

LECTURE 4

Chemical thermodynamics

We will consider such questions:

Energy changes in chemical reactions;

Heat effect of a chemical reaction;

Heat of formation of chemical compounds;

The laws of thermochemistry, thermochemical calculations;

Enthalpy, its change in different processes;

Entropy, its change at chemical processes and phase transitions;

Gibbs energy, its changes at chemical processes;

Conditions of spontaneous proceeding chemical processes;

The most important concepts and definitions of chemical thermodynamics

Thermodynamic parameters

**P- pressure, T- temperature V-volume, m -mass,
C- concentration**

In chemistry, IUPAC has changed the definition of standard temperature and pressure (STP) in 1982:

Until 1982, STP was defined as a temperature of 273.15 K (0 °C, 32 °F) and an absolute pressure of exactly 1 atm (1.01325×10^5 Pa).

Since 1982, STP is defined as a temperature of 273.15 K (0 °C, 32 °F) and an absolute pressure of exactly 10^5 Pa (100 kPa, 1 bar).

STP should not be confused with the standard state commonly used in thermodynamic evaluations of the Gibbs energy of a reaction

System is defined as the substance or combination of substances being considered

The **surroundings** – the substances surrounding the system, are opposed to a system.

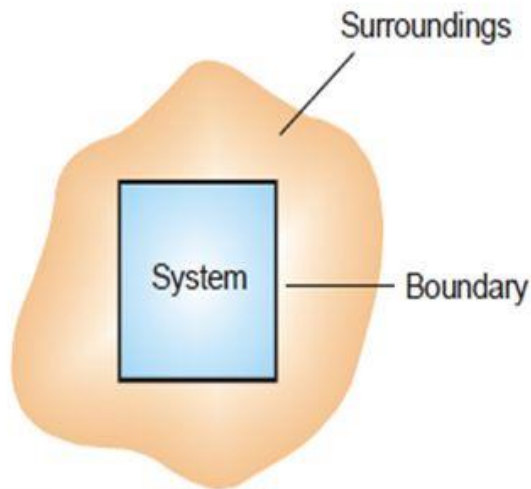
A system is usually separated physically from its surroundings.

Phase is meant a part of a system separated from its other parts by an interface upon passing through which the properties change in a jump.

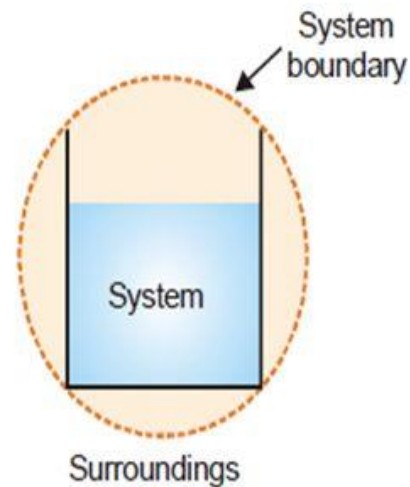
SYSTEM, BOUNDARY, SURROUNDINGS

A system is that part of the universe which is under thermodynamic study and the rest of the universe is surroundings.

The real or imaginary surface separating the system from the surroundings is called the boundary.



■ **Figure**
Thermodynamic system.



■ **Figure**
Water contained in a beaker constitutes a system.

Thermodynamic systems

by phase composition

Homogeneous

Heterogeneous



Thermodynamic systems



open

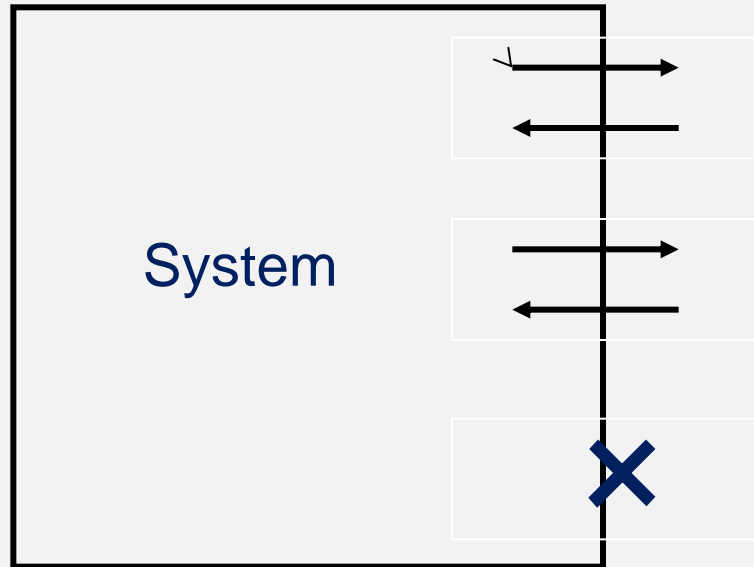


closed



isolated

Surroundings



Open system
-can exchange mass or energy with surroundings

Closed system
-can exchange only energy with surroundings

Isolated system
- No transfer of either energy or mass



**Thermodynamic
state 1**



**Thermodynamic
state 2**

Thermodynamic process

$P=\text{const}$

isobaric

$V=\text{const}$

isochoric

$T=\text{const}$

isothermal

$P=\text{const}, T=\text{const}$ isobaric-isothermal

State function

U - Internal energy J/mol

H - Enthalpy kJ/mol

S - Entropy J/mol

G - Gibbs energy J/mol

In thermodynamics, a **state function** or **function of state** is a function defined for a system relating several *state variables* or *state quantities* that depends only on the current equilibrium state of the system. State functions do not depend on the path by which the system arrived at its present state. A state function describes the equilibrium state of a system.

The first law of thermodynamics

Energy is conserved; it can not be neither created nor destroyed.

Mathematically, this is represented as

$$\Delta U = Q + W$$

ΔU is the total change in internal energy of a system,

Q is the heat exchanged between a system and its surroundings,

W is the work done by or on the system

For a chemical reaction proceeding at constant volume of the system, a change in the internal energy equals the heat effect of the reaction taken with the opposite sign

$$\Delta U = Q_v$$

The total heat content of a system is called its enthalpy. It can be regarded as the sum of the internal and external energies of the system determined by the relationship

$$H = U + pV$$

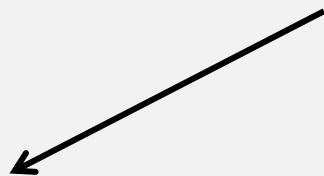
However, in chemistry we have to do with processes occurring at a constant pressure more often. Here it is convenient to use an enthalpy $\Delta H = \Delta U + p \Delta V$

At constant pressure and provided that only the work of expansion is performed in the course of a process, we have

$$\Delta H = Q_p$$

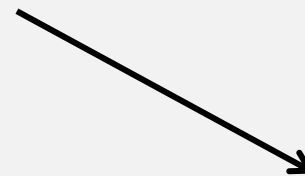
In a chemical reaction, the change in the enthalpy
Equals the heat effect of the reaction conducted at
a constant temperature and constant pressure with
opposite sign

Chemical reactions



$\Delta H < 0$ exothermic

**Reactions proceeding
with the liberation of
energy**



$\Delta H > 0$ endothermic

**Reactions in which
energy is absorbed**

Endothermic and Exothermic Reactions

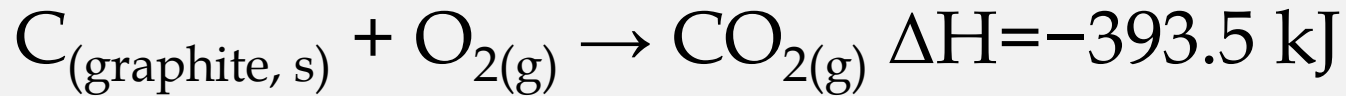
At **constant** pressure, the change in enthalpy of a system is the amount of energy released or absorbed

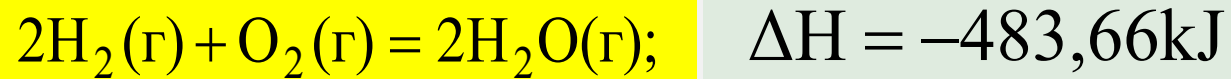
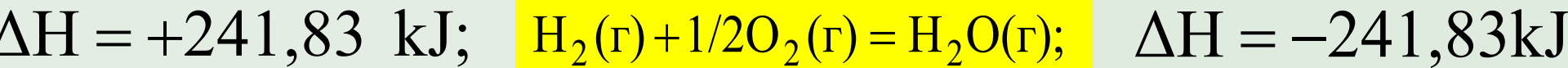
Standard reaction enthalpy, $\Delta H^\circ_{\text{rxn}}$: change in enthalpy when reactants in their standard states are changed to products in their standard states

Standard enthalpy of formation, $\Delta H^\circ_{\text{form}}$: change in enthalpy when one mole of product is formed from reactants in their standard states

Standard enthalpy of combustion, $\Delta H^\circ_{\text{comb}}$: change in enthalpy when one mole of reactant is burned completely in oxygen

A **Thermochemical Equation** is a balanced stoichiometric chemical equation that includes the enthalpy change, ΔH . In variable form





Hess's law states that the change of enthalpy in a chemical reaction (i.e. the heat of reaction at constant pressure) is independent of the pathway between the initial and final states.

$$\Delta H_{\text{reaction}}^{\ominus} = \sum \Delta H_{f(\text{products})}^{\ominus} - \sum \Delta H_{f(\text{reactants})}^{\ominus}$$

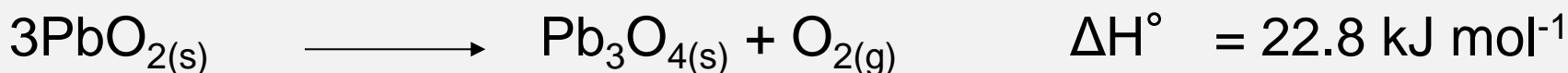
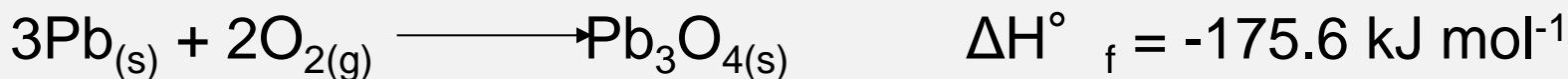
where ΔH_f^{\ominus} is an enthalpy of formation, and the $^{\ominus}$ superscript indicates standard state values. This may be considered as the sum of two (real or fictitious) reactions:

Example

Given that ΔH° for formation (ΔH°_f) of Pb_3O_4 is $-175.6 \text{ kJ mol}^{-1}$ and ΔH° for the reaction $3\text{PbO}_2 \rightarrow \text{Pb}_3\text{O}_4 + \text{O}_2$ is 22.8 kJ mol^{-1} . What is the ΔH°_f for PbO_2 (in kJ mol^{-1})?

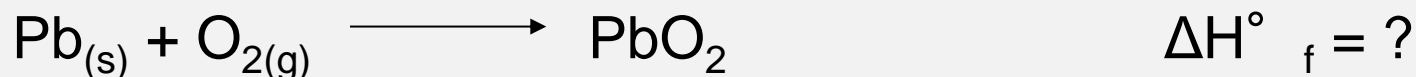
Step 1: Write equation for reactions given

Enthalpy of formation:

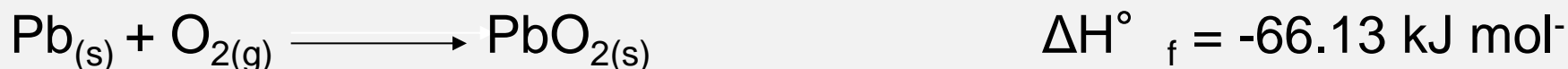
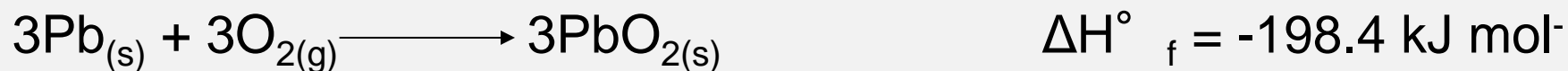
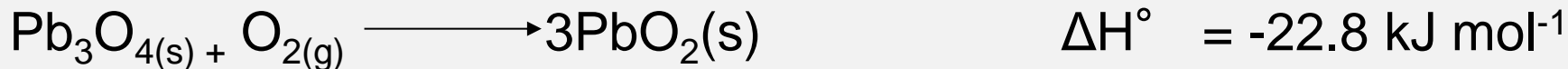
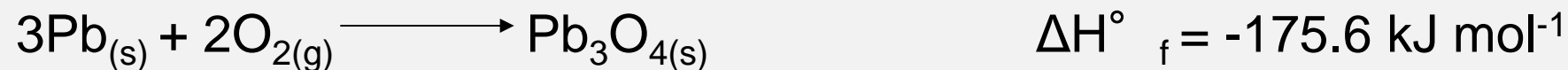


Step 2: Write down what you are looking for

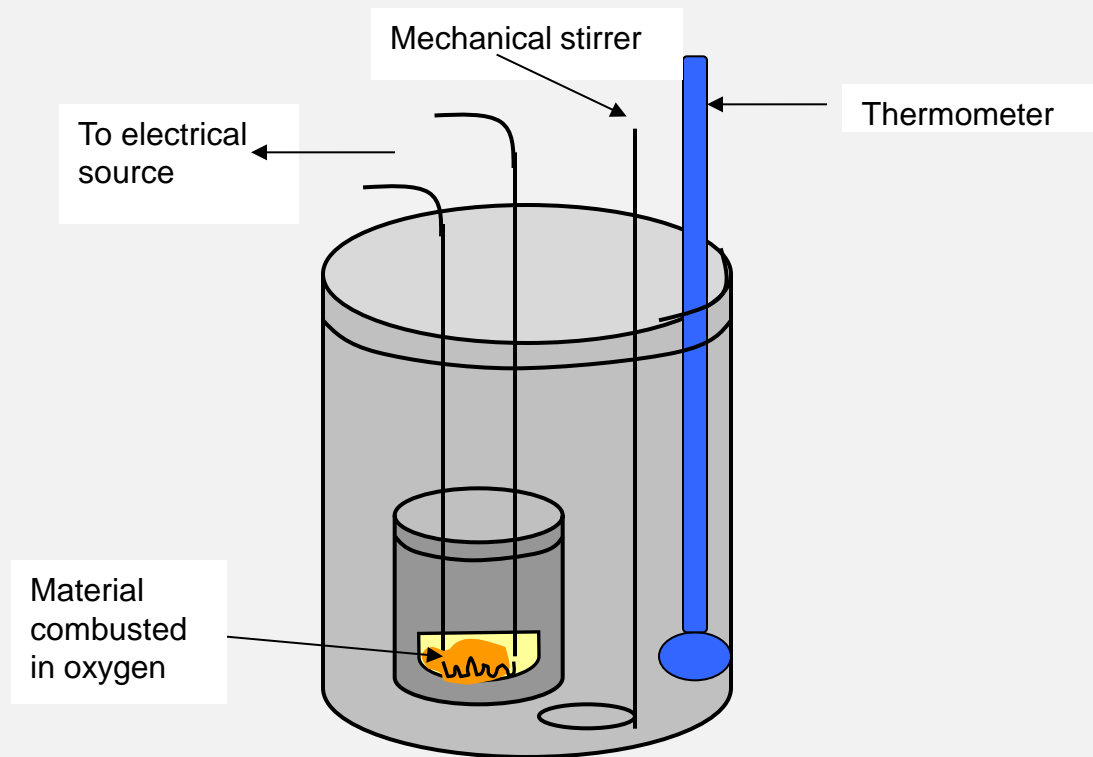
Enthalpy of formation of PbO_2 :



Step 3: Combine the equations we know to get the answer we require



By using a bomb calorimeter in the lab, we can determine the reaction enthalpy



The equation to calculate the heat change is

$$q = m s \Delta T$$

where q is the heat change

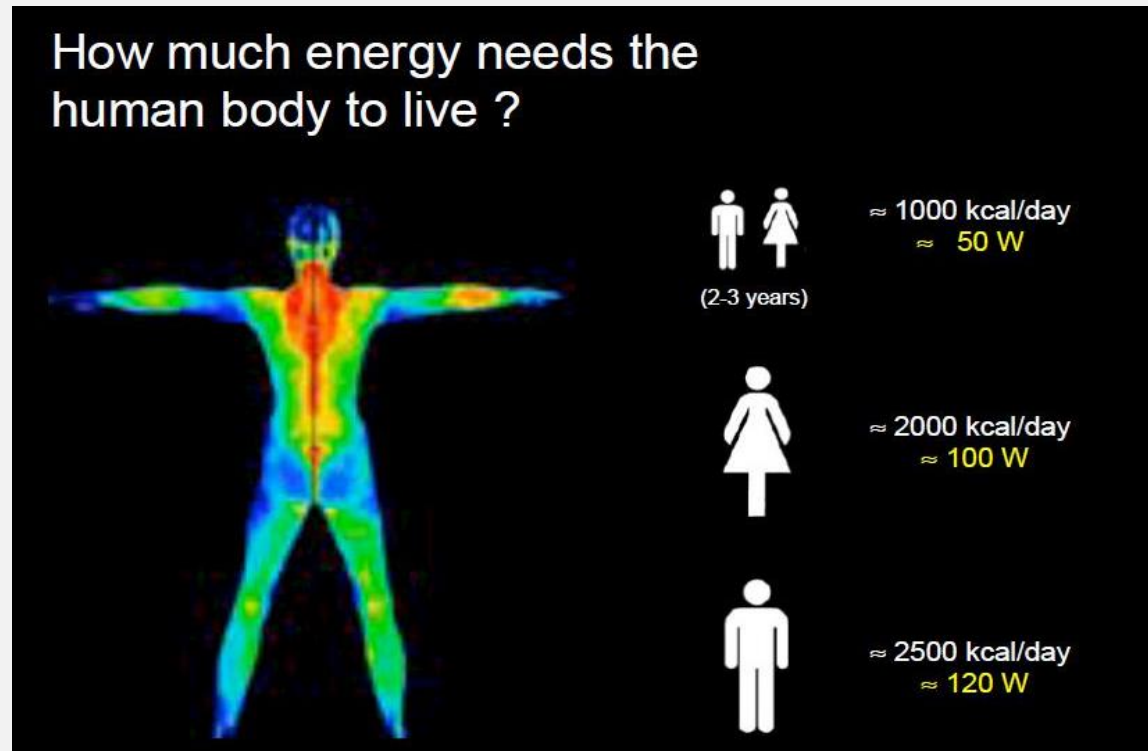
m is the mass of the sample

s is the specific heat of the sample

ΔT is the temperature change during reaction

The specific heat of a substance is the amount of heat required to raise the temperature of one gram of that substance by one degree Celsius

Calorie content of food



1g proteins– 4 kcal/g or 17 κ J/g

1g carbohydrates – 3,8-4 kcal/g or 16-17 κ J/g

1g fats – 9 kcal/g or 38 κ J/g

Entropy

- Measure of disorder of a system
- May be increased by increasing number of ways of arranging components. Explained by Boltzmann equation:
$$S = k \ln W$$
where S = entropy of system
 k = Boltzmann constant
 W = number of possible arrangements
- Has relationship with spontaneous change. Second Law of Thermodynamics: spontaneous processes (those which occur naturally without any external influence) are accompanied by an increase in entropy of the universe
- Absolute entropies may be determined from
- **Third Law of Thermodynamics**: At zero degrees Kelvin, the entropy of a perfect crystal is zero
- Because this starting point exists, can measure standard molar entropies: entropy change for 1 mol of a pure substance at 1 atm pressure (usually 25°C)

- A system with many equivalent ways to arrange its components (larger W) has relatively more disorder and high entropy.

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

This is the second law of thermodynamics.

Predicting Relative S^0 Values of a System



1. Temperature changes 

S^0 increases as the temperature rises.

2. Physical states and phase changes 

S^0 increases as a more ordered phase changes to a less ordered

phase.

3. Dissolution of a solid or liquid  

S^0 of a dissolved solid or liquid is usually greater than the S^0 of the pure solute. However, the extent depends upon the nature of the solute and solvent.

4. Dissolution of a gas 

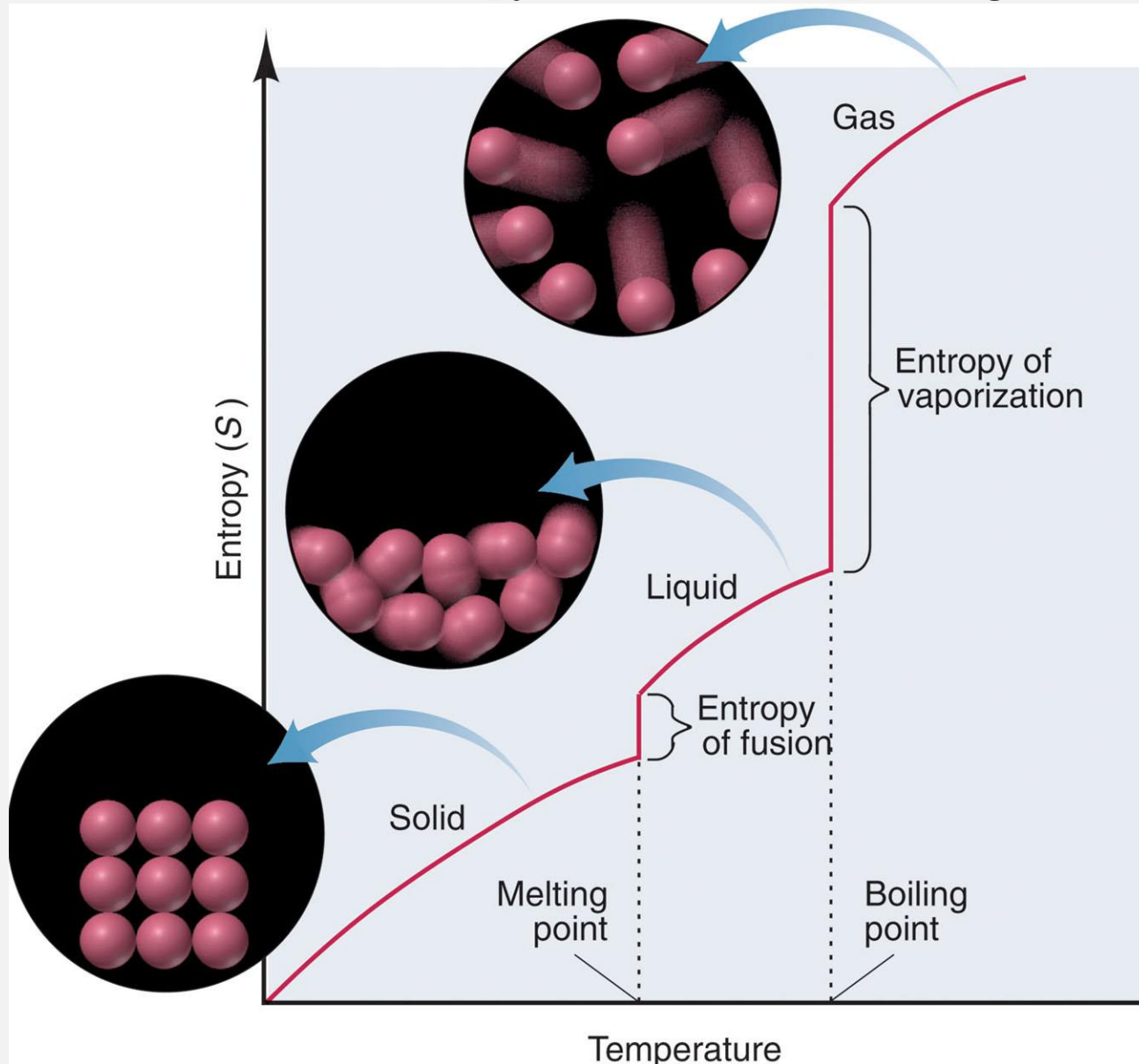
A gas becomes more ordered when it dissolves in a liquid or solid.

5. Atomic size or molecular complexity 

In similar substances, increases in mass relate directly to entropy.

In allotropic substances, increases in complexity (e.g. bond flexibility) relate directly to entropy.

The increase in entropy from solid to liquid to gas

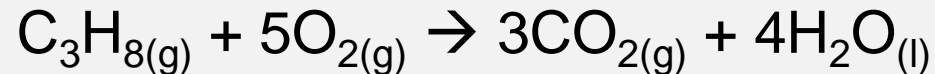


Predicting Entropy Changes

- An increase in temperature leads to greater kinetic energy of moving particles, more motion and hence greater S°
- Going from solid to liquid to gas (i.e. to less ordered systems) leads to an increase in S°
- For spontaneous change, ΔS must be greater than zero. For negative ΔS values, the process is spontaneous in the reverse direction

Example

Predict whether the entropy change for the following reaction will be positive or negative:



6 gas molecules \rightarrow 3 gas molecules + 4 liquid molecules

A decrease of the more disordered gas system indicates the entropy change for the reaction should be negative

Given the following information, calculate ΔS° for the reaction

S° (J / mol K)

CO₂ 213.7

H₂O 69.9

C₃H₈ 269.9

O₂ 205.0

$$\Delta S^\circ_{\text{rxn}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$= [(3 \text{ mol CO}_2)(S^\circ \text{ of CO}_2) + (4 \text{ mol H}_2\text{O})(S^\circ \text{ of H}_2\text{O})] - [(1 \text{ mol C}_3\text{H}_8)(S^\circ \text{ of C}_3\text{H}_8) + (5 \text{ mol O}_2)(S^\circ \text{ of O}_2)]$$

$$= [(3 \text{ mol})(213.7 \text{ J/molK}) + (4 \text{ mol})(69.9 \text{ J/molK})] - [(1 \text{ mol})(269.9 \text{ J/molK}) + (5 \text{ mol})(205.0 \text{ J/molK})]$$

$$= 641.1 \text{ J/K} + 279.6 \text{ J/K} - (269.9 \text{ J/K} + 1025 \text{ J/K})$$

$$= 920.7 \text{ J/K} - 1294.9 \text{ J/K}$$

$$= -374.2 \text{ J/K}$$

Spontaneity and Gibbs Free Energy

- Gibbs Free energy is a measure of the spontaneity of a process
- ΔG is the free energy change for a reaction under standard state conditions
- At constant temperature and pressure:

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

- an increase in ΔS leads to a decrease in ΔG
- if $\Delta G < 0$, the forward reaction is spontaneous
- if $\Delta G > 0$, the forward reaction is nonspontaneous
- if $\Delta G = 0$, the process is in equilibrium
- if ΔH and ΔS are positive, then ΔG will be negative only at high T , i.e. forward reaction spontaneous
- if ΔH is positive and ΔS is negative, ΔG will always be positive, i.e. forward reaction nonspontaneous
- if ΔH is negative and ΔS is positive, ΔG will always be negative, i.e. forward reaction spontaneous
- if ΔH and ΔS are negative, ΔG is negative only at low T , i.e. forward reaction spontaneous

Example

At 27°C, a reaction has $\Delta H = +10 \text{ kJ mol}^{-1}$ and $\Delta S = +30 \text{ J K}^{-1} \text{ mol}^{-1}$.

What is the value of ΔG ?

$$\Delta G = \Delta H - T\Delta S \quad T = 300 \text{ K}$$

$$\Delta G = (+10 \text{ kJ mol}^{-1}) - (300 \text{ K})(+30 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G = +10 \text{ kJ mol}^{-1} - 9000 \text{ J mol}^{-1}$$

$$\Delta G = +10 \text{ kJ mol}^{-1} - 9 \text{ kJ mol}^{-1}$$

$$\Delta G = + 1.0 \text{ kJ mol}^{-1}$$