropy***

Entropy is a State Function

As with ***enthalpy*** (***H***), entropy (***S***) is also a ***state function***. This, of course, means that ***ΔS*** for any transformation depends only on the final and initial states in its calculation and NOT on the path taken to get there:

$$\Delta S = \text{total } S_{products} - \text{total } S_{reactants} = S_{final} - S_{initial}$$

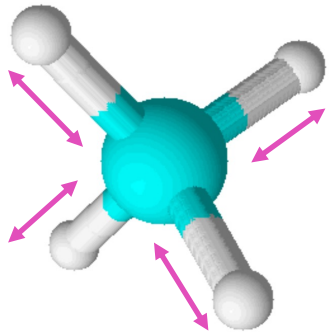
A more technically-correct way of writing this is:

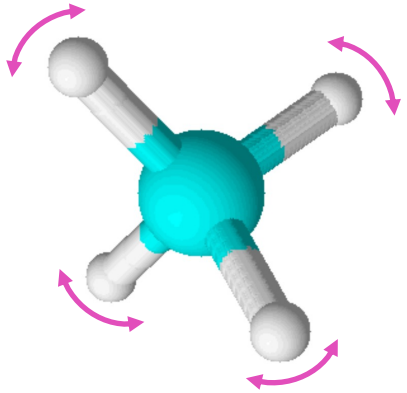
$$\Delta S_{rxn} = \Sigma n S_{products} - \Sigma n S_{reactants}$$

Entropy at Standard States

You might remember from an earlier video that the ***standard enthalpy of formation*** (***H°$_f$***) of any element in its ***standard state*** (solid, liquid, or gas) at 298 K and 1 atm is equal to zero kJ/mol.

This is NOT true of ***entropy***. Because all substances, including individual atoms, have some amount of motion and disorder, their ***entropies*** at 298 K and 1 atm (***S°***) are NOT zero kJ/mol. Furthermore, the ***S*** values for all substances CANNOT be negative!





Entropy at Standard States

Keeping this in mind, it should make sense that while ***S*** can *never* be zero or negative for any molecule, atom, or substance, ***ΔS*** CAN be either positive, negative, or equal to zero.

The reason is because ***ΔS*** is the *difference* between the total ***S*** values of products and reactants:

$$\Delta S_{rxn} = \Sigma n S_{products} - \Sigma n S_{reactants}$$

If ΔS_{rxn} is **positive**, than your products are more *disordered* than your reactants, and your reaction is *entropically favorable*. If ΔS_{rxn} is **negative**, than your products are more *ordered* than your reactants, and your reaction is *entropically unfavorable*.

Take-Homes

For the EXAM, you need to be able to predict if ***entropy*** increases or decreases for a reaction; in other words, if ***ΔS*** is positive or negative.

To do this, you basically just need to ask yourself, "Is the reaction more ordered on the right, or on the left?" If it's more ordered on the left, then its ***ΔS*** is positive, and the reaction is entropically favorable. If it's more ordered on the right, then its ***ΔS*** is negative, and the reaction is entropically unfavorable.

ΔS_{rxn}	Description	Significance
+	Products more disordered than reactants	Reaction is entropically favorable.
–	Reactants more disordered than products	Reaction is entropically unfavorable.

Take-Homes

You should also understand (and it should make sense), that:

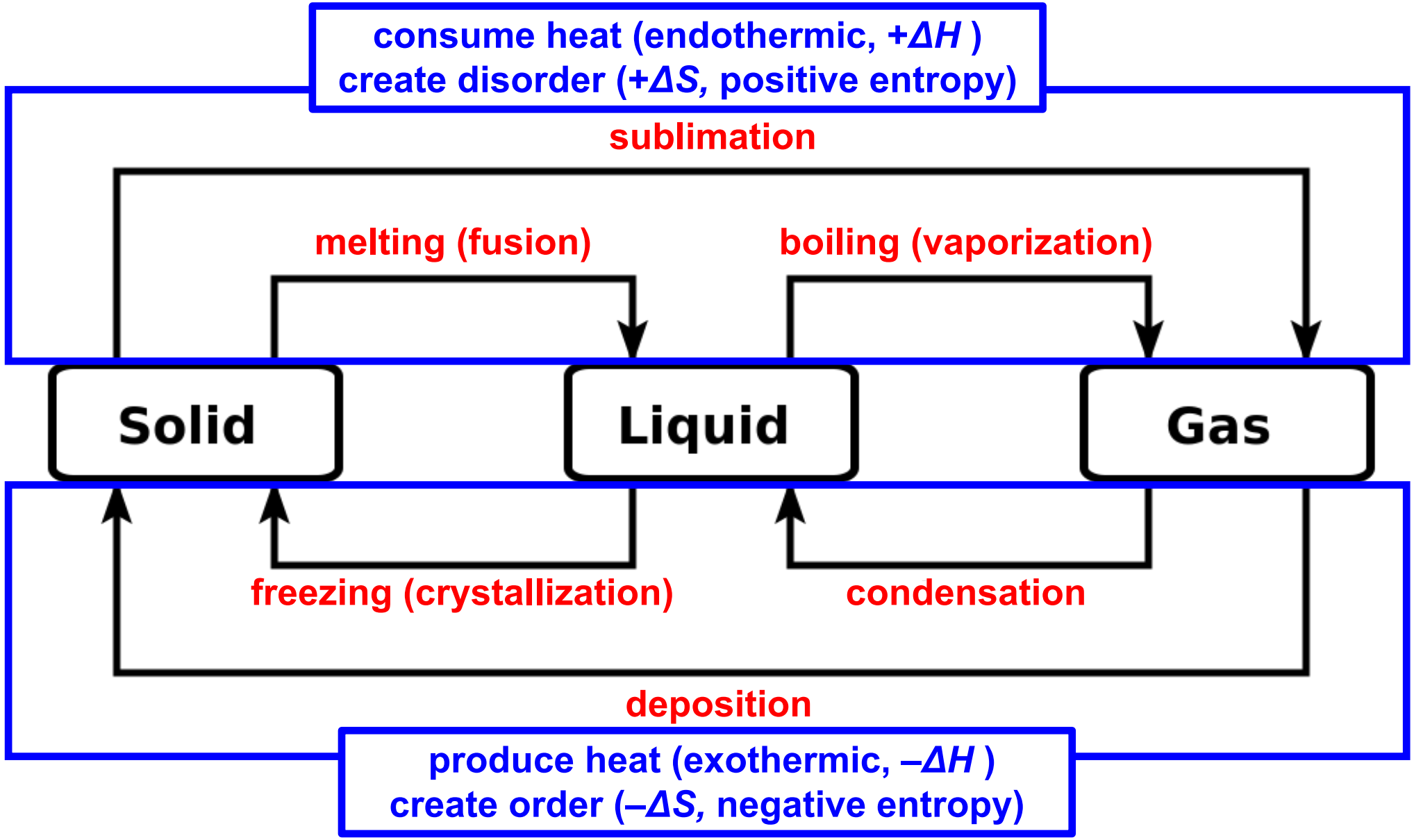
$$S_{solid} < S_{liquid} < S_{gas}$$

ΔS_{rxn}	Description	Significance
+	Products more disordered than reactants	Reaction is entropically favorable.
–	Reactants more disordered than products	Reaction is entropically unfavorable.

Take-Homes

Just so you know, whether or not a reaction will actually proceed is NOT determined completely by either ***ΔS*** *or* ***ΔH***. fact, a reaction's favorability is actually determined by both. Hence, some reactions that are ***entropically unfavorable*** will still occur spontaneously because they are sufficiently ***enthalpically favorable***, and vice versa. We'll talk more about this in a later video in this chapter.

Phase Changes



Phase Changes

Converting from a . . .	to a . . .	is called:	ΔH	ΔS
solid	liquid	fusion		
liquid	gas	vaporization	+ (endothermic)	+
solid	gas	sublimation		
gas	solid	deposition		
gas	liquid	condensation	– (exothermic)	–
liquid	solid	crystallization		

Questions

Please indicate if each of the following reactions or processes will have a positive or negative ***ΔS***, and if they are entropically favorable or entropically unfavorable:

- $C_3H_{8\,(g)} + 5\,O_{2\,(g)} \rightarrow 3\,CO_{2\,(g)} + 4\,H_2O_{\,(g)}$
- $NaCl_{\,(s)} \rightarrow NaCl_{\,(aq)}$
- $2\,NO_{2\,(g)} \rightarrow N_2O_{4\,(g)}$
- $BaF_{2\,(s)} \rightarrow Ba^{2+}_{\,(aq)} + 2\,F^-_{\,(aq)}$

Thermodynamics & Thermochemistry (Using Hess's Law to Calculate ΔH_{rxn})

Three Ways to Calculate ΔH_{rxn}

On the exam, there are three ways to calculate a reaction's overall ***enthalpy change***, or ΔH_{rxn}:

1. By using the formula: $\Delta H_{rxn} = \Sigma \Delta H°_{f\ products} - \Sigma \Delta H°_{f\ reactants}$, for which we did an example ($C_2H_5OH_{(g)} + 3\ O_{2\ (g)} \rightarrow 2\ CO_{2\ (g)} + 3\ H_2O_{(g)}$) in a previous video.

2. By adding reactions and their accompanying ΔH values together to arrive at a final target reaction and *its* ΔH_{rxn}.

this video

3. By using ***bond enthalpy values*** to calculate $\Delta H_{bonds\ broken}$ and $\Delta H_{bonds\ formed}$ and then using the formula: $\Delta H_{rxn} = \Delta H_{bonds\ broken} - \Delta H_{bonds\ formed}$.

later video

Hess's Law

Hess's Law says that if you add multiple reactions together, then the new *overall* reaction's ***ΔH*** is equal to the combined sum of all of the *individual* reactions' ***ΔH***'s. For example:

A + B → C **ΔH = –100 kJ**

C + D → E **ΔH = +50 kJ**

A + B + D → E **ΔH = –100 + 50**

ΔH = –50 kJ

Hess's Law

Because of ***Hess's law***, we can add reactions and their accompanying ***ΔH*** values together to arrive at a final target reaction and *its* ΔH_{rxn}. Before doing an example, we need to remember the following rules:

- If you reverse a reaction, the ***ΔH*** of the new, *reversed* reaction has the same value, but opposite sign. In other words, $\Delta H_{forward} = -\Delta H_{reverse}$.

- If you multiply a reaction by a coefficient, then its ***ΔH*** gets multiplied by that same coefficient. For example:

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \rightarrow H_2O_{\,(l)} \qquad \Delta H_{rxn} = -286\ kJ/mol$$

Thus:

$$2\,H_{2\,(g)} + O_{2\,(g)} \rightarrow 2\,H_2O_{\,(l)} \qquad \Delta H_{rxn} = 2\,(-286) = -572\ kJ/mol$$

Questions

Given the following enthalpy information:

$$Ca_{(s)} + H_{2\,(g)} + O_{2\,(g)} \rightarrow Ca(OH)_{2\,(s)} \qquad \Delta H°_f = -986\ kJ$$

$$\tfrac{1}{2}\,H_{2\,(g)} + \tfrac{1}{2}\,Cl_{2\,(g)} \rightarrow HCl_{\,(g)} \qquad \Delta H°_f = -92\ kJ$$

$$Ca_{(s)} + Cl_{2\,(g)} \rightarrow CaCl_{2\,(s)} \qquad \Delta H°_f = -796\ kJ$$

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \rightarrow H_2O_{\,(l)} \qquad \Delta H°_f = -286\ kJ$$

. . . What is ΔH_{rxn} for the following reaction:

$$Ca(OH)_{2\,(s)} + 2\,HCl_{\,(g)} \rightarrow CaCl_{2\,(s)} + 2\,H_2O_{\,(l)}$$

Thermodynamics & Thermochemistry (Using Bond Dissociation Energies to Calculate ΔH_{rxn})

Three Ways to Calculate ΔH_{rxn}

As I taught you in a previous video, on the EXAM, there are three ways to calculate a reaction's overall ***enthalpy change***, or ΔH_{rxn}:

1. By using the formula: $\Delta H_{rxn} = \Sigma \Delta H°_{f\ products} - \Sigma \Delta H°_{f\ reactants}$, for which we did an example ($C_2H_5OH_{(g)} + 3\ O_{2\ (g)} \rightarrow 2\ CO_{2\ (g)} + 3\ H_2O_{(g)}$) in a previous video.

2. By using ***Hess's Law*** to add reactions and their accompanying ΔH values together to arrive at a final target reaction and *its* ΔH_{rxn}.

prior video

3. By using ***bond enthalpy values*** to calculate $\Delta H_{bonds\ broken}$ and $\Delta H_{bonds\ formed}$ and then using the formula: $\Delta H_{rxn} = \Delta H_{bonds\ broken} - \Delta H_{bonds\ formed}$.

this video

Bond Enthalpies

Sometimes, we do not have ΔH°_f values available, so we can't use $\Delta H_{rxn} = \Sigma \Delta H^\circ_{f\ products} - \Sigma \Delta H^\circ_{f\ reactants}$ or ***Hess's law*** to calculate ΔH_{rxn}.

In such circumstances, we can instead calculate ΔH_{rxn} by:

- Drawing the ***Lewis structures*** of each reactant and product
- Writing down the ΔH value for each *bond* in those structures (these are called ***bond enthalpies***)
- Using the formula $\Delta H_{rxn} = \Delta H_{bonds\ broken} - \Delta H_{bonds\ formed}$

Bond Enthalpies

$$\Delta H_{rxn} = \underbrace{\Delta H_{bonds\ broken}}_{reactants} - \underbrace{\Delta H_{bonds\ formed}}_{products}$$

A few warnings:

- **This** term right here refers to ***reactants***, because it is the *reactants'* bonds that get broken in any chemical reaction. In contrast, **this** term refers to ***products***, because it is the *products'* bonds that get *formed* in any chemical reaction.

- This might seem confusing, because in $\Delta H_{rxn} = \Sigma \Delta H^\circ_{f\ products} - \Sigma \Delta H^\circ_{f\ reactants}$, the **products** appear to the left, and the **reactants** to the right. So, these are two different ways of calculating ΔH_{rxn}.

Bond Enthalpies

$$\Delta H_{rxn} = \underbrace{\Delta H_{bonds\ broken}}_{reactants} - \underbrace{\Delta H_{bonds\ formed}}_{products}$$

A few warnings:

- Using ***bond enthalpies*** to calculate ΔH_{rxn} is not as accurate as using ***enthalpies of formation*** (ΔH°_f). Hence, if you use the ***bond enthalpy*** approach, you will NOT get the exact same answer as you will by using the ΔH°_f approach.

  Thus, the ***bond enthalpy*** approach is somewhat of a ballpark approximation. Nevertheless, it is quite helpful when we lack ΔH°_f values.

Examples

Given the following enthalpy data:

Bond	Approximate ΔH_{bond} (bond enthalpy)
H−H	400 kJ
O=O	500 kJ
H−O	450 kJ

. . . What is ΔH_{rxn} for the following reaction:

$$2\ H_{2\ (g)} + O_{2\ (g)} \rightarrow 2\ H_2O_{\ (g)}$$

Examples

Given *this* enthalpy data:

Bond	Approximate ΔH_{bond} (bond enthalpy)
C−H	410 kJ
C−C	350 kJ
O=O	500 kJ
C=O	800 kJ
H−O	450 kJ

. . . What is ΔH_{rxn} for *this* reaction:

***n*-propane $_{(g)}$ + oxygen gas → carbon dioxide $_{(g)}$ + water $_{(g)}$**

Thermodynamics & Thermochemistry (Gibbs Free Energy: An Intro)

Reaction Spontaneity

In the world of ***thermodynamics*** and ***thermochemistry***, we often care about determining whether or a not a reaction will happen spontaneously, as written. A reaction that *does* proceed spontaneously is called a ***spontaneous reaction***, and one that does *not* is called a ***nonspontaneous reaction***.

In a past video, I mentioned that whether or not a reaction will actually proceed (that is, whether or not it's ***spontaneous***) is NOT determined solely by either ***ΔS*** (change in ***entropy***) or ***ΔH*** (change in ***enthalpy***). In reality, a reaction's ***spontaneity*** is actually determined by both ***ΔS*** and ***ΔH***.

Because of this, some reactions that have unfavorable ***ΔS*** values can *still happen*, if they have sufficiently favorable ***ΔH*** values, and vice versa.

Gibbs Free Energy

ΔS and ***ΔH*** come together in the following equation:

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

Where ***T*** is the reaction's temperature (in **K**), and ***ΔG*** is something called ***Gibbs Free Energy***.

If ***ΔG*** is negative, the reaction *will* occur spontaneously, as written. If ***ΔG*** is positive, then the reaction will *not* occur spontaneously. If ***ΔG*** = 0, then the reaction is at equilibrium.

ΔG	**Reaction is:**
negative	Spontaneous
positive	Nonspontaneous
zero	At equilibrium

Standard Conditions

Before continuing, I need to explain the difference between ***ΔG*** and ***ΔG°***. ***ΔG°*** (also called ***ΔG-naught***) is the change in ***Gibbs free energy*** under standard conditions.

Please do not confuse this with ***standard temperature pressure*** (***STP***). ***STP*** is 273 K (0°C), 1.0 atm, and no specific concentration.

Again, then, ***ΔG°*** is the change in ***Gibbs free energy*** specifically under standard conditions, while ***ΔG*** is more generic: the ***Gibbs free energy*** change under nonstandard conditions of any variety. By analogy, ***ΔS°*** and ***ΔH°*** are the changes in ***entropy*** and ***enthalpy***, respectively, under these same standard conditions. Thus, we can rewrite our equation as follows:

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

Gibbs Free Energy

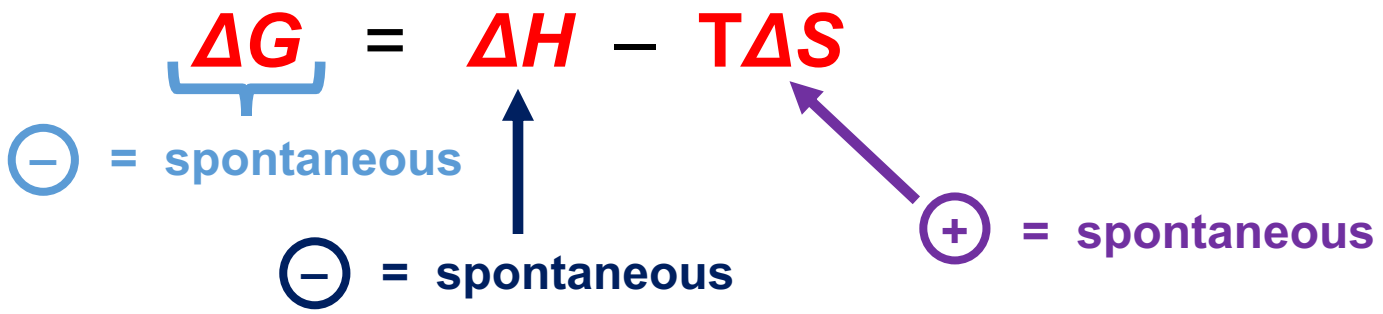
When it comes to determining if a reaction or process is ***spontaneous***, ***ΔG*** is the be-all-end-all. In other words, with regard to reaction ***spontaneity***, the buck stops here.

This chart summarizes the impact of each sign (either **+** or **–**) of ***ΔH*** and ***ΔS*** on ***ΔG*** and on your reaction's spontaneity. You need memorize the information on this chart for the EXAM.

ΔH	***ΔS***	***–TΔS***	***ΔG***	**Impact on the reaction**
–	**+**	**–**	**–**	spontaneous at all temperatures
+	**–**	**+**	**+**	nonspontaneous at all temperatures
–	**–**	**+**	depends	spontaneous at low temperatures
+	**+**	**–**	depends	spontaneous at high temperatures

Gibbs Free Energy

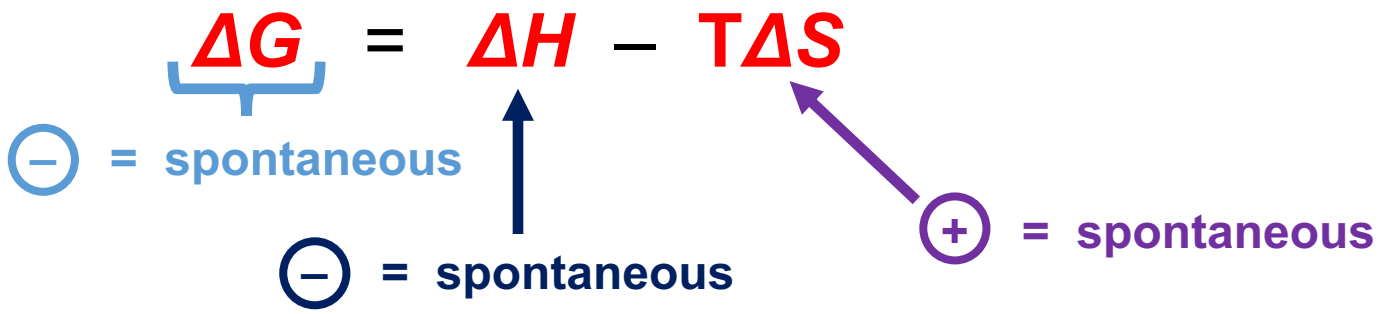
Now, if you prefer *not* to memorize the previous chart, then you can instead just memorize this equation and think about it mathematically:



Please remember: a negative ***ΔG*** means a spontaneous reaction. This is more mathematically likely if ***ΔH*** is also negative. But what about ***ΔS***? Well, if ***ΔH*** is negative, then having a positive ***ΔS*** will make the entire right side of the equation negative, because there is a **–** sign to the left of the ***ΔS*** term.

Gibbs Free Energy

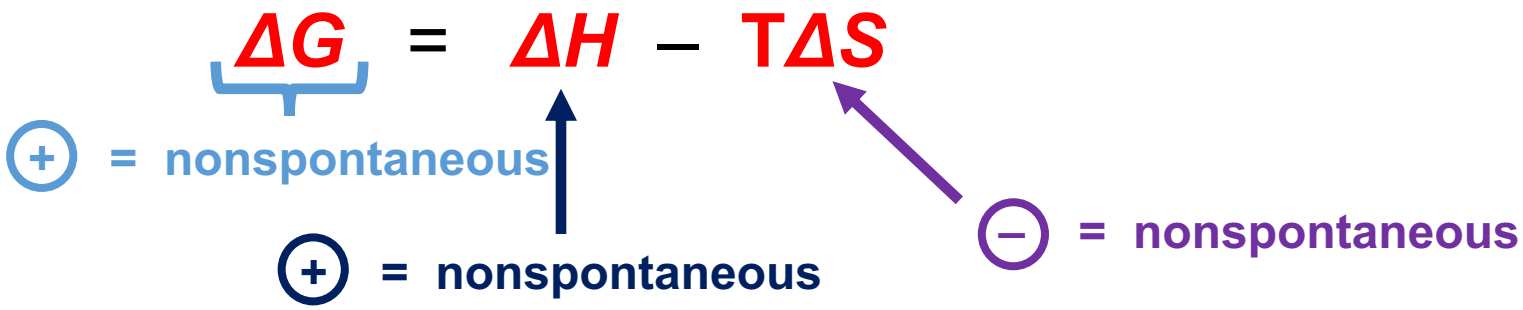
Now, if you prefer *not* to memorize the previous chart, then you can instead just memorize this equation and think about it mathematically:



In other words, a reaction that is ***exothermic*** (negative ***ΔH***) and *increases disorder* (positive ***ΔS***) will give a negative ***ΔG*** and therefore be ***spontaneous*** at any temperature ***T***.

Gibbs Free Energy

Now, if you prefer *not* to memorize the previous chart, then you can instead just memorize this equation and think about it mathematically:



By the same logic, ***endothermic*** reactions (positive ***ΔH***) with *increasing order* (negative ***ΔS***) give positive ***ΔG***'s and are therefore ***nonspontaneous*** at all temperatures ***T***.

Gibbs Free Energy

I'm suggesting, then, that if you can just think about this equation mathematically, then you don't have to memorize the table.

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

You can see that having a **+ΔH** and a **+ΔS**, or vice versa, complicates matters. In such cases, the sign of **ΔG** (either **+** or **–**) will depend on how large **ΔH** and **ΔS** are.

ΔH	ΔS	–TΔS	ΔG	Impact on the reaction
–	+	–	–	spontaneous at all temperatures
+	–	+	+	nonspontaneous at all temperatures
–	–	+	depends	spontaneous at low temperatures
+	+	–	depends	spontaneous at high temperatures

Equation Details

When using this equation:

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

. . . You can hopefully see that, algebraically, $T = (\Delta H / \Delta S)$ when $\Delta G = 0$.

Additionally, when using this equation, make sure that the units for ΔH and ΔS match. Typically ΔH is given in units of kJ, while ΔS is given in units of J, so you will get the wrong answer if you don't make sure your units match!

Questions

Based on your experience with the following physical transformation (the melting of ice):

$$H_2O_{(s)} \rightarrow H_2O_{(l)}$$

- Is ***ΔH*** for this phase change positive or negative at room temperature (25 °C)?
- Is ***ΔS*** for this phase change positive or negative?
- Considering your answers to the previous questions, does this phase change occur spontaneously at room temperature? Is its ***ΔG*** positive or negative?

Questions

$$H_2O_{(s)} \rightarrow H_2O_{(l)}$$

- Is ***ΔH*** for this phase change positive or negative at room temperature (25 °C)?

  feels cold = endothermic = ***ΔH*** is positive

- Is ***ΔS*** for this phase change positive or negative?

  solid → liquid = becoming more disordered = ***ΔS*** is positive

- Considering your answers to the previous questions, does this phase change occur spontaneously at room temperature? Is its ***ΔG*** positive or negative?

$$\underbrace{\Delta G}_{\ominus = \text{spontaneous}} = \Delta H - T\Delta S$$

ΔH: $+$

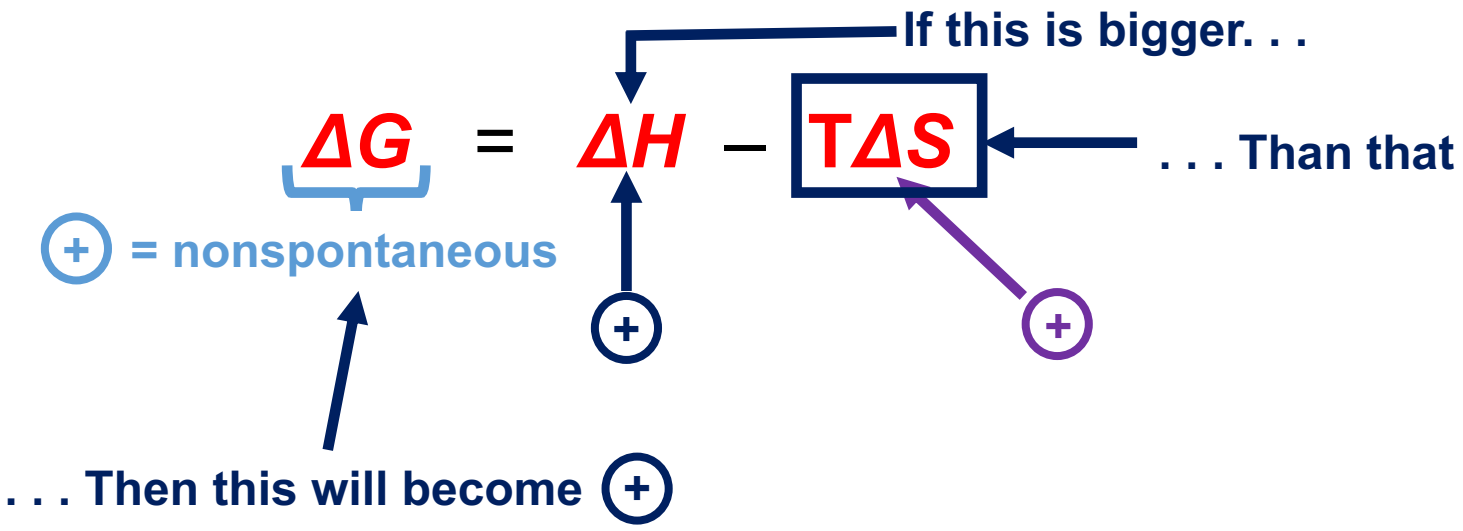
$T\Delta S$: $+$

Questions

Given that this reaction is spontaneous at room temperature (298K, 25 °C), what could you do to make it nonspontaneous?

$$H_2O_{(s)} \rightarrow H_2O_{(l)}$$

Answer:



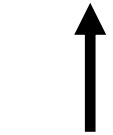
Questions

Given that this reaction is spontaneous at room temperature (298K, 25 °C), what could you do to make it nonspontaneous?

$$H_2O_{(s)} \rightarrow H_2O_{(l)}$$

Answer:

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



make *T* smaller

Questions

What can be said about an endothermic reaction that is accompanied by an increase in entropy?

$$\Delta G = \Delta H - T\Delta S$$ ← (+)

X A. The Gibbs free energy change of the reaction has a negative value at all temperatures.

X B. The reaction will be spontaneous at all temperatures.

C. The reaction will be spontaneous above a certain temperature.

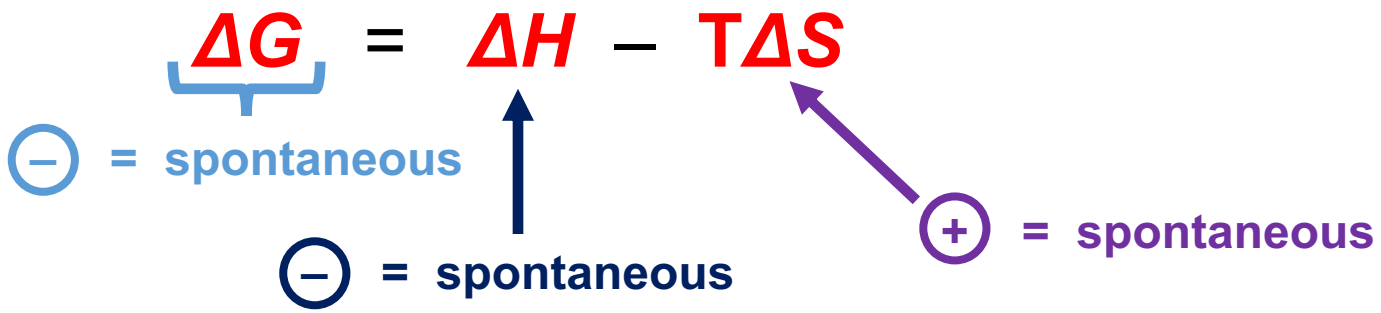
X D. The reaction will be spontaneous below a certain temperature.

X E. The reaction is spontaneous only at 25 °C.

Thermodynamics & Thermochemistry (Gibbs Free Energy: Conclusions)

To Review

In our last video, I taught you about ***Gibbs free energy***, which is calculated using the following equation:



I also taught you that a negative ***ΔG*** means your reaction is spontaneous, which is more mathematically likely if ***ΔH*** is also negative. But what about ***ΔS****?* Well, if ***ΔH*** is negative, then having a positive ***ΔS*** will make the entire right side of the equation negative, because there is a **–** sign to the left of the ***ΔS*** term.

To Review

I summarized this all in the following chart, which you need either memorize or be able to derive by mathematically analyzing the ***Gibbs equation***.

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

The tricky part is this section, where spontaneity depends on which term (either ΔH or ΔS) is larger.

ΔH	ΔS	$-T\Delta S$	ΔG	Impact on the reaction
–	+	–	–	spontaneous at all temperatures
+	–	+	+	nonspontaneous at all temperatures
–	–	+	depends	spontaneous at low temperatures
+	+	–	depends	spontaneous at high temperatures

To Review

I also taught you the difference between ***ΔG*** and ***ΔG°***. ***ΔG°*** (also called ***ΔG-naught***) is the change in ***Gibbs free energy*** under standard conditions. Standard conditions are 298 K (25 °C), 1.0 atm, and 1.0 M concentration.

Do NOT confuse ***standard conditions*** with ***standard temperature pressure*** (***STP***). ***STP*** is 273 K (0°C), 1.0 atm, and no specific concentration.

Again, ***ΔG°*** is the change in ***Gibbs free energy*** specifically under standard conditions, while ***ΔG*** is just the ***Gibbs free energy*** change under nonstandard conditions of any variety. By analogy, ***ΔS°*** and ***ΔH°*** are the changes in ***entropy*** and ***enthalpy***, respectively, under these same standard conditions. Thus, we can rewrite our equation as follows:

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

Relating ΔG to ΔG°

We can mathematically interrelate ***ΔG*** and ***ΔG°*** by using the following equation:

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

Where:

- ***R*** is the ideal gas constant, 8.314 J/mol-K (not to be confused with the *other* version of the ***ideal gas constant***, 0.0821 L-atm/mol-K)
- ***Q*** is the reaction quotient. We talked about this in our past chapter on chemical equilibrium. ***Q*** is just like ***K*** (a ratio of products over reactants), except that ***Q*** may or may not be at equilibrium, while ***K*** (the equilibrium rate constant) is.

Relating ΔG to ΔG°

We can mathematically interrelate ***ΔG*** and ***ΔG°*** by using the following equation:

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

This equation is useful because real-life reactions are almost never run at *standard conditions*, so it's helpful to be able to convert nonstandard results into tabulatable, standard ones.

With that said, it is very unlikely that you will encounter any calculation questions involving this equation on the exam. However, it is important to understand that when ***ΔG* = 0**, your reaction is at equilibrium, but that is not necessarily true when ***ΔG°* = 0**. When ***ΔG°* = 0**, your reaction is at equilibrium under *standard conditions*, but not necessarily under *all* conditions. Because ***ΔG*** has a broader meaning, ***ΔG* = 0** indicates that your reaction is at equilibrium under all conditions.

K, *Q*, ΔG, and ΔG°

As I just mentioned, the ***reaction quotient*** ***Q*** is just like ***K*** (that is, a specific ratio of products over reactants), except that ***Q*** may or may not be at equilibrium, but ***K*** specifically is.

Now, as I *also* just mentioned, if ΔG (not ΔG°) is equal to zero, then your reaction is at equilibrium. When this happens, we can rearrange the following equation:

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

. . . To become:

$$0 = \Delta G^\circ + RT \ln(K)$$

K, *Q*, ΔG, and ΔG°

As I just mentioned, the ***reaction quotient*** ***Q*** is just like ***K*** (that is, a specific ratio of products over reactants), except that ***Q*** may or may not be at equilibrium, but ***K*** specifically is.

Now, as I *also* just mentioned, if ΔG (not ΔG°) is equal to zero, then your reaction is at equilibrium. When this happens, we can rearrange the following equation:

$$0 = \Delta G^\circ + RT \ln(K)$$

This equation can be rearranged further to give:

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

K, *Q*, ΔG, and ΔG°

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

I need to explain a little bit more about ***K*** here. To review (and you should remember this from a past video in our chemical equilibrium chapter), for any generic reaction:

Its ***equilibrium rate constant*** (in terms of concentration), K_c, is:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K, Q, ΔG, and ΔG°

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

You should also remember (and it should make sense) that when $K > 1$, products are favored at equilibrium. When $K < 1$, reactants are favored at equilibrium. When $K = 1$, reactants and products are equally favored at equilibrium.

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K, Q, ΔG, and ΔG°

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

With this in mind, it should also make sense that when $K > 1$, the reaction will be spontaneous in the *forward direction, toward products*. When $K < 1$, reactants are favored, so the reaction wants to drift left toward the reactants, *so the reaction will be nonspontaneous*.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K, *Q*, ΔG, and ΔG°

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

This is all summarized in the following table:

ΔG°	K_{eq}	significance
negative	$K > 1$	Reaction is spontaneous as written; products favored
positive	$K < 1$	Reaction is nonspontaneous as written; reactants favored
zero	$K = 1$	Reactants and products equally favored