CHEMISTRY
PHYSICAL CHEMISTRY
&
THERMODYNAMICS

Lesson 2

by
Dr. Suchandra Chatterjee
Department of Chemistry
Surendranath College

THERMODYNAMICS

Main Theme: It deals with scientific study of work, heat and the related properties of chemical and mechanical systems. The word comes from two Greek words: ‘dunamikos, meaning movement and ‘thermos’ meaning heat or energy. So thermodynamics as a whole deals with the flow (movement/dynamics) of heat; conversion of heat to other utilizable forms; and more precisely getting work from heat.

Background: You have learnt since10th grade, that all forms of energy ultimately get converted into heat and this conversion is sometimes 100% and thus we have a huge source of heat with us! Also there is huge solar energy coming from the sun in the form of heat. However, coming to the reverse process, when we want to convert heat to other forms of energy or work, we face severe restrictions and we can not ever fully transform heat into other forms/work. And this is the reason we study thermodynamics, actually to learn the strategies to convert heat most efficiently to work, with minimal loss/waste of energy. So this is the main motto.

THERMODYNAMIC SYSTEMS

An important concept in thermodynamics is this **thermodynamic system**. A thermodynamic system is one that interacts and exchanges energy with the area around it (transformation of energy). As thermodynamics is a macroscopic science, it **loves to see everything from a bulk view, regards everything as a system, not moving into its microscopic/molecular details of the constituents**. This system could be as simple as a block of metal, a container filled with gas, chair, table anything, or as complex as a compartment fire. Outside the system are its surroundings. The system and its surroundings as a whole comprise the universe.

System: A region of the universe that we direct our attention to, actually a part of the universe that is separated from the rest of it by a definite wall or boundary.

Surrounding: Everything outside a system is called surroundings, where from we actually make our observations.

Boundary: An imaginary or physical thing/wall that separates a system from its surroundings.

Universe: Overall physical space comprising of system and surrounding.

TYPES OF SYSTEMS

Open systems: These systems are separated from the surrounding by a **porous wall** that can **exchange both matter and energy** with an outside system. They are actually portions of larger systems and in intimate contact with that larger system. Our body, room, house etc. are open systems.

Closed systems: These systems are separated from the surrounding by a **dia-thermal wall** that can **exchange energy but not matter** with the outside system. Though they are also typically portions of larger systems, they are not in complete contact with that larger system. The Earth is essentially a closed system; it obtains lots of energy from the sun but the exchange of matter with the outside is almost zero.

Isolated systems: These systems are separated from the surrounding by an **adiabatic wall** that can **exchange neither energy nor matter** with the outside system. While they also may be portions of larger systems, but do not communicate with the outside in any way both in context of matter and energy. The physical universe as a whole, is an isolated system; a closed thermos bottle is essentially an isolated system too (though its insulation is not perfect!). **Properly isolated systems are only idealization, we don't have such systems in reality.**

THERMODYNAMIC PROPERTIES

As thermodynamics being a macroscopic science, doesn't bother at all about the molecular picture of the constituents, it recognises and defines all the systems by their relevant **properties.** These properties may be **measurable** or may be **immeasurable.**

Measurable properties: Properties that can be measured like pressure, volume, temperature, density, surface tension, viscosity etc. **Among them 8 properties are used to describe thermodynamic systems.** They are **pressure, temperature, volume, entropy, internal energy, enthalpy, Gibbs function and Helmholtz function**. So they are called thermodynamic properties.

Immeasurable properties: Properties that can not be measured like colour, odour, softness, hardness etc.

Note: It's obvious that we would prefer the measurable ones over the immeasurable as they would help us to **measure the changes in these properties during any change or transformation**. These measurable properties again may be **intensive** or **extensive**.

EXTENSIVE OR INTENSIVE?

Intensive Properties: That are independent of the amount of mass present. e.g., pressure, temperature, density, molar volume, molecular weight etc.

Extensive Properties: Whose value depend on the mass of the system. e.g., mass, volume etc.

Trick: The easiest way to check whether a property is intensive or not, is to perform two steps;

1. **Check whether the value of that property is same every where through out the system.**
2. **Check whether its value remains the same even in a small block if cut from the system.**
3. **If for both the cases, the answer is positive, then the property is definitely intensive and vice versa.**

✓ **Things to Remember:** Please do remember, that except pressure and temperature all the other six thermodynamic properties mentioned earlier, i,e., volume, entropy, internal energy, enthalpy, Gibbs function and Helmholtz function are essentially **extensive**!

STATE AND PATH FUNCTIONS

State Function: The property that **depends only upon the final state of the system and not on the path traversed by it to reach that final state** is a **state property or state function**. e.g., pressure, temperature, volume, entropy, enthalpy, free energy etc.

Path Function: The property that **depends not only on the initial and final states of the system but on the path also, by which it has reached that final state,** is a **path property or path function** e.g., work, heat, heat capacity, molar heat capacity etc.

Note: All the **8 thermodynamic functions mentioned earlier are essentially state functions** and hence not dependant on the path. However, fortunately or unfortunately **heat and work** these two properties (that are major concern of thermodynamics) are **path functions**. **So by changing the path, there remains some scope/chance to change the values of these functions that could have not been done it the functions were state functions!** Hence we all study thermodynamics very seriously even today, with the aim to choose the best (most efficient) path for getting maximum work from heat with minimum loss/waste of energy.

PATH FOR THERMODYNAMIC CHANGE

The path/process to reach the final state from the initial state of a particular system may be mainly of two types – reversible and irreversible.

Reversible Processes are those;

✓That are carried out **infinitely slowly** with **infinite numbers** of **infinitesimally small** steps.
✓That **does not disturb the equilibrium** between system and surrounding through out the process at any point.
✓For which, the **driving force is just a little more than the opposing force** since the process proceeds in smaller steps.
✓That **can be made to proceed both in forward and backward directions** just by changing the driving force slightly.
✓That helps in **bringing back the system exactly to its initial original state** without leaving any effect in the surrounding. That means both the system and surroundings are restored to their original states.
✓That **produces maximum amount work** as an output**.**

Note: Its obviously an idealisation. We can not ever have perfectly reversible processes, just like perfectly isolated systems stated earlier!

MORE ON PATH

Irreversible processes are those;

✓That are actually very fast as carried out **abruptly with finite number of relatively larger steps.**
✓That **do disturb the equilibrium** between system and surrounding in one or more steps.
✓For which, the **difference between the driving and opposing forces is larger** since the process proceeds in bigger steps.
✓That **can not be made to proceed both in forward and backward directions** just by changing the driving force but actually **unidirectional**.
✓That **can not return back both the system and the surrounding to the original condition** if the process is some how reversed.
✓That **produce work which is definitely lesser than their reversible analogues.**

Note: All the natural and spontaneous processes are essentially irreversible. Hence they are fast, happens in one or two steps and generally can not be reverted back to the original state following exactly the same path.

THANK YOU!

ANY QUESTION ?