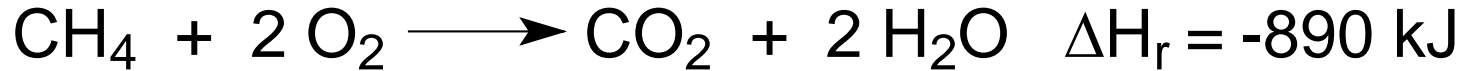


Chemical Thermodynamics

studies energy changes during the process of chemical and physical changes in matter

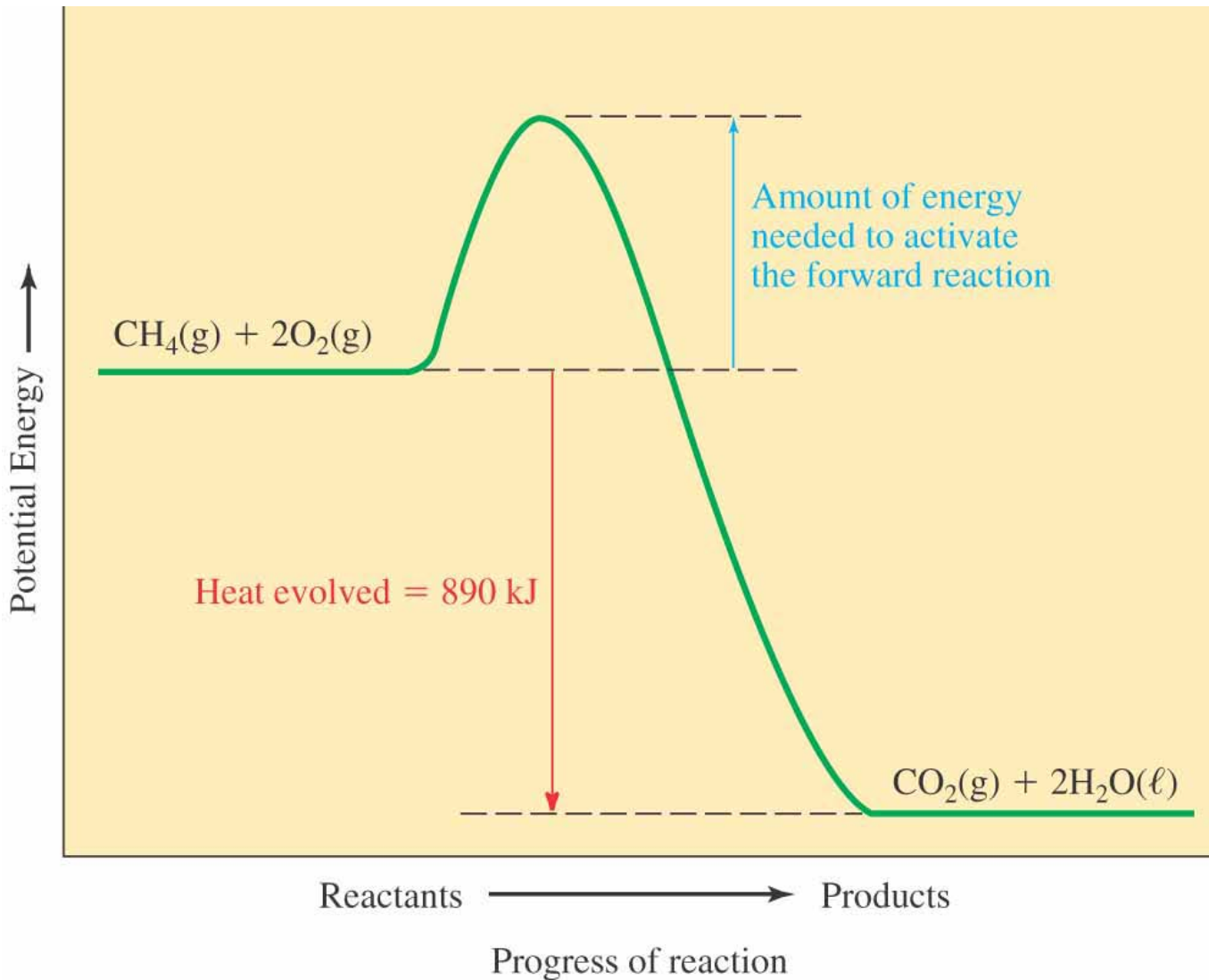
Recall endothermic and exothermic reactions mentioned in chemistry 1

An Example



are both examples of ways to represent
an **exothermic** reaction

An Energy Diagram



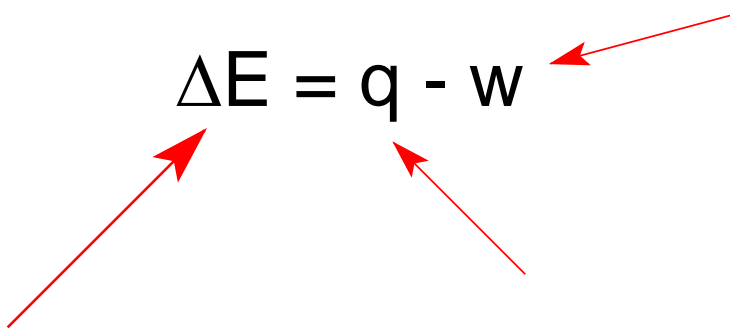
The Universe

According to thermodynamics the universe is made of two parts:

The 1st Law of Thermodynamics

is the Law of Conservation of Energy

can be stated as

$$\Delta E = q - w$$


State Functions

properties that define a state

indicated by capital letters ...

usually expressed as a change in state

ΔE ΔH ΔG ΔS

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

An analogy

"A car has traveled for 70 miles" is a scalar quantity.

We don't know how or why, just a value.

"In going from Austin to San Antonio,
a distance of 70 miles is traversed."

This is a state function.

The final state of the system is San Antonio and the initial state is Austin. Because of this change of state, a difference of 70 miles results.

Calorimetry

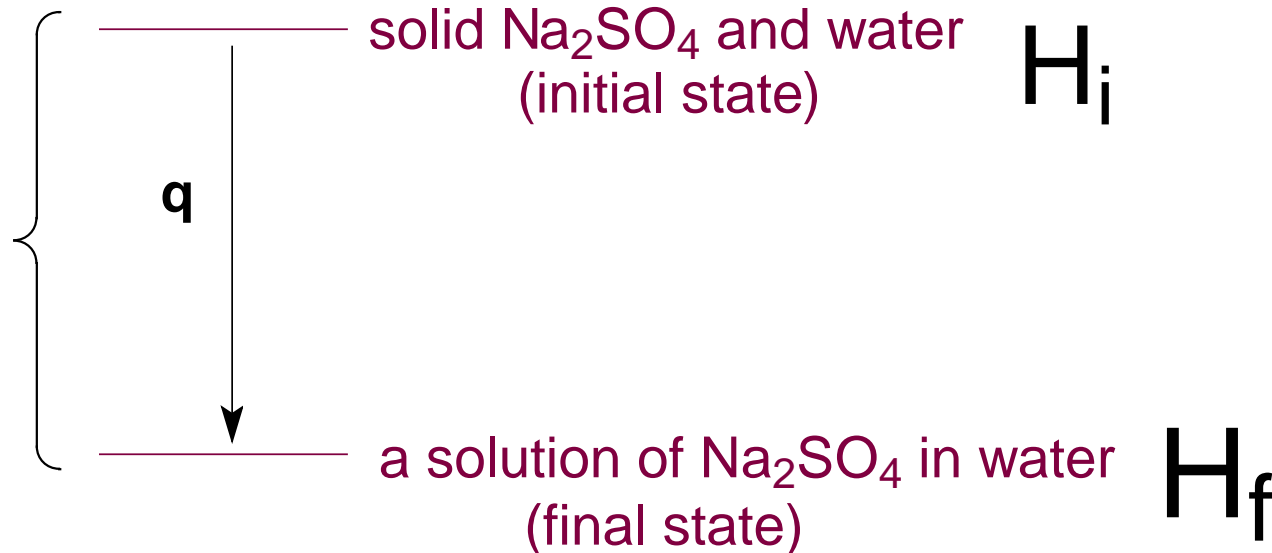
$$\Delta H = H_f - H_i = q$$

is a statement seen in most experiments on calorimetry

Dissolving Na_2SO_4 into water releases heat.

The heat released is q (an amount).

It is the result of changing the system:



Standard States

Since state functions vary with conditions, a standard set of conditions are specified:

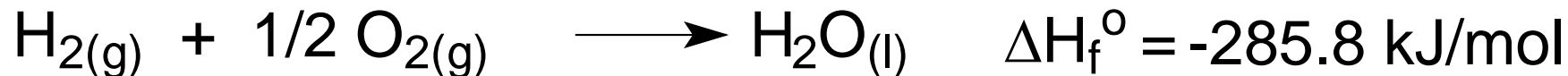
1. for pure substances, it is their most stable state @ 25°C ($\text{H}_{2(g)}$, $\text{Fe}_{(s)}$, etc.)
2. for gases, 1 atm pressure
3. for solutions, 1M

Standard Enthalpies (Heats) of Formation

Measuring the heat absorbed or released from forming
1 mol of a compound from the elements in their standard state.

We assign a value of 0 to all elements in their standard states.

an equation to show this:



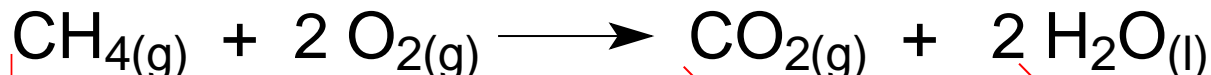
Heats of Reaction

The heat released or absorbed can be calculated for a reaction from a table of standard enthalpies of formation (a table in the back of your text)

$$\Delta H_r^\circ = \sum(\Delta H_f^\circ)_{\text{products}} - \sum(\Delta H_f^\circ)_{\text{reactants}}$$

Example:

Calculate ΔH_r° for the following equation



$$\Delta H_r^\circ = [(1 \text{ mol})\Delta H_{f\text{CO}_2}^\circ + (2 \text{ mol})\Delta H_{f\text{H}_2\text{O}}^\circ] - [(1 \text{ mol})\Delta H_{f\text{CH}_4}^\circ + (2 \text{ mol})\Delta H_{f\text{O}_2}^\circ]$$

Continuing

$$\Delta H_r^\circ = [(1 \text{ mol})\Delta H_f^\circ \text{CO}_2 + (2 \text{ mol})\Delta H_f^\circ \text{H}_2\text{O}] - [(1 \text{ mol})\Delta H_f^\circ \text{CH}_4 + (2 \text{ mol})\Delta H_f^\circ \text{O}_2]$$

$$\Delta H_r^\circ = [(1 \text{ mol})(-393.5 \text{ kJ/mol} + (2 \text{ mol})(-285.8 \text{ kJ/mol})]$$

$$- [(1 \text{ mol})(-74.81 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})]$$



$$\Delta H_r^\circ = [(-393.5 + (-571.6))] - [(-74.81 + 0)] \text{ kJ}$$

$$= (-965.1) - (-74.81) \text{ kJ}$$

$$\Delta H_r^\circ = \mathbf{-890.3 \text{ kJ}}$$

Try One

Q1

Calculate ΔH_r° for the following, using the table of Enthalpies of Formation:



Hess' Law

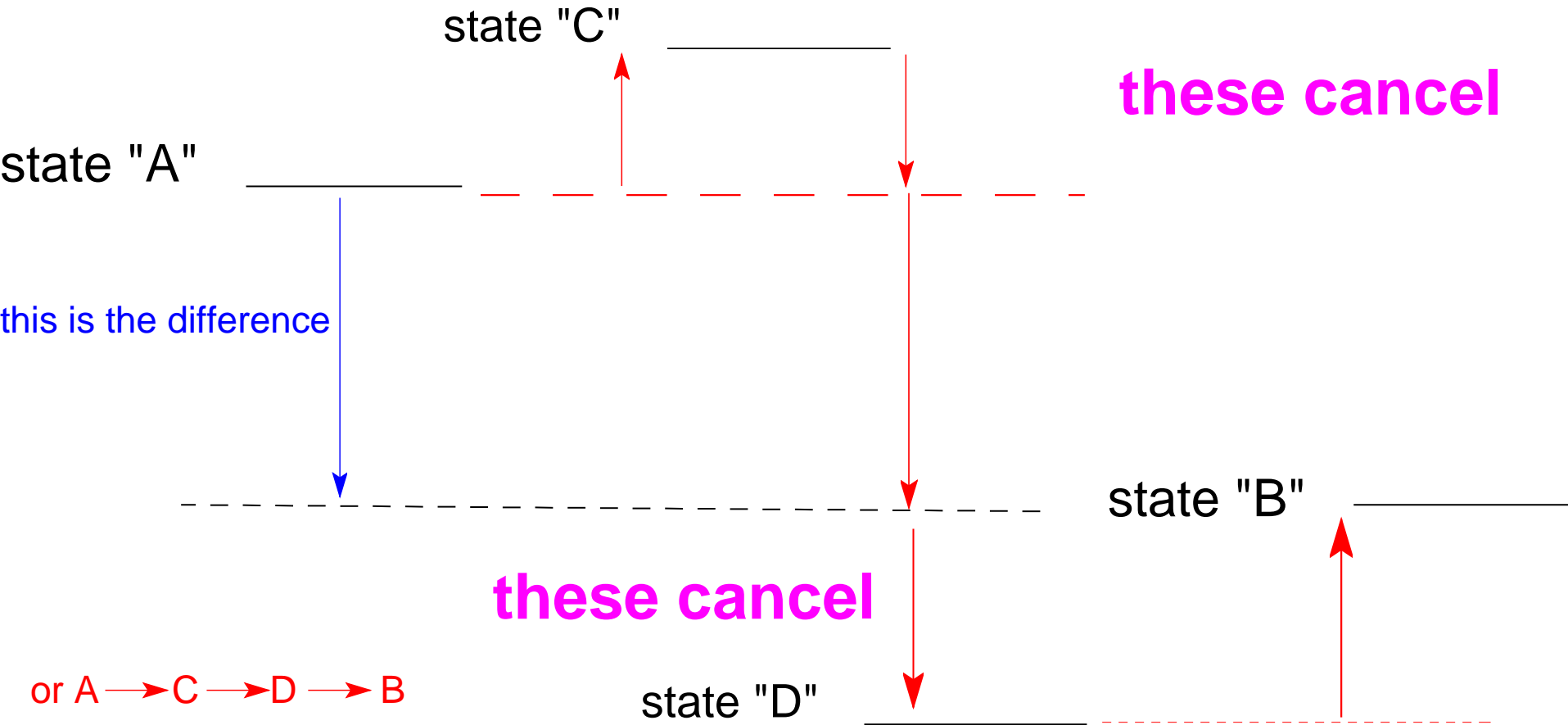
"The enthalpy change for a reaction is the same whether it occurs in one step or by any series of steps."

"pathway independence"

any way you get there must have the same energy involved
(the Law of Conservation of Energy)

An Example

Whether we go directly from A to B ($A \rightarrow B$)



we started at A and ended at B
and the difference must be the same,
regardless of the path taken!

An analogy

If you start a trip in Austin and travel directly to San Antonio on I 35, you are 70 miles from where you started.

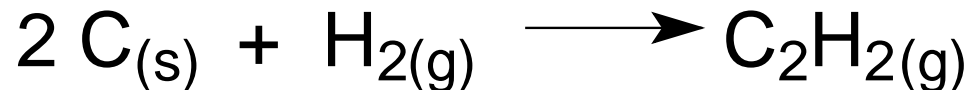
If you started in Austin, drove to Dallas, then to Houston and then to San Antonio, you would still be only 70 miles from where you started!

An Application of Hess' Law

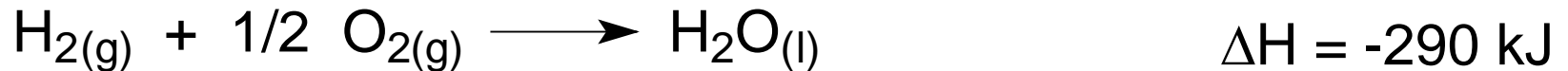
Not only are pathways independent, but
you can manipulate equations
(add together, multiply, reverse them)
to get other equations' energy values

Example

Calculate ΔH for the following equation:



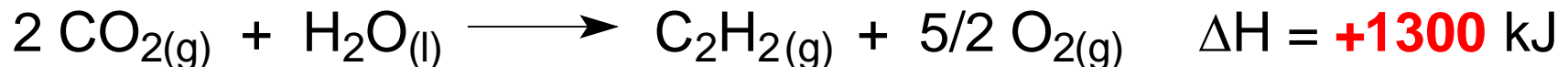
from the following equations:



Strategy

Reverse the first equation to have $\text{C}_2\text{H}_2(\text{g})$ on the right side of the arrow.

(When you reverse an equation, change the sign of ΔH !!)



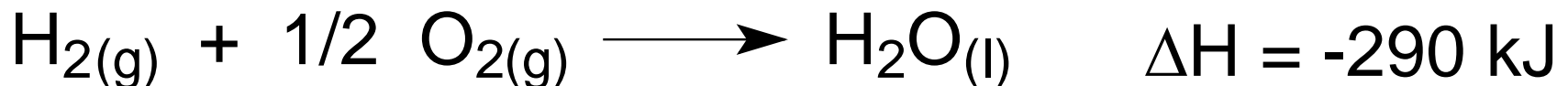
We must get rid of 2 mols CO_2 on the left.

Use the second equation as written, but double all coefficients.

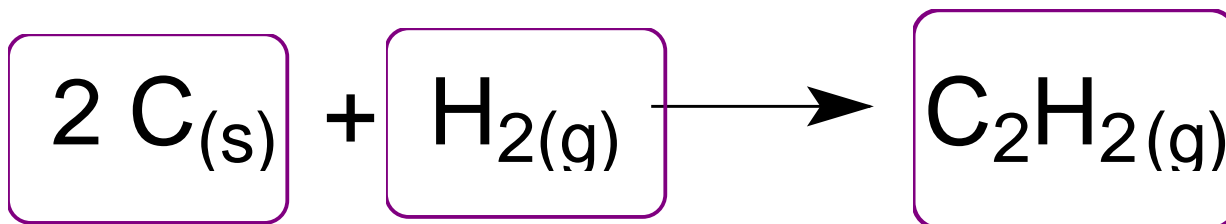
(When you multiply coefficients, multiply ΔH by the same factor!!)



write the third equation as is



Add the Equations

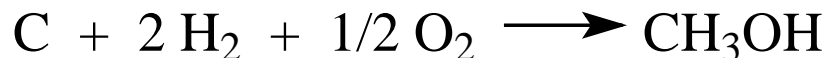


$$\Delta H_r = (+1300 \text{ kJ}) + (-780 \text{ kJ}) + (-290 \text{ kJ}) = \mathbf{+230 \text{ kJ}}$$

Try One

Q2

Calculate ΔH_r for the following:



using the following equations:

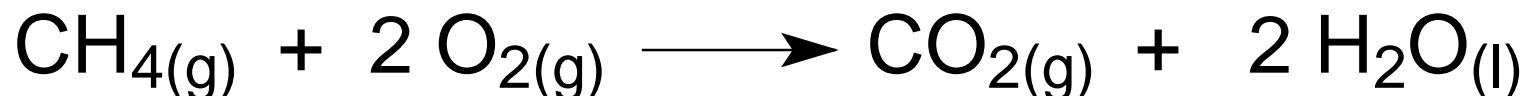


Solution

Bond Energies

During the process of chemical reactions, reactant bonds break and new bonds form.

For every covalent bond there is an energy associated with breaking or forming that bond *"homolytically"* (one electron to each atom)



Lewis structures:

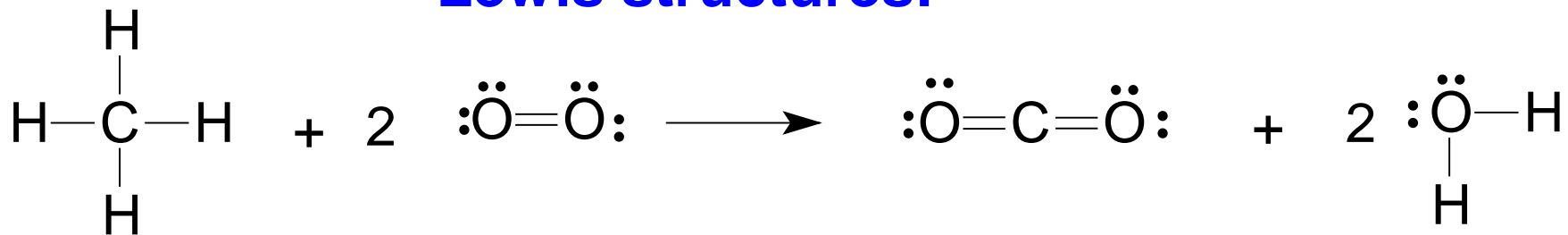


Table of Bond Energies

Average Bond Enthalpies (kJ/mol)

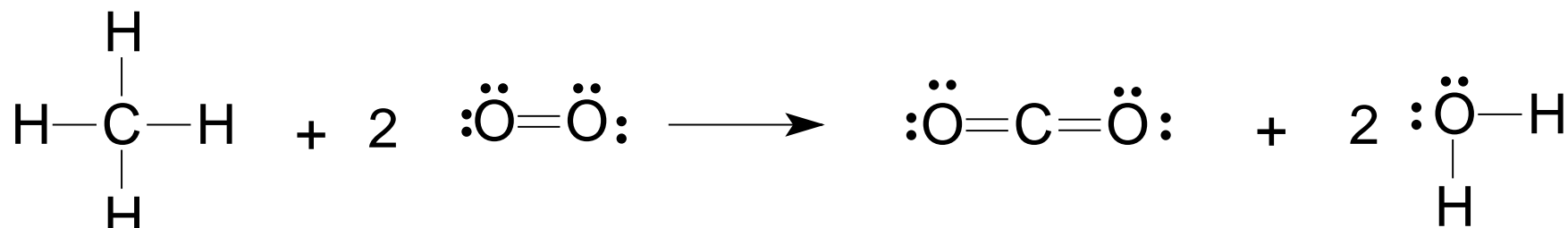
Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941		
C=N	615			S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Continuing



break:

$$4 \text{ C}-\text{H} \quad 4(+413 \text{ kJ}) = +1652 \text{ kJ}$$

$$2 \text{ O}=\text{O} \quad 2(+495 \text{ kJ}) = +990 \text{ kJ}$$

$$+2642 \text{ kJ}$$

form:

$$2 \text{ C}=\text{O} \quad 2(-799 \text{ kJ}) = -1598 \text{ kJ}$$

$$4 \text{ O}-\text{H} \quad 4(-463 \text{ kJ}) = -1852 \text{ kJ}$$

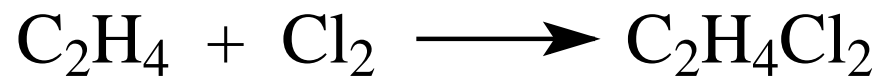
$$-3450 \text{ kJ}$$

$$+2642 \text{ kJ} - 3450 \text{ kJ} = -808 \text{ kJ}$$

Try One

Q3

Calculate ΔH for the following equation, using tables of bond energies.



Entropy

Some processes occur on their own, with no additional "help" by the surroundings.

These events are said to be **spontaneous**

Examples:

a drop of food coloring into a glass of water
diffuses until a uniform color is seen

water freezes at temperatures below the freezing point

ice melts at temperatures above its melting point

Spontaneity

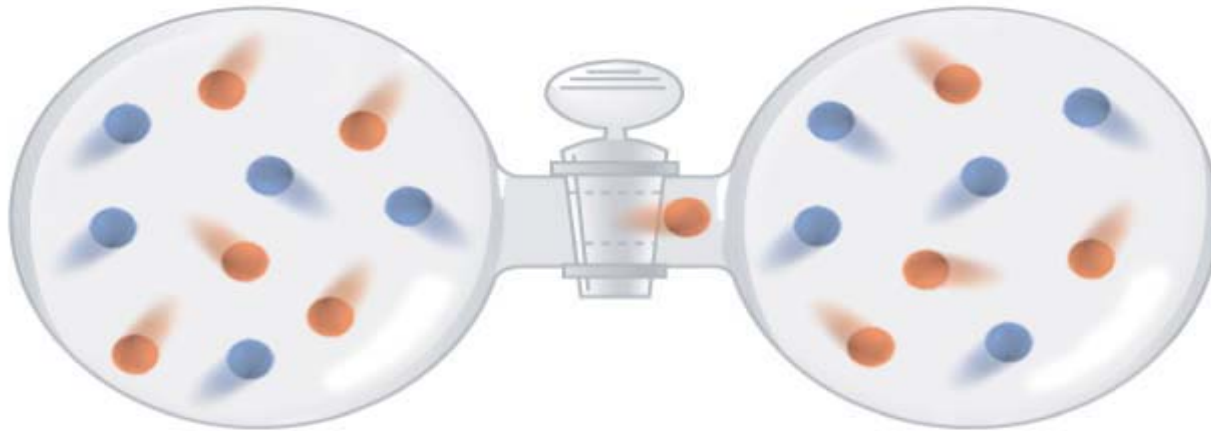
During any physical or chemical change

1. spontaneity is favored when heat is released by the process
2. spontaneity is favored when an increase in disorder or energy distribution occurs

An Illustration



(a) Stopcock closed



(b) Stopcock open

Disorder

Systems tend to distribute their energies and also become more random. This measure of energy distribution and randomness is called **entropy**

This is the Second Law of Thermodynamics

"Every spontaneous change results in an increase in entropy of the universe."

Everything Has Some Entropy

The Third Law of Thermodynamics:

"The entropy of a perfect crystal at absolute zero is "0".

ΔS

Calculated from a table of
"absolute entropies"

TABLE 15-5

*Absolute
Entropies at
298 K for a
Few Common
Substances*

Substance	S^0 (J/mol·K)
C(diamond)	2.38
C(g)	158.0
H ₂ O(l)	69.91
H ₂ O(g)	188.7
I ₂ (s)	116.1
I ₂ (g)	260.6

Don't Forget about Energy!

Systems tend toward low energy (exothermic)

When water freezes spontaneously it releases heat but it becomes more ordered as a crystal. The system has become less random. However the release of heat goes to making the surroundings more random with a broader distribution of energy.

The entropy of the universe (system + surroundings) increases

When ice melts spontaneously, it absorbs heat but becomes less ordered as a liquid, with a broader distribution of energy within the system.

Free Energy (ΔG)

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

ΔG

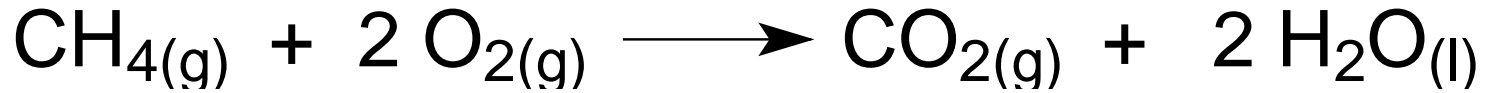
Changes in (Gibbs) free energy determine whether or not a process is spontaneous.

$\Delta G (-)$	spontaneous
$\Delta G(+)$	not spontaneous
$\Delta G(0)$	at equilibrium

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

ΔH	ΔS	ΔG	
-	+	-	(exothermic and more random) <i>most favorable for both</i>
+	-	+	(endothermic and less random) <i>least favorable for both</i>
-	-	?	exothermic and less random depends on which dominates <i>(temperature can be the final influence)</i>
+	+	?	endothermic and more random depends on which dominates <i>(temperature can be the final influence)</i>

An Example



Calculate ΔG° for the reaction at 25°C

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

ΔH_r° has already been calculated $\Delta H_r^\circ = -890.3 \text{ kJ}$

$$\Delta S_r^\circ = \Sigma(S_f^\circ)_{\text{products}} - \Sigma(S_f^\circ)_{\text{reactants}}$$

$$\Delta S_r^\circ = [(1 \text{ mol})S^\circ_{\text{CO}_2} + (2 \text{ mol})S^\circ_{\text{H}_2\text{O}(\text{l})}] - [(1 \text{ mol})S^\circ_{\text{CH}_4} + (2 \text{ mol})S^\circ_{\text{O}_2}]$$

Continuing

$$\Delta S_r^{\circ} = [(1 \text{ mol})213.6 \text{ Jmol}^{-1}\text{K}^{-1} + (2 \text{ mol})(69.91 \text{ Jmol}^{-1}\text{K}^{-1})] \\ - [(1 \text{ mol})186.2\text{Jmol}^{-1}\text{K}^{-1} + (2 \text{ mol})(205.0\text{Jmol}^{-1}\text{K}^{-1})]$$

$$\Delta S_r^{\circ} = [353.42 \text{ JK}^{-1}] - [596.2 \text{ JK}^{-1}]$$

$$\Delta S_r^{\circ} = -242.8 \text{ JK}^{-1} \quad \Delta S_r^{\circ} = -242.8 \text{ JK}^{-1} \left(\frac{1 \text{ kJ}}{1 \times 10^3 \text{ J}} \right) = \mathbf{-0.2428 \text{ kJK}^{-1}}$$

$$\Delta G_r^{\circ} = \Delta H_r^{\circ} - T\Delta S_r^{\circ}$$

$$\Delta G_r^{\circ} = (-890.3 \text{ kJ}) - (298\text{K})(-0.2428 \text{ kJK}^{-1}) \\ = (-890.3 \text{ kJ}) - (-72.4 \text{ kJ}) \\ = \mathbf{-817.9 \text{ kJ}}$$

Try One

Q4

Calculate ΔG_r° for the following:

