CHEM 1035 – Lecture 18

Energy in Chemical Reactions

At the beginning of the semester, we said that Chemistry was the study of matter and its properties, the changes that matter undergoes, and the energy associated with those changes. Thus far we have only considered the changes in matter and the physical properties of matter. The energy associated with chemical change is a very important aspect of Chemistry

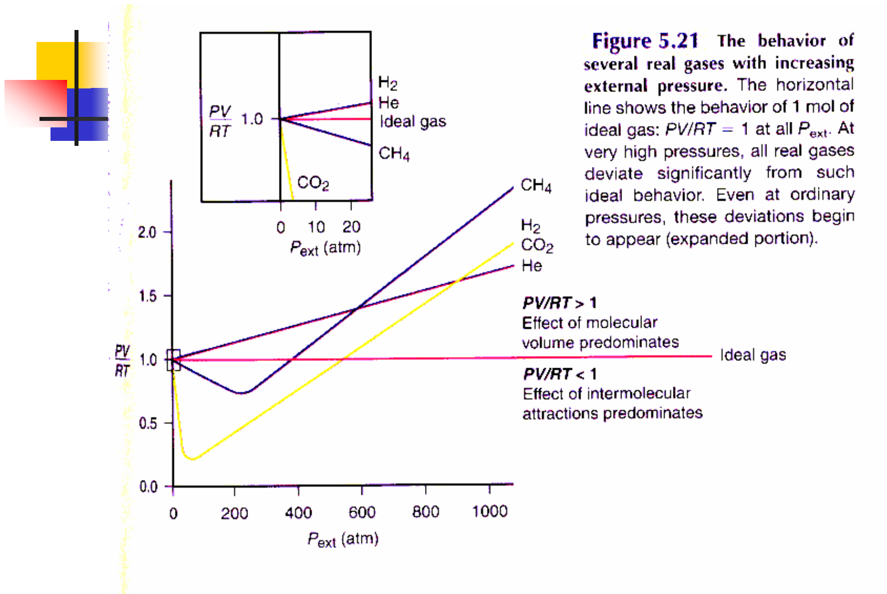

Figure 5.21 **The behavior of several real gases with increasing external pressure.** The horizontal line shows the behavior of 1 mol of ideal gas: $PV/RT = 1$ at all P_{ext}. At very high pressures, all real gases deviate significantly from such ideal behavior. Even at ordinary pressures, these deviations begin to appear (expanded portion).

The y-axis is PV/RT and the x-axis is the pressure. The Ideal gas has a constant value at all pressure (because the Volume and Temperature scale appropriately). A real-gas has deviations from the ideal behavior – dipping below the ideal value (due to intermolecular interactions, or rising above the ideal behavior due to molecular volume.

Thermochemistry

- A branch of Thermodynamics that studies the heat involved in chemical reactions. More specifically, the heat involved in a chemical reaction is part of the energy associated with the reaction.

Terms:
System
Surroundings
Universe

Thermodynamics – the study of energy flow during a chemical process.

To monitor the heat flow in a chemical reaction, we need to understand where the heat is flowing to, or where it is coming from. The Universe refers to everything. The system is that part of the Universe that we are observing. The part whose chemical or physical properties are undergoing the changes that we are observing. Once the system has been defined, then the surroundings are everything else in the Universe. Typically, however, we limit our view of the surroundings to those things in direct contact with the chemical system.

Energy of the System

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

E refers to the internal energy of the system.

The internal energy (E) of a chemical reaction is composed of the kinetic energy and potential energy of the reactants (initial state) and products (final state)

The dynamic part of thermodynamics tells us that the surroundings undergoes a change in internal energy that is equal to, but opposite in sign from the change in the internal energy of the system.

If (delta)E<0, then the system has lost energy to the surroudings.

If (delta)E > 0, then the system has gained energy from the surroundings.

So the energy of a chemical process is not gained nor lost – it is simply exchanged between the system and the surroundings.a This is known as the First Law of Thermodynamics

First Law of Thermodynamics

The total Energy of the Universe is Constant.

- This is also known as the Law of Conservation of Energy

Law of Conservation of Mass – mass is neither created nor destroyed during a chemical reaction. Einstein tells us that $E=mc^2$. So mass and energy are the same according to Einstein. So the conservation of mass and energy are (in many respects) the same law.

Types of energy transferred

$$E = w + q$$

Where: w = the work

q = the heat

Convention: q is positive if heat is added to the system (e.g. heat flows from surroundings into the system) and is negative if the heat is given up by the system (e.g. flows into the surroundings). Similarly, w is positive if work is done by the surrounding onto the system, and w is negative if work is done by the system on the surroundings.

The direction of heat flow is usually indicated by the temperature change associated with the chemical system. If the system gets colder during the chemical change, then heat is being removed from the surroundings. If the system gets hotter during the chemical change, then heat is being released from the surroundings.

Work is more difficult to describe because it can take many different forms (mechanical, electrical, etc.). One common description is Pressure-Volume work (consistent with our recent discussion of gases). Generally in PV work, we consider what happens to the system volume if the pressure inside the system container increases (while the pressure outside the container remains constant). If the system internal pressure increases, then the volume will increase – pushing back on the surroundings (e.g. work is done by the system on the surroundings). If the internal system pressure decreases, then the volume of the system will decrease (e.g. work is done on the system by the surroundings).

SI unit for Energy

- Joule = $\frac{kg - m^2}{\sec^2}$

Work = Force x distance

Other common units for work:

Calorie = energy required to raise the temperature of 1gm of water by 1°C = 4.184 J

Nutritional Calorie (e.g. how many Calories are in that pizza you had for dinner) = 1000 calories

Remember the value of the gas constant (R=8.3145 J/K-mole) was used when relating the temperature to the kinetic energy of gas molecules/atoms. So we've previously had exposure to the J

Thermodynamic State Function

The Internal Energy (E) of a chemical system is a State Function.

State Function – a property whose value depends only on the current state of the system.

The value of a state function is determined only by the state of the system (e.g. composition, temperature, pressure, and volume) and does not matter how the system arrived at those conditions.

Enthalpy – Heat of Reaction

- Focus our attention on the heat flow during a Chemical process

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

Where the reaction Enthalpy is symbolized by H

Measuring changes in the heat are relatively simple (e.g. monitoring the temperature), but monitoring the "work" of a chemical process is very difficult. We can focus our attention on the heat by limiting our attention to processes that occur at constant pressure. This is easy to do because we don't have to work very hard to maintain constant pressure – nature provides that for us , e.g. atmospheric pressure.

Given this definition for the change in Enthalpy during a chemical process, how does this isolate our attention onto heat flow? Consider that work done by the system on the surroundings is given by $-P\Delta V$, then (delta)E = q_p +w = q_p –P(delta)V

And q_p = (delta)E + P(delta)V

Enthalpy is a state function

$$\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants}$$

If: $\Delta H_{reaction} > 0$ the reaction is Endothermic

$\Delta H_{reaction} < 0$ the reaction is Exothermic

As is the case with all state functions, the value of the reaction enthalpy is independent of the path that the reaction takes – it only depends on the properties of the initial and final conditions of the chemical system.

If heat (q) flows into the system from the surroundings, then the chemical process is said to be Endothermic. If heat (q) flows out of the system into the surroundings, then the chemical process is said to be Exothermic