

# *GENERAL CHEMISTRY*

## *Chapter 4* **Thermochemistry**

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# The Nature of Energy

## Kinetic Energy and Potential Energy

- Kinetic energy is the energy of motion:

$$E_k = \frac{1}{2}mv^2$$

- Potential energy is the energy an object possesses by virtue of its position.
- Potential energy can be converted into kinetic energy.  
Example: a bicyclist at the top of a hill.

# The Nature of Energy

## Kinetic Energy and Potential Energy

- Electrostatic potential energy,  $E_d$ , is the attraction between two oppositely charged particles,  $Q_1$  and  $Q_2$ , a distance  $d$  apart:

$$E_d = \frac{\kappa Q_1 Q_2}{d}$$

- The constant  $\kappa = 8.99 \times 10^9 \text{ J-m/C}^2$ .
- If the two particles are of opposite charge, then  $E_d$  is the electrostatic attraction between them.
- Force:  $\propto 1/d^2$
- Energy: work: integration  $F dl \rightarrow \propto 1/d$

# Units of Energy

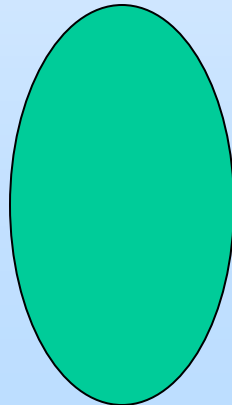
- SI Unit for energy is the joule, J:
- We sometimes use the calorie instead of the joule:
- 1 cal = 4.184 J (exactly)
- A nutritional Calorie:
- 1 Cal = 1000 cal = 1 kcal

$$\begin{aligned} E_k &= \frac{1}{2}mv^2 = \frac{1}{2}(2 \text{ kg})(1 \text{ m/s})^2 \\ &= 1 \text{ kg} \cdot \text{m/s}^2 = 1 \text{ J} \end{aligned}$$

# Systems and Surroundings

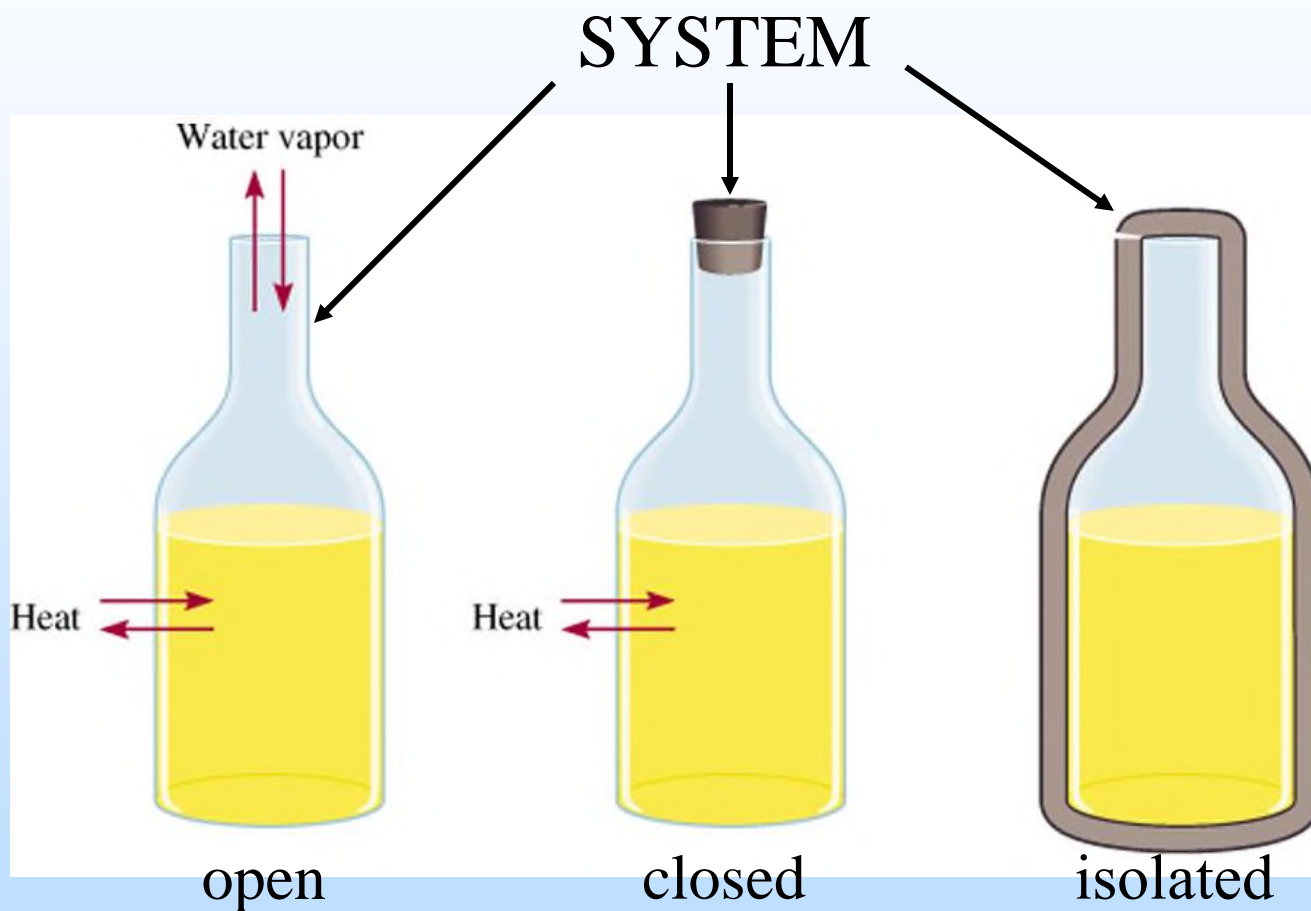
## Analyzing Energy Changes

- System: part of the universe we are interested in.
- Surroundings: the rest of the universe.
- $\text{Sys.} + \text{Surr.} = \text{Universe}$



**Thermochemistry** is the study of heat change in chemical reactions.

The **system** is the specific part of the universe that is of interest in the study.



**Exchange:**    mass & energy

energy

nothing

# Transferring Energy

## Work and Heat

- Force is a push or pull on an object.
- Work is the product of force applied to an object over a distance:

$$w = F \times d = \int Fdl$$

- Energy is the work done to move an object against a force.
- Heat is the transfer of energy between two objects.
- **Energy** is the capacity to do work or transfer heat.
- Quality: work is better in quality (direction)

# The First Law of Thermodynamics

Energy is neither created or destroyed

- Total energy lost by a system equals the total energy gained by a surrounding.
- **Internal Energy:** total energy of a system (kinetic + potential).
- Cannot measure absolute internal energy.
- Example: Cup of water: bonding energy
- Estimate change in internal energy,  $\Delta E = E_{\text{final}} - E_{\text{initial}}$

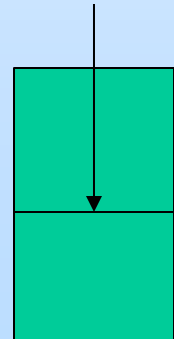




# Relating $\Delta E$ to Heat and Work

- Energy of (system + surroundings) is constant.
- Any energy transferred from a system must be transferred to the surroundings (and *vice versa*).
- From the first law of thermodynamics:  
**when a system undergoes a physical or chemical change, the change in internal energy is given by the heat added to or absorbed by the system plus the work done on the system:**

$$\Delta E = q + w$$



**System**

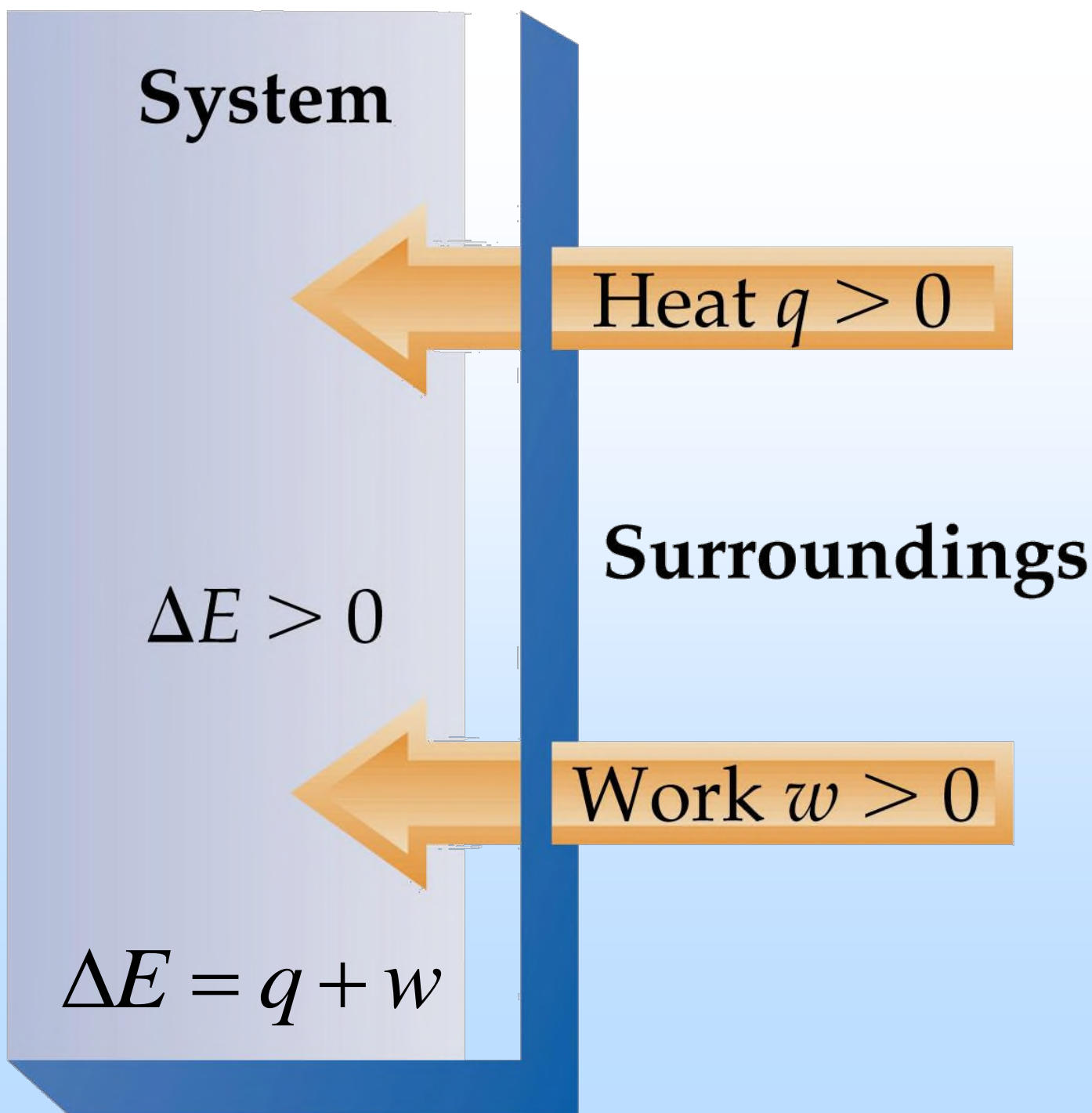
Heat  $q > 0$

$$\Delta E > 0$$

**Surroundings**

Work  $w > 0$

$$\Delta E = q + w$$



# Sign Conventions

## Sign Convention for $q$ :

$q > 0$ : Heat is transferred from the surroundings to the system

$q < 0$ : Heat is transferred from the system to the surroundings

## Sign Convention for $w$ :

$w > 0$ : Work is done by the surroundings on the system

$w < 0$ : Work is done by the system on the surroundings

## Sign of $\Delta E = q + w$

$q > 0$  and  $w > 0$ :  $\Delta E > 0$

$q > 0$  and  $w < 0$ : The sign of  $\Delta E$  depends on the magnitudes of  $q$  and  $w$

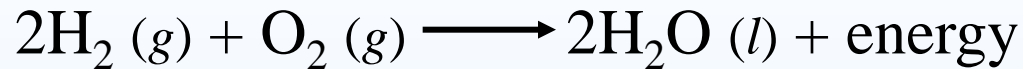
$q < 0$  and  $w > 0$ : The sign of  $\Delta E$  depends on the magnitudes of  $q$  and  $w$

$q < 0$  and  $w < 0$ :  $\Delta E < 0$

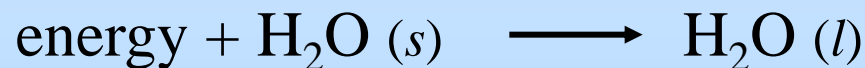
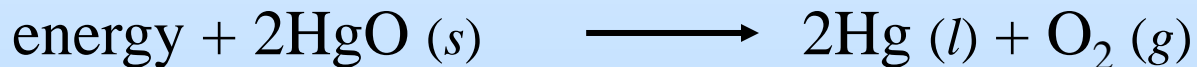
# Exothermic and Endothermic Processes

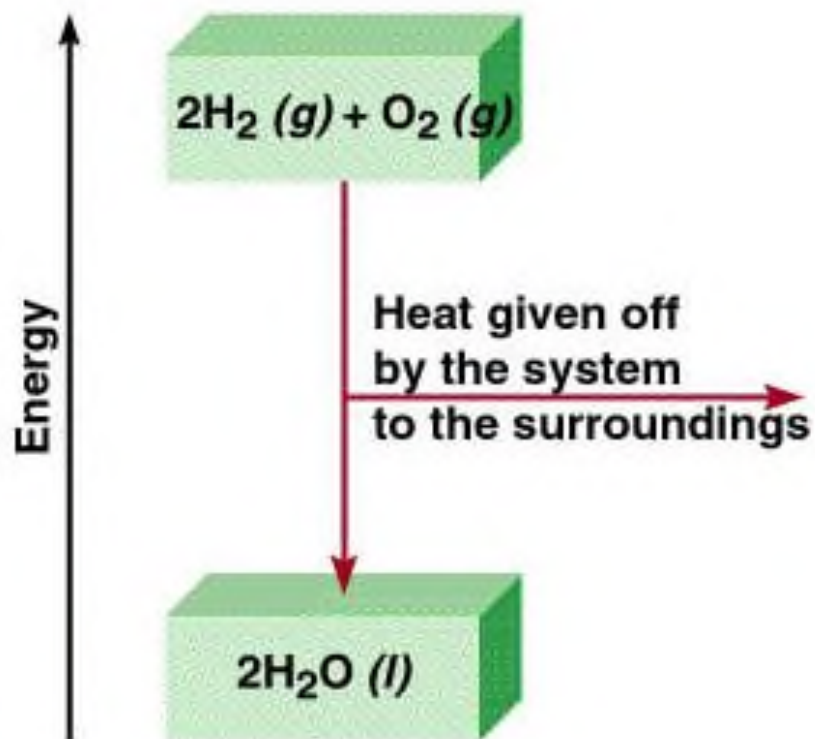
- **Endothermic**: absorbs heat from the surroundings.
- **Exothermic**: transfers heat to the surroundings.
- An endothermic reaction feels cold.
- An exothermic reaction feels hot.

***Exothermic process*** is any process that gives off heat – transfers thermal energy from the system to the surroundings.

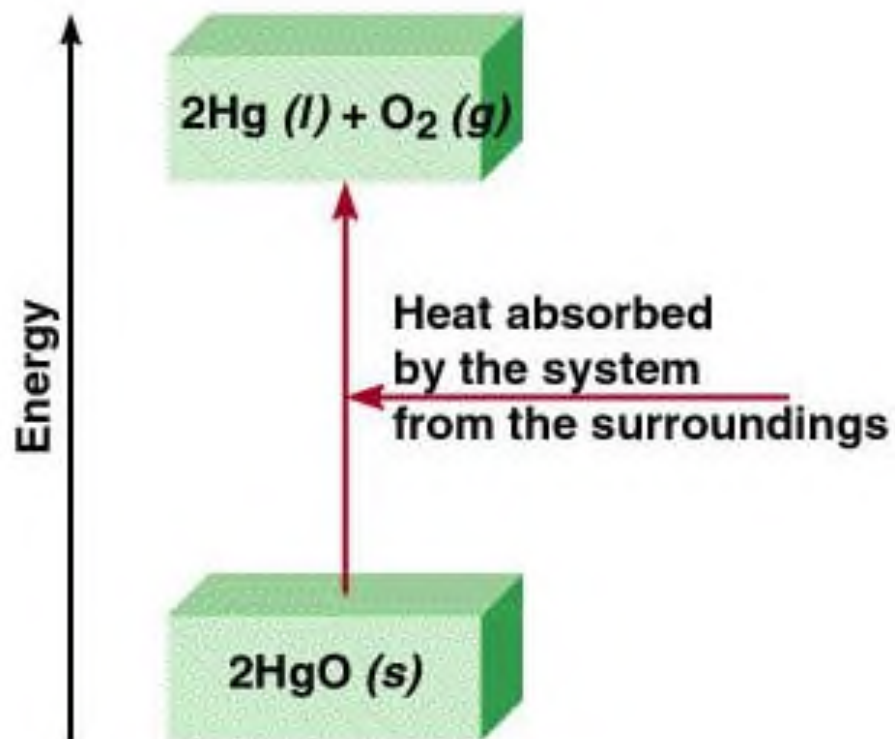


***Endothermic process*** is any process in which heat has to be supplied to the system from the surroundings.





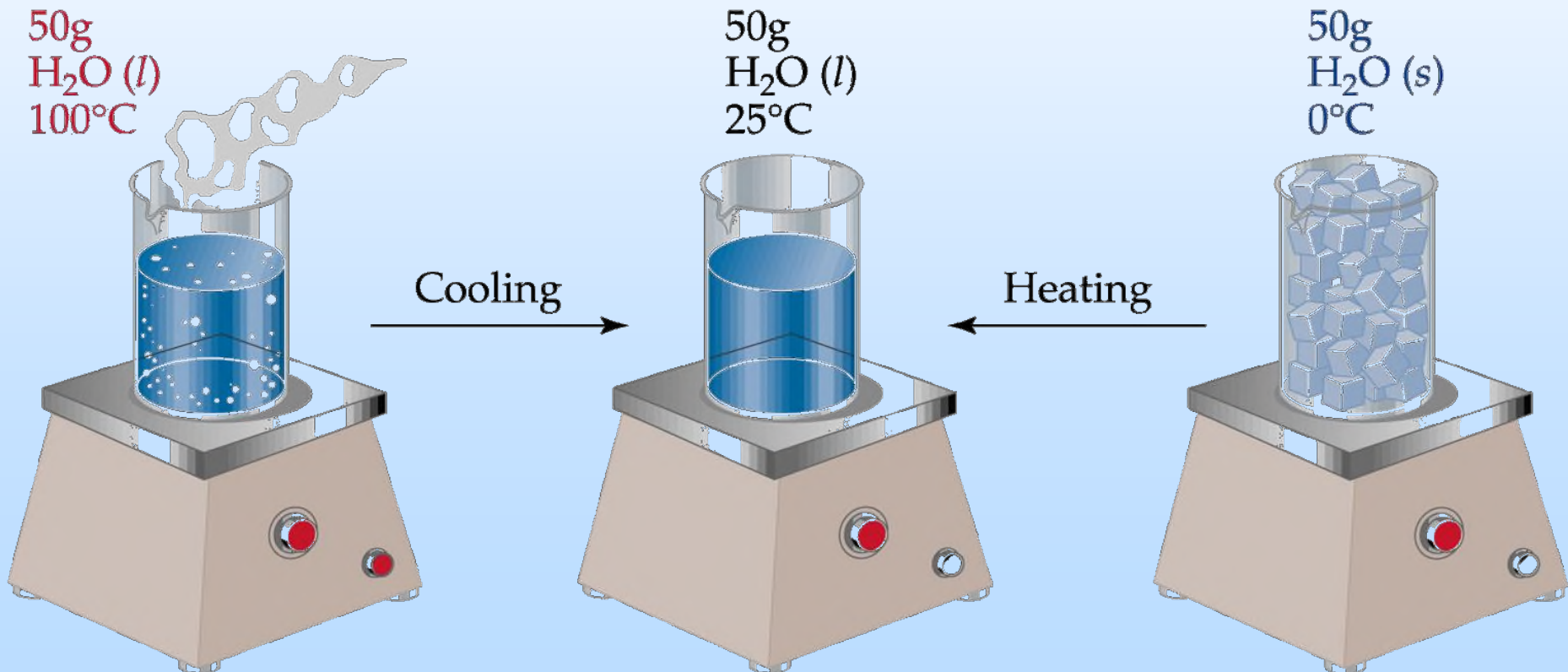
Exothermic



Endothermic

# State Functions

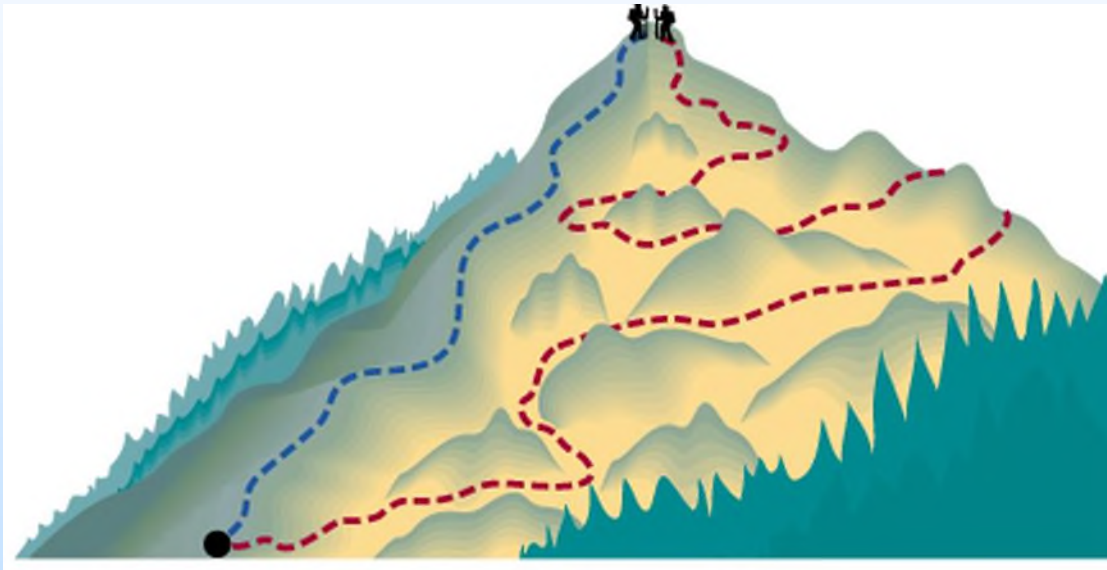
- State function: depends only on the initial and final states of system, not on how the internal energy is used.



# Thermodynamics

*State functions* are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy , pressure, volume, temperature, concentration



$$\Delta E = E_{final} - E_{initial}$$

$$\Delta P = P_{final} - P_{initial}$$

$$\Delta V = V_{final} - V_{initial}$$

$$\Delta T = T_{final} - T_{initial}$$

Potential energy of **hiker 1** and **hiker 2** is the same even though they took different paths.

state parameters = state function



# Work of chemical rxn

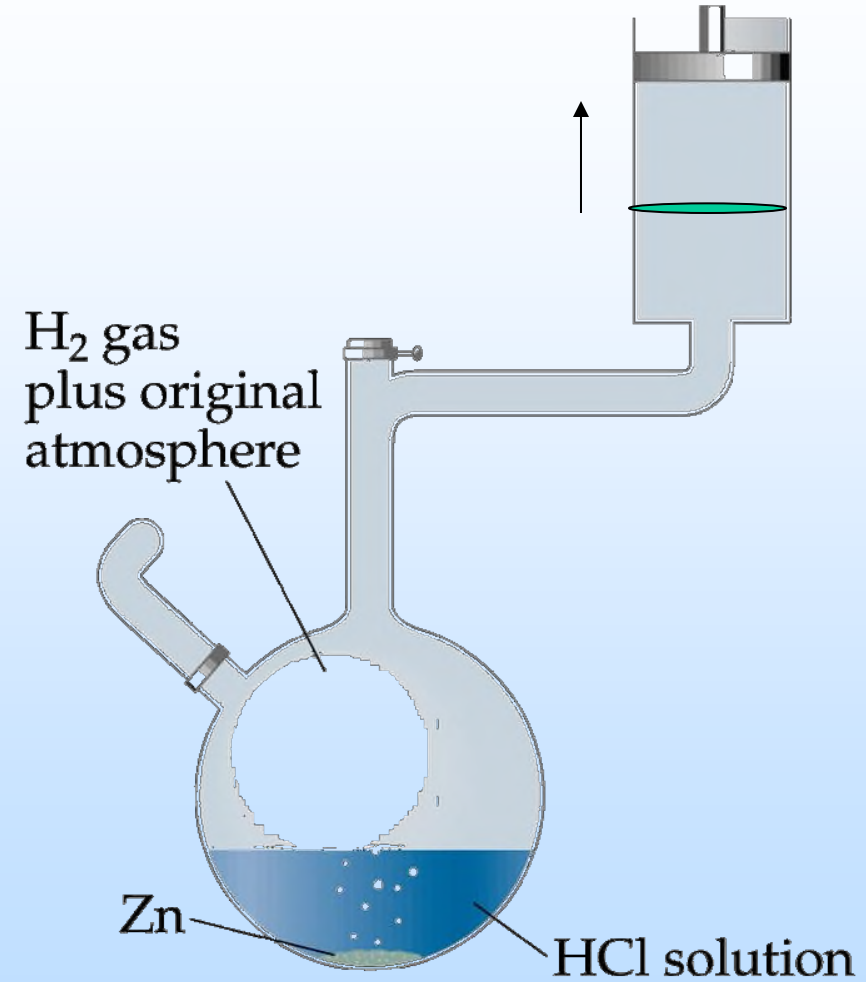
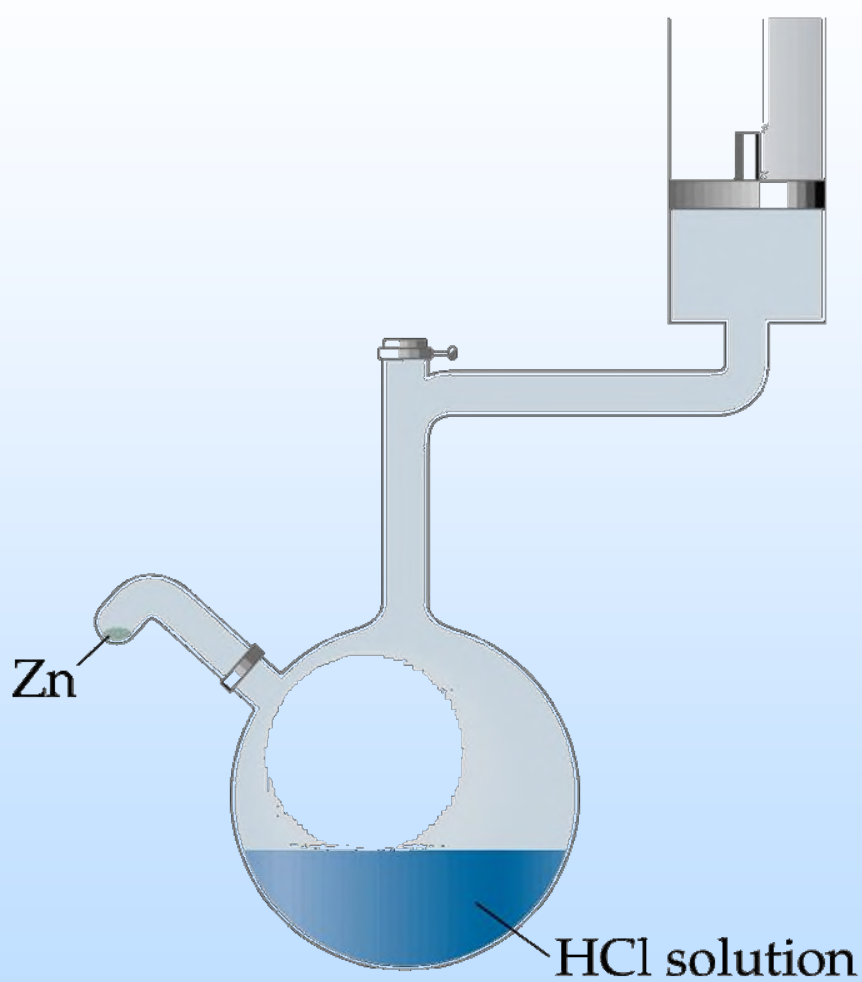
- Chemical reactions can absorb or release heat.
- However, they also have the ability to do work.
- For example, when a gas is produced, then the gas produced can be used to push a piston, thus doing work.



- The work performed by the above reaction is called *pressure-volume* work.
- When the pressure is constant,

$$w = -P\Delta V$$

$$w = - \int_1^2 F dl = - \int_1^2 P S dl = - \int_1^2 P dV$$



$$w = - \int_1^2 P dV$$

- 1<sup>st</sup> Law of thermodynamic:  $\Delta E = q + w$
- When system under  $V = \text{const}$ ,  $dV = 0$ ,  $w = 0$ ,  $q_V = \Delta E$
- Under  $P = \text{const}$ ,  $w = -P\Delta V$ ,  $q_P = \Delta E + P\Delta V = \Delta(E + PV) = \Delta H$
- $H = E + PV$ : enthalpy
- $\Delta H$ : Heat of the system (under constant pressure)
- Usually: chemical rxn carried out under  $P = \text{const}$

# Enthalpy

- Enthalpy,  $H$ : Heat transferred between the system and surroundings carried out under **constant pressure**.

$$H = E + PV$$

- Enthalpy is a state function.
- If the process occurs at constant pressure,

$$\begin{aligned} q_P &= \Delta H = \Delta(E + PV) \\ &= \Delta E + P\Delta V \end{aligned}$$

# Enthalpy

- We can write

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

$$q_P = q_V + w$$

$$w = (\Delta n_{gas})RT$$

$$\Delta n_{gas} = (c + d) - (a + b) \Big|_{gas}$$

- $R = 8.314 \text{ J/(mol.K)}$
- $\Delta V: V_{\text{final}} - V_{\text{initial}} = V_{\text{products}} - V_{\text{reactants}} \quad pV = nRT$
- When  $\Delta H$ , is positive, the system gains heat from the surroundings.
- When  $\Delta H$ , is negative, the surroundings gain heat from the system.

# Enthalpy

Surroundings

System



$$\Delta H > 0$$

Endothermic

Surroundings

System

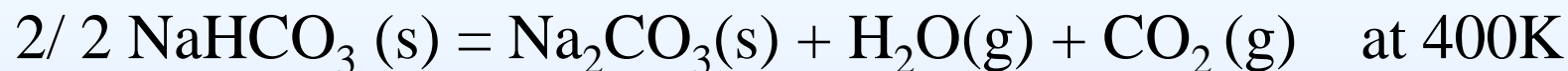


$$\Delta H < 0$$

Exothermic

# Exercise

Determine  $q_p - q_v$  of the following rxn

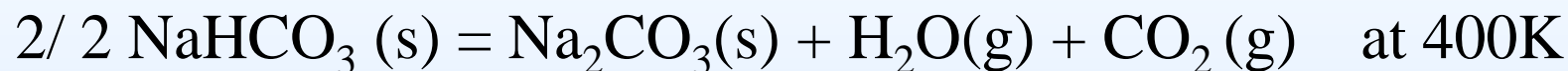
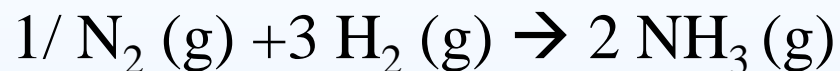


$q_p$  and  $q_v$  : energy (J)

$R = 8.314 \text{ J}/(\text{mol.K}) \quad 0.082 \text{ atm.L}/(\text{mol.K})$

# Exercise

Determine  $q_p - q_v$  of the following rxn at 298K



$$q_p - q_v = \Delta H - \Delta E = \Delta n_{\text{gas}} RT$$

$$1/ \Delta n_{\text{gas}} = -2$$

$$2/ \Delta n_{\text{gas}} = +2$$

$$R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$$

Usually, rxn under  $P = \text{const}$ , heat =  $\Delta H$       kJ

Rxn under  $V = \text{const}$ , heat =  $\Delta E$ ,      kJ

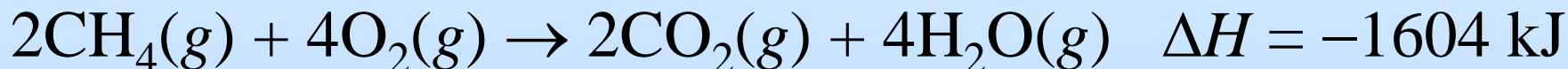


# Enthalpies of Reaction

- For a reaction:

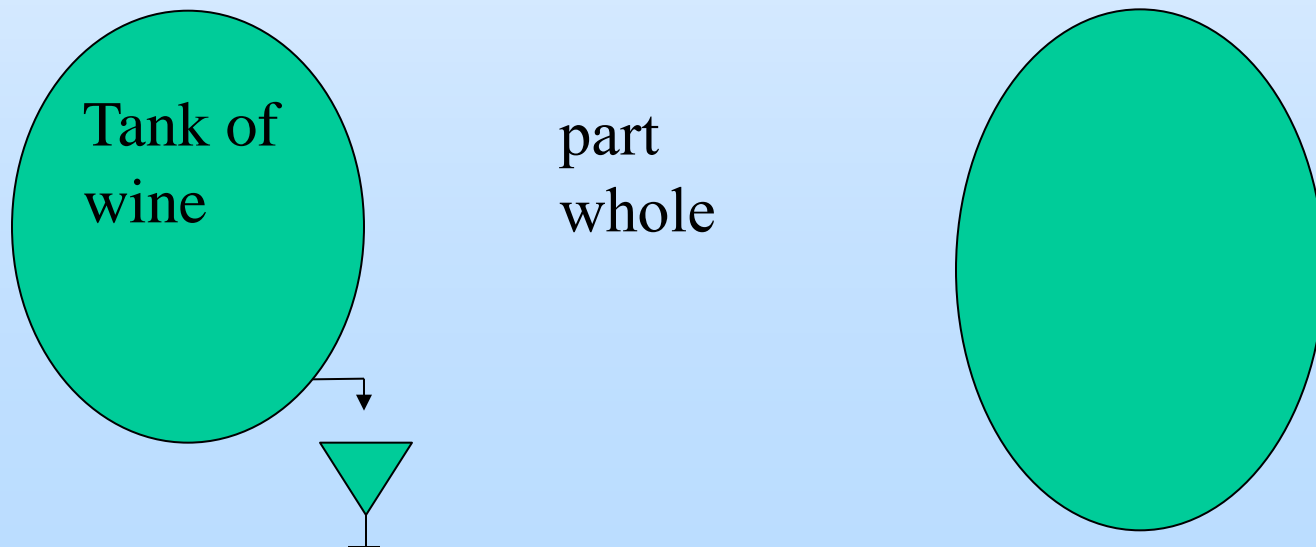
$$\begin{aligned}\Delta H &= H_{\text{final}} - H_{\text{initial}} \\ &= H_{\text{products}} - H_{\text{reactants}}\end{aligned}$$

- Enthalpy is an *extensive* property (magnitude  $\Delta H$  is directly proportional to amount):



# Intensive and extensive

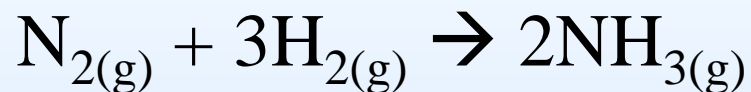
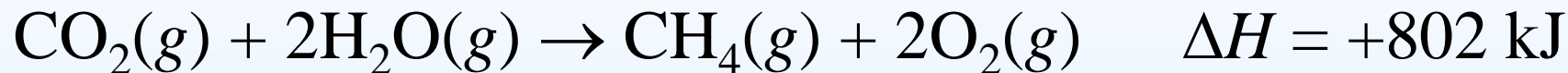
- Intensive properties:  
depend on the nature of  
the system
- P, T, density, specific  
heat capacity, specific  
volume, molar volume,  
concentration ....
- Extensive properties:  
depend on the amount of  
the system
- m, V, E,  $H=E+PV$ , ....



# Enthalpies of Reaction

- When we reverse a reaction, we change the sign of  $\Delta H$ :  
$$\text{CO}_2(g) + 2\text{H}_2\text{O}(g) \rightarrow \text{CH}_4(g) + 2\text{O}_2(g) \quad \Delta H = +802 \text{ kJ}$$
- Change in enthalpy depends on state:  
$$\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H = -88 \text{ kJ}$$
- Thermal chemical reaction equation: reaction equation +  
state of the compounds + enthalpy

# Enthalpies of Reaction

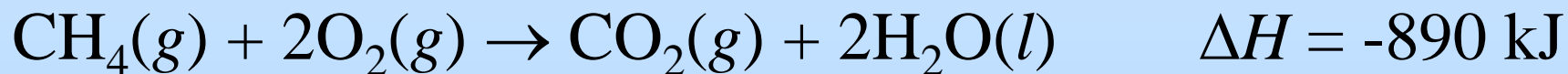
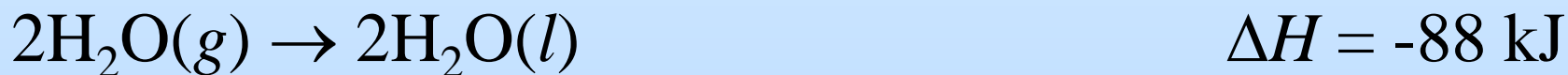


- Find the difference between  $\Delta H$  and  $\Delta E$   
 $q_P$  and  $q_V$

At  $25^\circ\text{C}$   $R=8.314 \text{ J}/(\text{mol.K})$

# Hess's Law

- **Hess's law:** if a reaction is carried out in a number of steps,  $\Delta H$  for the overall reaction is the sum of  $\Delta H$  for each individual step.
- Correct for any state function: E, H, ....
- For example:



# Hess's Law

- Discovered by looking at a lot exp. data from a lot of rxn (heat of rxn)

heat = enthalpy : state function  $\rightarrow$  correct

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# heat = enthalpies state function

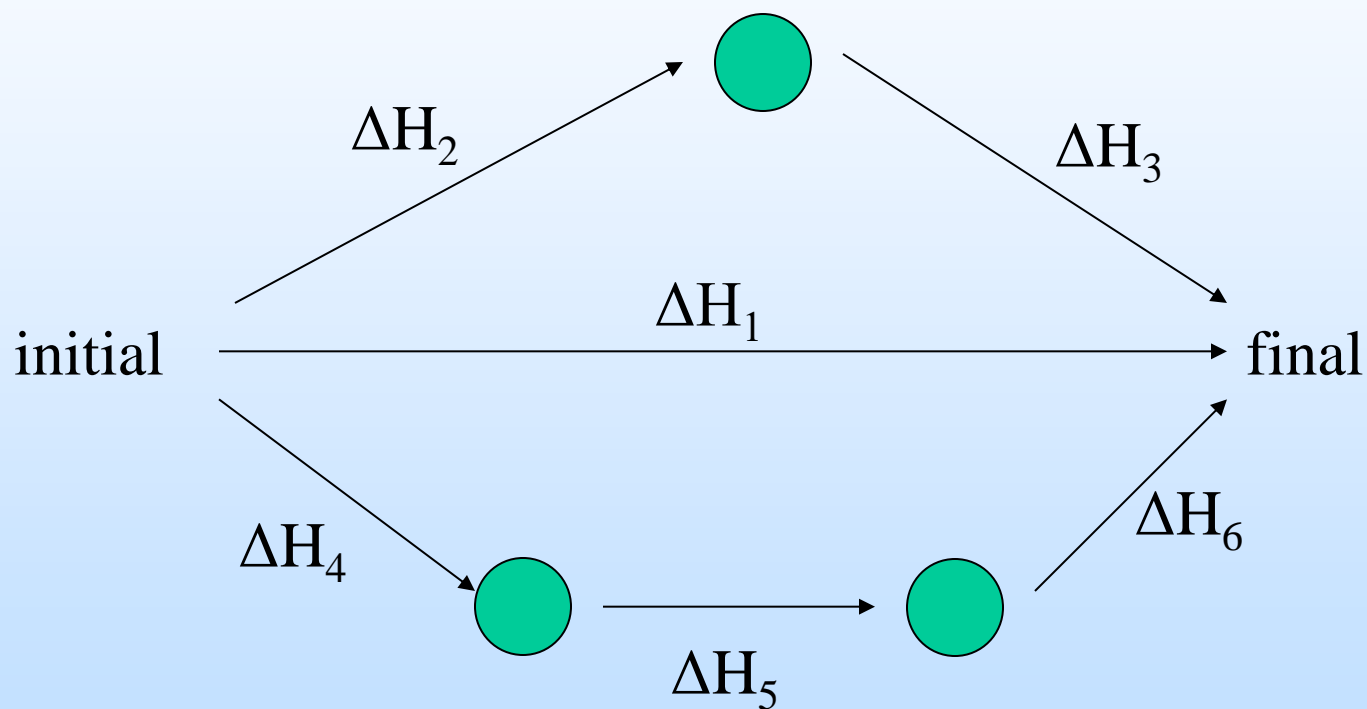
- **Hess's law:** if a reaction is carried out in a number of steps,  $\Delta H$  for the overall reaction is the sum of  $\Delta H$  for each individual step.
- $\Delta H$  depends only on initial and final state, independent on the path between reactants and products
- Correct for any state function: E, H, ....
- (1) and (2): equivalent

# Hess's Law

- **Hess's law:** if a reaction is carried out in a number of steps,  $\Delta H$  for the overall reaction is the sum of  $\Delta H$  for each individual step.
  - $\Delta H$  of a rxn depend on initial and final state, independent on the pathway between initial and final state
  - Correct for all state function
-



# Diagram form of Hess' Law



$$\Delta H_1 = \Delta H_2 + \Delta H_3 = \Delta H_4 + \Delta H_5 + \Delta H_6$$

# Algebraic form of Hess' law

- We can manipulate thermal chemical reaction similar to algebraic equation

$$(\Sigma) = \sum m_i (i)$$

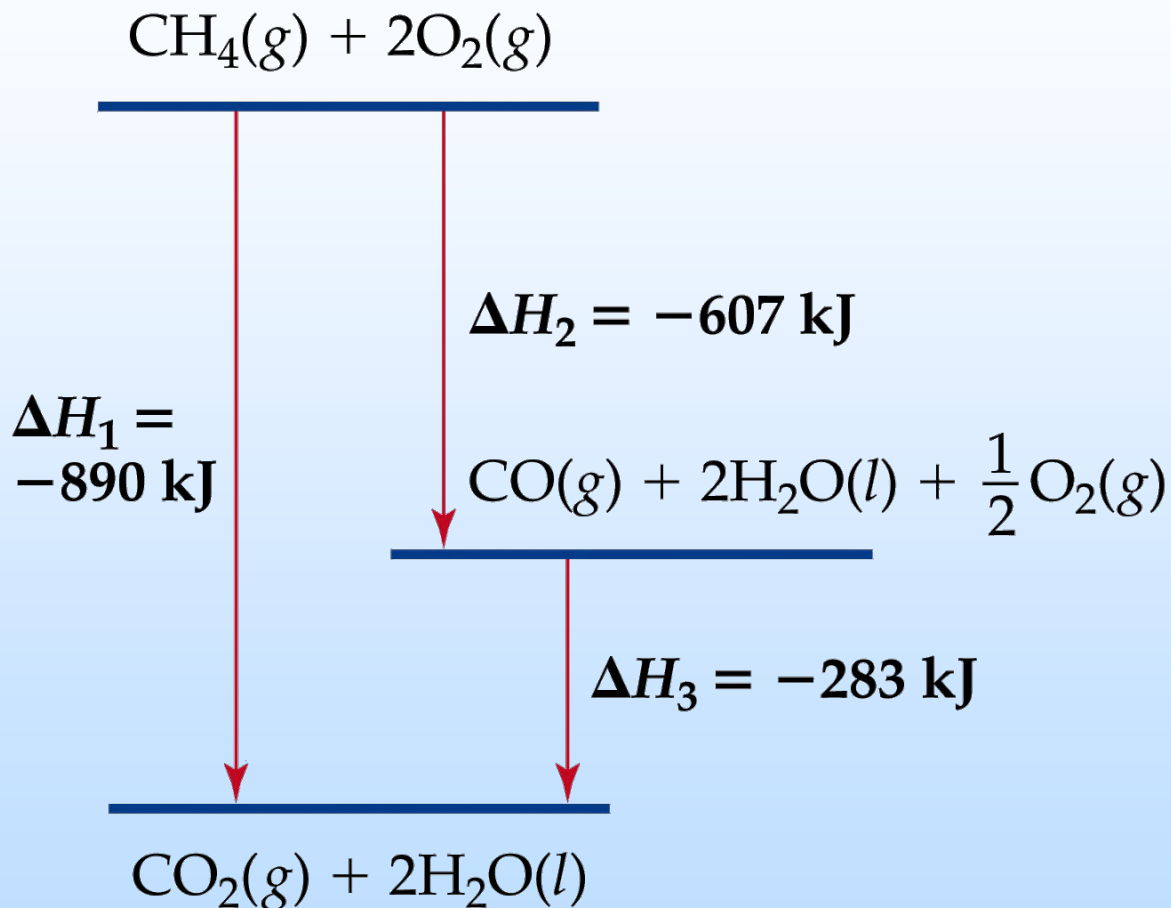
$$\Delta H_{\Sigma} = \sum m_i \times \Delta H_i$$

# Hess's Law

Note that:

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

Enthalpy ↑



# Enthalpies of Formation

- If 1 mol of a compound is formed from its constituent elements, then the enthalpy change for the reaction is called the **enthalpy of formation**,  $\Delta H_f^\circ$ .
- Standard conditions (standard state): 1 atm and 25 °C (298 K).
- Standard enthalpy,  $\Delta H^\circ$ , is the enthalpy measured when everything is in its standard state.
- Standard enthalpy of formation: 1 mol of compound is formed from substances in their standard states.

# Enthalpies of Formation

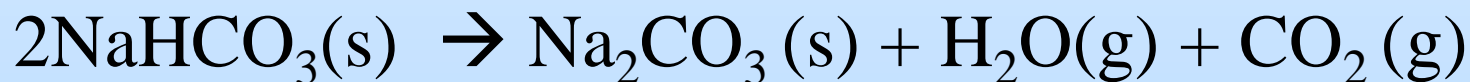
- Its constituent elements, stable form  $\rightarrow$  1 mol of a **compound**
- $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{f, compound}}$
- $2 \text{ C}(\text{gr}) + 3 \text{ H}_2(\text{g}) + 1/2 \text{ O}_2(\text{g}) \rightarrow 1 \text{ C}_2\text{H}_5\text{OH}_{(\text{l})}$

# Enthalpies of Formation

- If there is more than one state for a substance under standard conditions, the most stable one is used.
- Standard enthalpy of formation of **the most stable** form of an element is zero.
- itself  $\rightarrow$  1 mol compound  $\Delta H^\circ_{\text{rxn}} = 0 = \Delta H^\circ_{\text{f}}$
- $\Delta H^\circ_{\text{f, O2(g)}}=0$ , but  $\Delta H^\circ_{\text{f, O3(g)}}$  is not 0
- $\Delta H^\circ_{\text{f, C(gr)}}=0$ , but  $\Delta H^\circ_{\text{f, C(diamond)}}$  is not 0

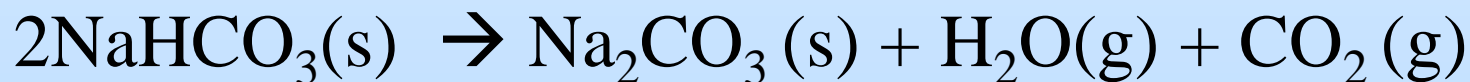
# Standard Enthalpies of Formation at 298 K

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)	Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	-92.30
Ammonia	$NH_3(g)$	-46.19	Hydrogen fluoride	$HF(g)$	-268.6
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	-1207.1	Methane	$CH_4(g)$	-74.8
Calcium oxide	$CaO(s)$	-635.5	Methanol	$CH_3OH(l)$	-238.6
Carbon dioxide	$CO_2(g)$	-393.5	Propane	$C_3H_8(g)$	-103.85
Carbon monoxide	$CO(g)$	-110.5	Silver chloride	$AgCl(s)$	-127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	-947.7
Ethane	$C_2H_6(g)$	-84.68	Sodium carbonate	$Na_2CO_3(s)$	-1130.9
Ethanol	$C_2H_5OH(l)$	-277.7	Sodium chloride	$NaCl(s)$	-410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	-2221
Glucose	$C_6H_{12}O_6(s)$	-1273	Water	$H_2O(l)$	-285.8
Hydrogen bromide	$HBr(g)$	-36.23	Water vapor	$H_2O(g)$	-241.8



# Standard Enthalpies of Formation at 298 K

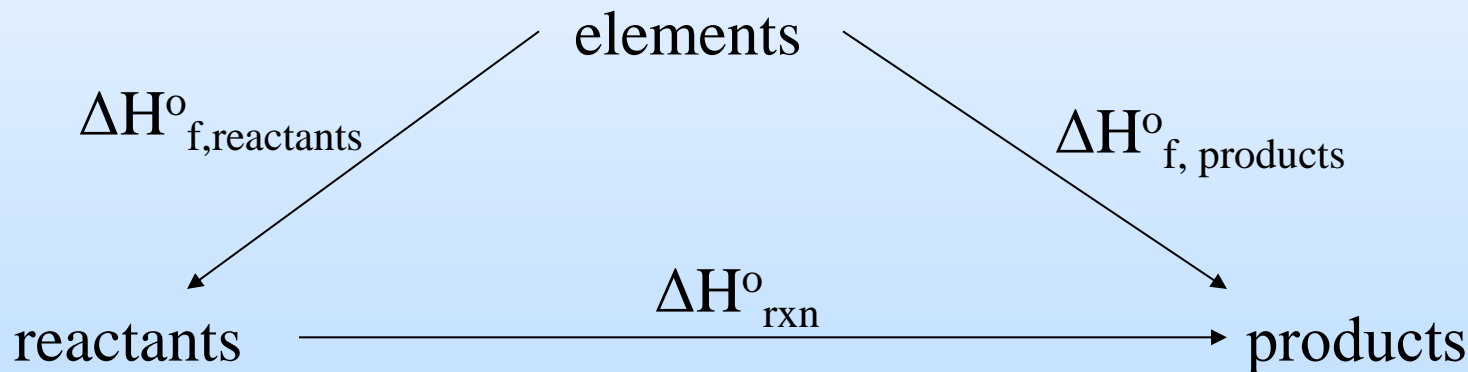
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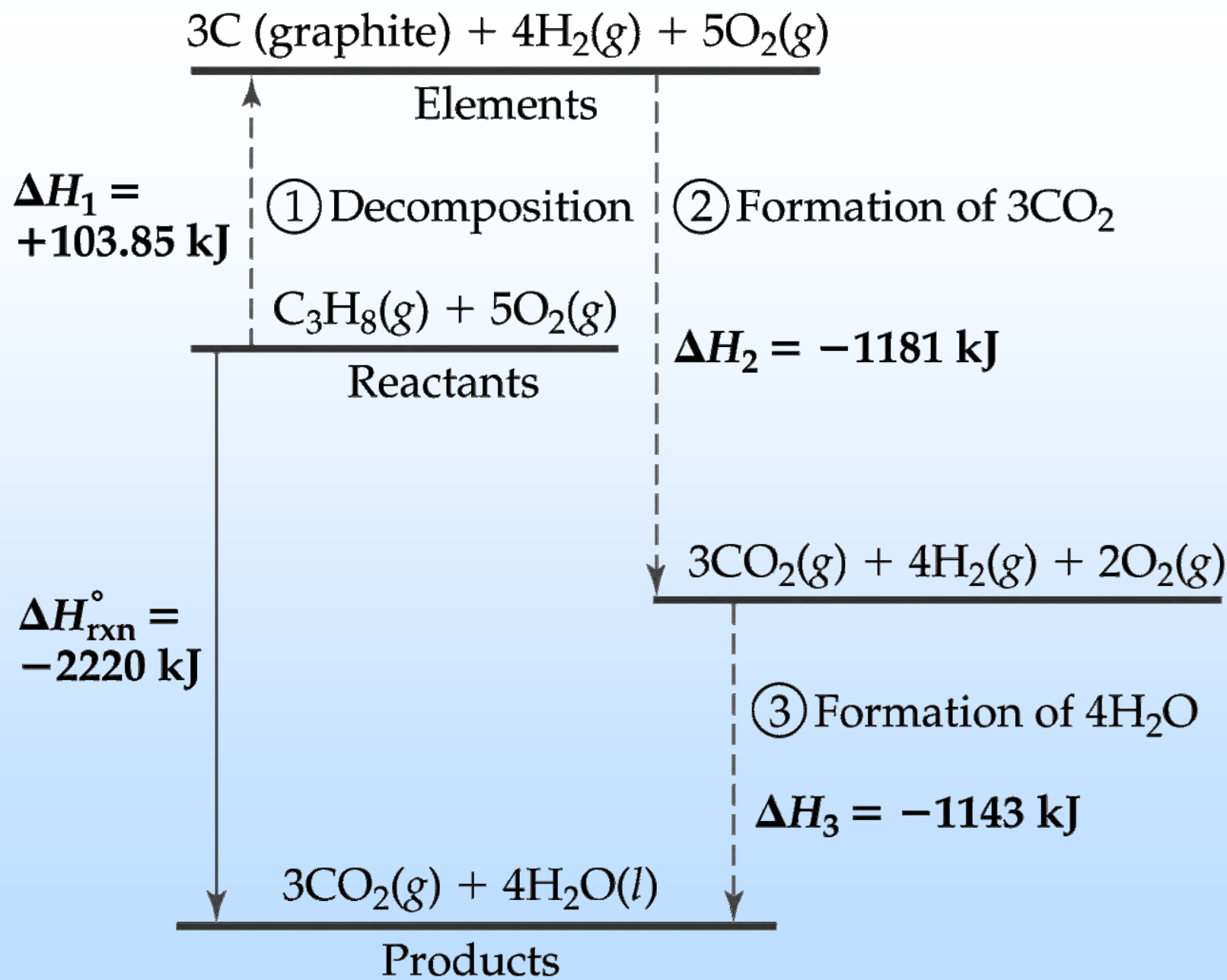
# Using Enthalpies of Formation of Calculate Enthalpies of Reaction

- We use Hess' Law to calculate enthalpies of a reaction from enthalpies of formation.



$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f (\text{products}) - \sum m \Delta H^\circ_f (\text{reactants})$$

Enthalpy  $\uparrow$



# Using Enthalpies of Formation of Calculate Enthalpies of Reaction

- For a reaction

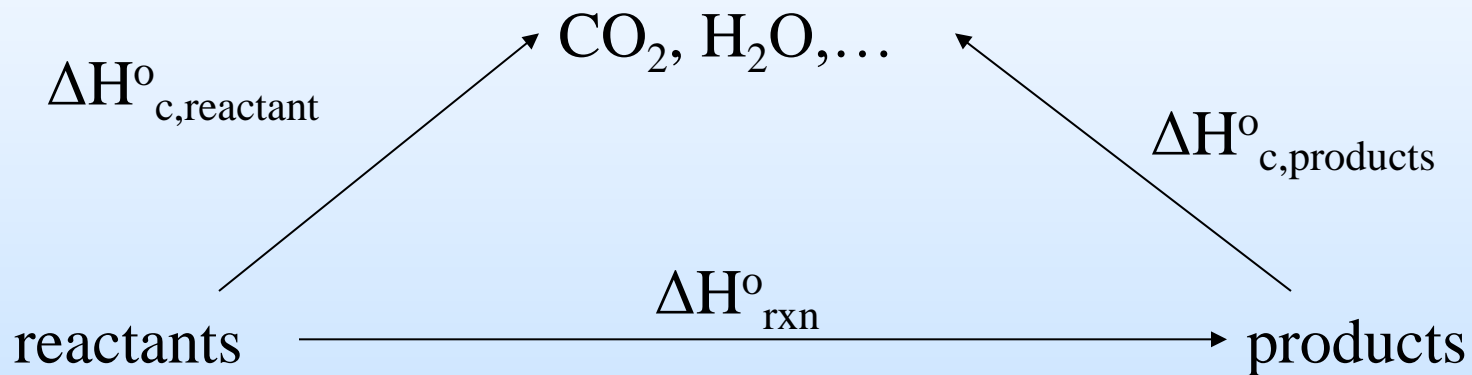
$$\Delta H^{\circ}_{\text{rxn}} = \sum n\Delta H^{\circ}_f(\text{products}) - \sum m\Delta H^{\circ}_f(\text{reactants})$$

# Heat of Combustion

The **heat of combustion** ( $\Delta H_c^\circ$ ) is the energy released as heat when one mole of a compound undergoes complete combustion with oxygen. The chemical reaction is typically a hydrocarbon or fuel reacting with oxygen to form carbon dioxide (gas), water (liquid) and heat.

For a reaction:

$$\Delta H^\circ_{\text{rxn}} = \sum m \Delta H_c^\circ (\text{reactants}) - \sum n \Delta H_c^\circ (\text{products})$$



$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_c (\text{reactants}) - \sum m \Delta H^\circ_c (\text{products})$$

## Heat of Combustion for some common fuels

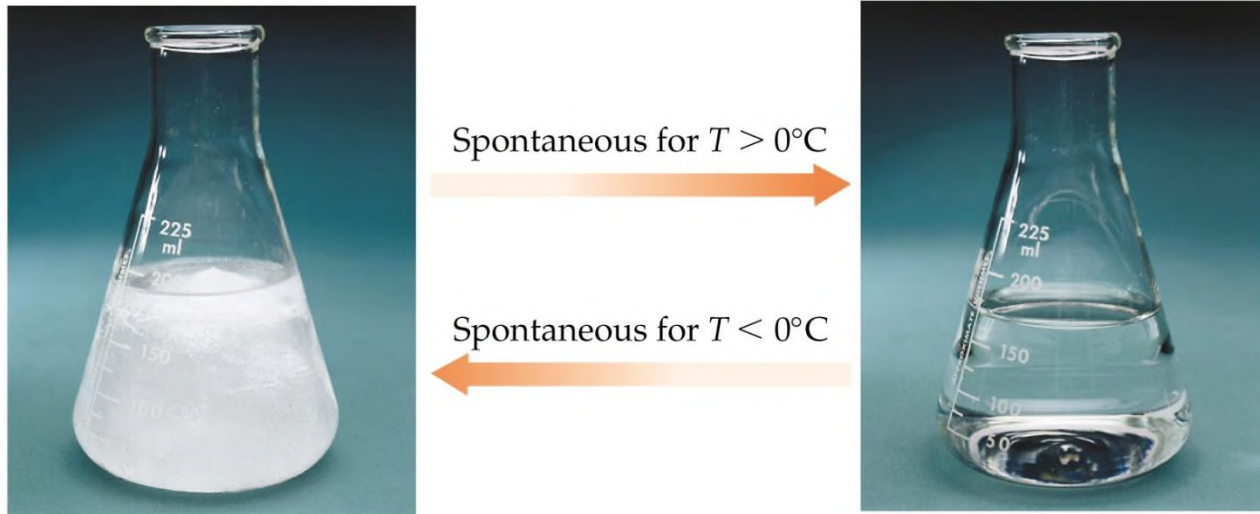
Fuel	kJ/g	kcal/g	BTU/lb
Hydrogen	141.9	33.9	61,000
Gasoline	47.0	11.3	20,000
Diesel	45.0	10.7	19,300
Ethanol	29.8	7.1	12,000
Propane	49.9	11.9	21,000
Butane	49.2	11.8	21,200
Wood	15.0	3.6	6,000
Coal (Lignite)	15.0	4.4	8,000
Coal (Anthracite)	27.0	7.8	14,000
Natural Gas	54.0	13.0	23,000

# Spontaneous Processes

- First Law of Thermodynamics: energy is conserved.
  - $\Delta E = q + w$ , where
    - $\Delta E$  = internal energy change
    - $q$  = heat absorbed (endothermic – exothermic)
    - $w$  = the work done
- Any process that occurs without outside intervention is spontaneous.
- When two eggs are dropped they spontaneously break.
- The reverse reaction is not spontaneous.
- We can conclude that a spontaneous process has a direction.

# Spontaneous Processes Direction

- A process that is spontaneous in one direction is not spontaneous in the opposite direction.
- The direction of a spontaneous process can depend on temperature: Ice turning to water is spontaneous at  $T > 0^{\circ}\text{C}$ , Water turning to ice is spontaneous at  $T < 0^{\circ}\text{C}$ .





# Class Example Problem

- Predict whether the following processes are spontaneous as described, are spontaneous in the reverse direction, or are in equilibrium:
- (a) When a piece of metal heated to  $150\text{ }^{\circ}\text{C}$  is added to water at  $40\text{ }^{\circ}\text{C}$ , the water gets hotter.
- (b) Water at room temperature decomposes into  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$ .
- (c) Benzene vapor at a pressure of 1 atm condenses to liquid benzene at the normal boiling point of benzene,  $80.1\text{ }^{\circ}\text{C}$ .

# Reversible Processes

- A **reversible process** is one that can go back and forth between states along the same path.
  - Chemical systems in equilibrium are reversible.
    - They can interconvert between reactants and products
    - For example, consider the interconversion of water and ice at 0 °C.
  - There is only one reversible path between any two states of a system.
- Reversible = equilibrium
- Spontaneous = direction = irreversible

# Irreversible Processes

- A **irreversible process** is one that cannot be reversed to restore the system to its original state.
  - To get back to the original state a different pathway must be followed.
  - In any spontaneous process, the path between reactants and products is irreversible.
- Thermodynamics gives us the direction of a process. It cannot predict the speed at which the process will occur.
- Why do spontaneous reactions occur? Driving force?
- Dynamic: drive the rxn?

# Entropy

- Entropy,  $S$ , is a measure of the disorder of a system.
- Spontaneous reactions proceed to lower energy or higher entropy (i.e., the more disorder the higher the entropy of the system).
- For example, ice molecules are very well ordered because of the H-bonds. Thus, ice has a low entropy.
- As ice melts, the intermolecular forces are broken (requires energy), but the order is interrupted (so entropy increases).
- Water is more random than ice, so ice spontaneously melts at room temperature.

# Expressing Entropy

- Entropy is a state function and an extensive property.
- For a system,  $\Delta S = S_{\text{final}} - S_{\text{initial}}$ .
- If  $\Delta S > 0$  the randomness increases, if  $\Delta S < 0$  the order increases.

# Class Example Problem

- By considering the disorder in the reactants and products, predict whether the change in entropy,  $\Delta S$ , is positive or negative for each of the following processes:
  - (a)  $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$
  - (b)  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$
  - (c)  $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{Fe}_2\text{O}_3(\text{s})$

# Class Example Problem

- By considering the disorder in the reactants and products, predict whether entropy,  $\Delta S$ , is positive or negative for each of the following processes:
  - (a)  $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$  ( $\Delta S$ : +)
  - (b)  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$  ( $\Delta S$ : -)
  - (c)  $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{Fe}_2\text{O}_3(\text{s})$  ( $\Delta S$ : -)

aq.: aqueous solution (solution with  $\text{H}_2\text{O}$  as solvent)

# The Change in Entropy

- Suppose a system changes reversibly between state 1 and state 2. Then, the change in entropy is given by

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} \quad (\text{constant } T)$$

- at constant  $T$  where  $q_{\text{rev}}$  is the amount of heat added reversibly to the system. (Example: a phase change occurs at constant  $T$  with the reversible addition of heat.)

$$\Delta S_{\text{sys}} \geq \frac{q}{T} \quad (\text{constant } T)$$

= for reversible process, > for the irreversible process



# Boltzmann formula

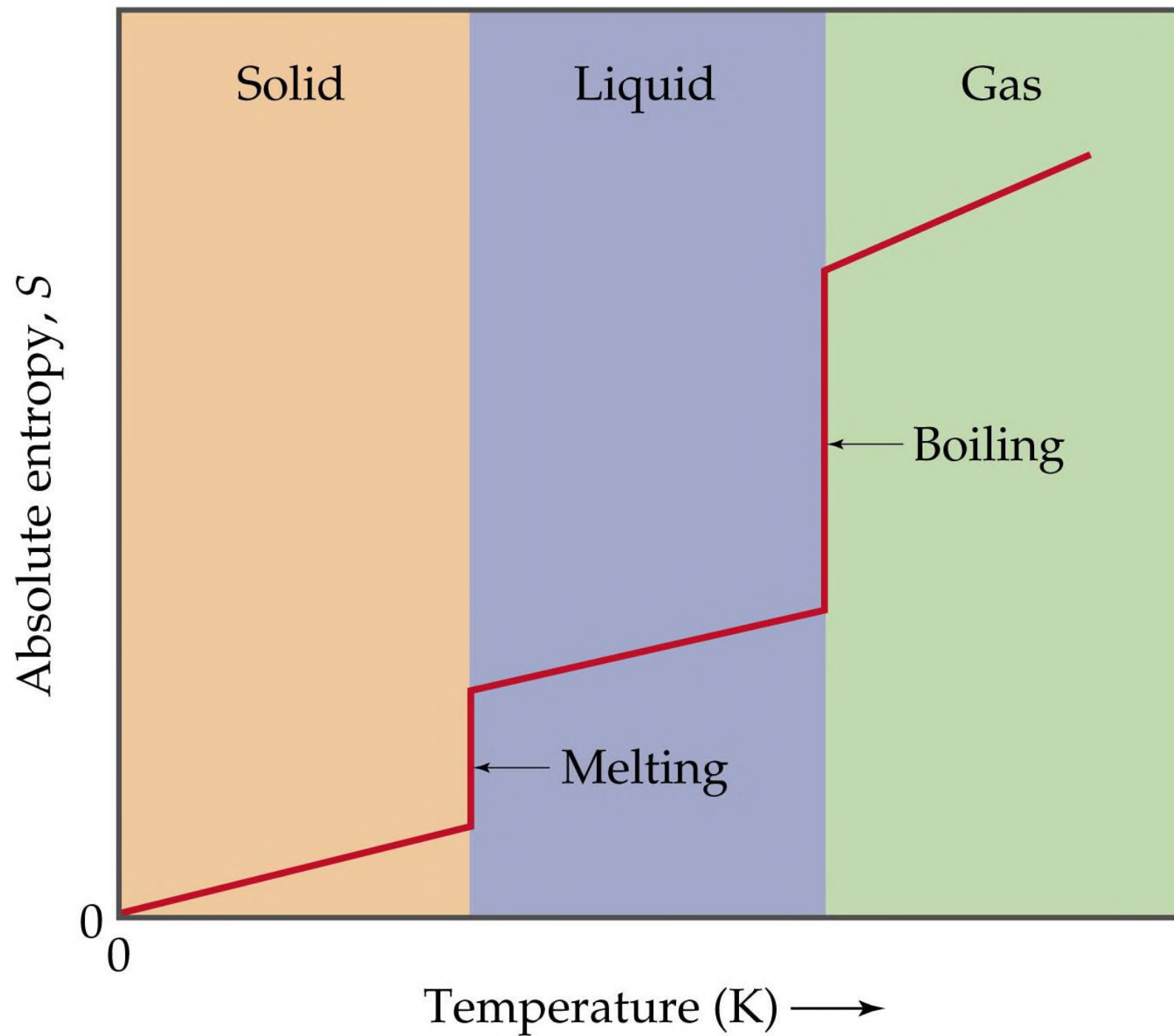
## Entropy

$$S = k_B \ln W$$

- $W$ : number of possible arrangement
- $W$  increases  $\rightarrow$  more disorder  $\rightarrow$  higher entropy

# Third Law of Thermodynamics

- Third Law of Thermodynamics: the entropy of a perfect crystal at 0 K is zero. ( $W=1$ )
- Estimate absolute  $S$  at any temperature
- Entropy changes dramatically at a phase change.
- As we heat a substance from absolute zero, the entropy must increase.
- If there are two different solid state forms of a substance, then the entropy increases at the solid state phase change.



# Properties of entropy

- S is a state function → apply Hess' Law
- Extensive properties: depends on the amount of the system
- State function: Hess' law
- intensive: p, T, concentration, density, molar volume, ..
- extensive: depend on amount of system: m, V, E, H, S, ...

# Absolute Entropy Changes in Chemical Reactions

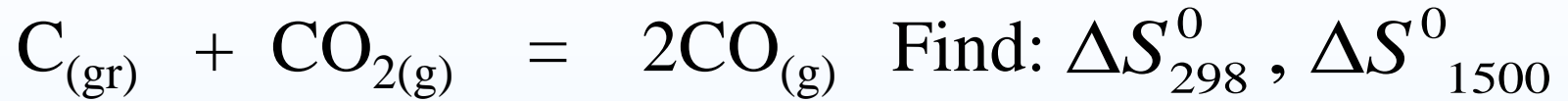
- Absolute entropy can be determined from complicated measurements.
- Standard molar entropy,  $S^\circ$ : entropy of a substance in its standard state. Similar in concept to  $\Delta H^\circ$ .
- Units: J/mol-K. Note units of  $\Delta H$ : kJ/mol.
- Standard molar entropies of elements are not zero.  $S^\circ_{\text{H}_2}$  not zero
- For a chemical reaction which produces  $n$  moles of products from  $m$  moles of reactants:

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

**SAMPLE EXERCISE 19.2 Calculating  $\Delta S$  for a Phase Change**

The element mercury, Hg, is a silvery liquid at room temperature. The normal freezing point of mercury is  $-38.9^{\circ}\text{C}$ , and its molar enthalpy of fusion is  $\Delta H_{\text{fusion}} = 2.29 \text{ kJ/mol}$ . What is the entropy change of the system when 50.0 g of Hg(l) freezes at the normal freezing point?

## Example



$$S_{298}^0 \quad 5.74 \quad 213.68 \quad 197.54 \text{ (J/mol.K)}$$

$$S_{1500}^0 \quad 33.44 \quad 291.76 \quad 248.71 \text{ (J/mol.K)}$$

# Second Law of Thermodynamics

- The **second law of thermodynamics** explains why spontaneous processes have a direction.
  - The second law is usually expressed in terms of entropy.
  - **In any spontaneous process, the entropy of the universe increases.**
- The total change in entropy
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ : the change in entropy of the universe is the sum of the change in entropy of the system and the change in entropy of the surroundings.
- Unlike energy, entropy is not conserved:  $S_{\text{univ}}$  is continually increasing ( $\Delta S_{\text{univ}} > 0$  or non-negative).



# Reversible and Irreversible Processes

- For a reversible process (equilibrium):  $\Delta S_{\text{univ}} = 0$ .
- For a spontaneous process (i.e. irreversible):  $\Delta S_{\text{univ}} > 0$ .
- Note: the second law states that the entropy of the universe must increase in a spontaneous process. It is possible for the entropy of a system to decrease as long as the entropy of the surroundings increases.
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$
- For an isolated system,  $\Delta S_{\text{sys}} = 0$  for a reversible process and  $\Delta S_{\text{sys}} > 0$  for a spontaneous process. ( $\Delta S_{\text{surr.}} = 0$ )

# Gibbs Free Energy

- For a spontaneous reaction the entropy of the universe must increase.
- Reactions with large negative  $\Delta H$  values are spontaneous.
- How do we balance  $\Delta S$  and  $\Delta H$  to predict whether a reaction is spontaneous?

- Gibbs free energy,  $G$ , of a state is

$$G = H - TS$$

- For a process occurring at constant temperature

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

# Conditions of Gibbs Free Energy

- There are three important conditions:
  - If  $\Delta G < 0$  then the forward reaction is spontaneous.
  - If  $\Delta G = 0$  then reaction is at equilibrium and no net reaction will occur.
  - If  $\Delta G > 0$  then the forward reaction is not spontaneous. If  $\Delta G > 0$ , work must be supplied from the surroundings to drive the reaction.
- For a reaction the free energy of the reactants decreases to a minimum (equilibrium) and then increases to the free energy of the products.

# Properties of Gibbs Free Energy

- $G = H - TS$
- $G$  is a state function  $\rightarrow$  apply Hess' Law
- $G$  is an extensive properties

- Its elements  $\rightarrow$  **1 mol** compound

- $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{f, that compound}}$

- $\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{f, that compound}}$

$$\Delta G^\circ = G_{\text{products}} - G_{\text{reactants}}$$

$$\Delta G^\circ = \sum n \Delta G^\circ_f (\text{products}) - \sum m \Delta G^\circ_f (\text{reactants})$$

# Standard Free-Energy Changes

- We can tabulate standard free-energies of formation,  $\Delta G^\circ_f$  (c.f. standard enthalpies of formation).
- Standard states are: pure solid, pure liquid, 1 atm (gas), 1  $M$  concentration (solution), and  $\Delta G^\circ_f = 0$  for elements (most stable form).
- $\Delta G^\circ$  for a process is given by

$$\Delta G^\circ = \sum n \Delta G^\circ_f (\text{products}) - \sum m \Delta G^\circ_f (\text{reactants})$$

- The quantity  $\Delta G^\circ$  for a reaction tells us whether a mixture of substances will spontaneously react to produce more reactants ( $\Delta G^\circ > 0$ ) or products ( $\Delta G^\circ < 0$ ).

# Free Energy and Temperature

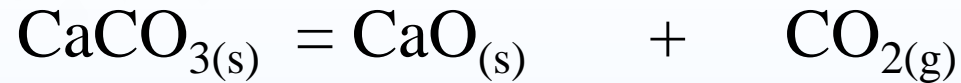
- Focus on  $\Delta G = \Delta H - T\Delta S$ :
  - If  $\Delta H < 0$  and  $\Delta S > 0$ , then  $\Delta G$  is always negative.
  - If  $\Delta H > 0$  and  $\Delta S < 0$ , then  $\Delta G$  is always positive. (That is, the reverse of 1.)
  - If  $\Delta H < 0$  and  $\Delta S < 0$ , then  $\Delta G$  is negative at low temperatures.
  - If  $\Delta H > 0$  and  $\Delta S > 0$ , then  $\Delta G$  is negative at high temperatures.
- Even though a reaction has a negative  $\Delta G$  it may occur too slowly to be observed. ( $\text{H}_2 + 0.5 \text{O}_2 \rightarrow \text{H}_2\text{O}$ )

# Free Energy and Temperature Chart

TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
–	+	–	Always negative	Spontaneous at all temperatures	$2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$
+	–	+	Always positive	Nonspontaneous at all temperatures; reverse reaction always spontaneous	$3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
–	–	+	Negative at low $T$ ; positive at high $T$	Spontaneous at low $T$ ; becomes nonspontaneous at high $T$	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$
+	+	–	Positive at low $T$ ; negative at high $T$	Nonspontaneous at low $T$ ; becomes spontaneous at high $T$	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$

**Example:** Find  $\Delta G_{298}^0, \Delta G_{1500}^0$  ?



$\Delta H_{298,f}^0 (kJ / mol)$	-1205.93	-634.94	-392.92
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$S_{298}^0 (J / mol.K)$	92.63	39.71	213.31
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$\Delta G_{298,f}^0 (kJ / mol)$	-1129	-604	-394.38
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