

# Introduction to Physical Chemistry – Lecture 4

## I. LECTURE OVERVIEW

In this lecture, we will formulate and study the First Law of Thermodynamics. We will then go on to consider various thermodynamic functions.

We should point out that, starting with this lecture, the next few lectures may not perfectly overlap with what will be taught in section for the given week. This is simply due to the theoretical background material that I would like to cover in class. However, both the class and section material should be “in sync” again by the sixth week or so (though they may fall “out of sync” again during the semester).

## II. INTERNAL ENERGY

Consider some object which from very far away appears to be a solid object. If this object has a mass  $M$ , and its center of mass has a velocity  $v$ , then this object has a kinetic energy of  $\frac{1}{2}Mv^2$ .

However, as we approach the object and look at it

more closely, we notice that it is in fact composed of numerous smaller objects (atoms, molecules, etc.), each of which have their own velocities  $\vec{v}_1, \dots, \vec{v}_N$ , where  $\vec{v}_i = (v_{ix}, v_{iy}, v_{iz})$  denotes the velocity vector of the  $i^{\text{th}}$  particle.

The kinetic energy of the system is then  $\sum_{i=1}^N \frac{1}{2}m_i\vec{v}_i^2$ . In general, this will not equal  $\frac{1}{2}Mv^2$ . So, what is going on here?

We can break apart the kinetic energy by redefining some terms to make a physically more useful picture. We begin by defining the total mass  $M = m_1 + \dots + m_N$ , and the *average* velocity  $\vec{v} = (m_1\vec{v}_1 + \dots + m_N\vec{v}_N)/M$  (note that this is a *weighted* average, since the mass of the object affects its contribution to the average velocity). Also, for object  $i$ , define its *relative* velocity to be  $\Delta\vec{v}_i = \vec{v}_i - \vec{v}$ .

Note that  $\vec{v}$  is simply the velocity of the center of mass of the collection of particles. To see this, if  $\vec{x}_i$  denotes the coordinates of the  $i^{\text{th}}$  object, then the center of mass  $\vec{x} = (m_1\vec{x}_1 + \dots + m_N\vec{x}_N)/M$ , so that the velocity of the center of mass is  $\dot{\vec{x}} = (m_1\dot{\vec{x}}_1 + \dots + m_N\dot{\vec{x}}_N)/M = \vec{v}$ .

Now, we have,

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$$\begin{aligned}\sum_{i=1}^N \frac{1}{2}m_i\vec{v}_i^2 &= \sum_{i=1}^N \frac{1}{2}m_i(\vec{v} + \Delta\vec{v}_i)^2 \\ &= \frac{1}{2}\left(\sum_{i=1}^N m_i\right)\vec{v}^2 + \sum_{i=1}^N m_i(\vec{v} \cdot \Delta\vec{v}_i) + \sum_{i=1}^N \frac{1}{2}m_i\Delta\vec{v}_i^2 \\ &= \frac{1}{2}M\vec{v}^2 + \vec{v} \cdot \left(\sum_{i=1}^N m_i\Delta\vec{v}_i\right) + \sum_{i=1}^N \frac{1}{2}m_i\Delta\vec{v}_i^2 \\ &= \frac{1}{2}M\vec{v}^2 + \sum_{i=1}^N \frac{1}{2}m_i\Delta\vec{v}_i^2\end{aligned}\tag{1}$$

since  $\sum_{i=1}^N m_i\Delta\vec{v}_i = \sum_{i=1}^N m_i\vec{v}_i - \vec{v}\sum_{i=1}^N m_i = M\vec{v} - M\vec{v} = 0$ .

Note then that the kinetic energy of the object may be composed into two parts: (1) The *macroscopic* kinetic energy, or the kinetic energy due to the overall motion of the object. When viewed from far away, this is simply the motion of the center of mass, so the kinetic energy is given by  $\frac{1}{2}M\vec{v}^2$ . (2) The *internal* kinetic energy, given by  $\sum_{i=1}^N \frac{1}{2}m_i\Delta\vec{v}_i^2$ . This is the kinetic energy of the internal motions of the particles.

If the center of mass of the object is not moving, then from far away the object will appear stationary. Nevertheless, the internal motions of the particles relative to

each other means that the object will still have an internal kinetic energy.

Therefore, in addition to kinetic energy, a macroscopic object may possess additional energy which we call *internal energy*. Although our derivation was for kinetic energy only, if the particles have interactions between each other, and if the object is placed in an external field (say gravitational), then we can perform such a decomposition for potential energy as well. In general then, if the energy state of an object is a function of the positions and velocities of all its constituent particles, then we may decompose the energy into an external energy that depends only on the center of mass coordinates and velocities of the object, and an internal energy that de-

depends only on the deviation of the individual particles

from the center of mass and velocity. We have,

$$E(\vec{x}_1, \dots, \vec{x}_N, \vec{v}_1, \dots, \vec{v}_N) = E_{ext}(\vec{x}, \vec{v}) + E_{int}(\Delta\vec{x}_1, \dots, \Delta\vec{x}_N, \Delta\vec{v}_1, \dots, \Delta\vec{v}_N) \quad (2)$$

The internal energy  $E_{int}$  is often denoted by the symbol  $U$ .

### III. THE FIRST LAW OF THERMODYNAMICS

We now consider the First Law of Thermodynamics, which is nothing more than the principle of energy conservation applied to heat and work flows on macroscopic systems. Before stating the First Law, we need to first introduce some definitions.

#### A. The concept of system and surroundings

The universe is a pretty big place. For many problems of interest (the functioning of heat engines, boiling of water, fluid flows, flying of airplanes, etc.), we are not interested in the behavior of the universe as a whole, but rather in a small part of it.

The region of space which is the focus of our attention for a given problem is known as a *system*. The rest of the universe is known as the *surroundings*. A system may interact with its surroundings, via heat and mass flows.

A simple illustration of this concept is water in a glass. We may define the interior of the glass to be the system, and everything else to be the surroundings. If we pour water into the glass, then there is a mass flow from the surroundings into the system. Conversely, if we pour water out of the glass, then there is a mass flow from the system to the surroundings. If we heat the water in the glass, then there is energy flow from the surroundings into the system. Conversely, if we cool the water in the glass, then there is energy flow from the system to the surroundings.

A system may be *isolated*, *closed*, or *open*. An isolated system has no interactions with its environment. A closed system allows only thermal interactions (i.e. heat flows). An open system allows for both heat and mass flows.

We are now in a position to state the First Law of Thermodynamics.

#### B. The statement of the first law

The First Law of Thermodynamics may be stated as follows: The change in internal energy of a system is given by the heat flow into the system minus the work done by the system on the surroundings.

Mathematically, the law may be expressed as follows:

$$\Delta U = Q - W \quad (3)$$

There is a sign convention here that is worth mentioning. Here, we take  $W$  to be positive if the work is done *by the system* on the surroundings. Thus, a positive value of  $W$  corresponds to a loss in the internal energy of the system.

However, you may find texts (and I may forget this convention and flip back and forth at various points in the course :-)) where the expression is  $\Delta U = Q + W$ . Both equations are correct. In the second case,  $W$  is positive if the work is done *on the system* by the surroundings. Thus, a positive value of  $W$  corresponds to a gain in the internal energy of the system.

Therefore, the first law may be stated mathematically in two distinct but equivalent ways:

$$\begin{aligned} \Delta U = Q - W \text{ if } W > 0 \text{ implies that work is done by the system on the surroundings} \\ \Delta U = Q + W \text{ if } W > 0 \text{ implies that work is done on the system by the surroundings} \end{aligned} \quad (4)$$

To illustrate this law for a concrete example, consider an ideal gas in a box. However, assume that one side of the box can move, as with a piston (see Figure 1). Let the gas in the box be at a volume  $V$ , temperature  $T$ , and pressure  $P$ . Since the piston is stationary, the external

pressure acting on the movable wall must be  $P$  as well. If the area of the piston is  $A$ , and if the piston moves outward a distance  $\Delta x$ , then the total work done by the

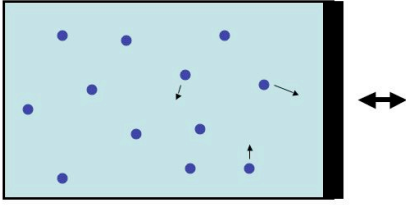


FIG. 1: An ideal gas sitting in a container with a movable wall.

system is,

$$W = F\Delta x = P\Delta V \quad (5)$$

where  $\Delta V$  denotes the change in volume of the box. In this context, the first law gives,

$$\Delta U = Q - P\Delta V \quad (6)$$

In differential form, this becomes,

$$dU = \delta Q - PdV \quad (7)$$

where  $\delta Q$  denotes that  $Q$  is not an exact differential, while  $dU$  is an exact differential. We will discuss this notation a bit later.

We should point out that if other kinds of work are done on the system (electrical work, say), then these terms must be added in as well. However, for the bulk of this course, we will simply focus on what is known as  $PV$ -work.

## IV. STATE FUNCTIONS

### A. Definition and examples

A *state* function is a function that only depends on the state of the system, and not on how that state was achieved. We illustrate what we mean with two examples:

*Example 1 – A particle in a gravitational field:* If we consider a uniform gravitational field, for simplicity, then we have shown earlier that the change in potential energy of the object in moving it from height coordinate  $z_1$  to  $z_2$  is simply  $mg(z_2 - z_1)$ . Note that this energy change does not depend on how the object was moved from  $z_1$  to  $z_2$ . We could start at  $z_1$ , move it up some, then down some, side to side, at a diagonal, etc. The point is that the *path from  $z_1$  to  $z_2$  is irrelevant*. The change in potential

energy only depends on the initial and final states of the object.

This independence of path allows us to define the potential energy function as a state function of the object: We pick an arbitrary reference point to be the origin of our coordinate system, and set the energy at this reference point to be 0 (since we can only measure energy differences and not energy itself, this is a valid step). We then define the potential energy of an object at a height  $z$  to be the potential energy change in moving the object from the origin to the height  $z$ . Since the energy change is independent of path, we get one answer, namely  $mgz$ .

A force field that admits a potential energy function which is a state function of the system is known as a *conservative* force field. The reason for this terminology is that a particle moving in a conservative force field will obey energy conservation (potential plus kinetic remains constant).

*Example 2 – Energy lost due to friction:* Friction is an example where the path does matter in determining energy changes. For example, suppose we have an object on some table, and we wish to move it a distance of  $1m$  to the right. We can either move it directly, or we can first move it up  $0.5m$ , to the right  $1m$ , and then down  $0.5m$ . If there is a retarding frictional force  $1N$  on the object, then the first path requires an energy input of  $1N \times 1m = 1J$ , while the second path requires an energy input of  $1N \times 2m = 2J$ . So, in this case, we cannot assign a “friction” energy function to the object, because the amount of work done on the object due to friction is path-dependent.

Internal energy is a state function, because it is the total energy associated with the motions and interactions of the constituent particles of the system. Thus, by the exact differential  $dU$ , we mean an infinitesimal change in the internal energy of the system associated with an infinitesimal change in the state.

Note that because  $P$  and  $V$  are state functions,  $PV$ -work is a state function as well.

Heat, however, is not a state function, because heat is not something that an object possesses. Rather, heat is a form of energy that is given off or taken in by a system during changes in the internal state of a system. Since heat is associated with changes in the internal state of a system, the amount of heat given off will generally be path-dependent. Therefore, we do not use  $dQ$  to denote small heat transfers, but rather  $\delta Q$ , to make the path-dependent nature of heat transfer clear.

### B. Mathematical definition

In the first homework set, you were given various differentials and asked to determine if they were exact differentials or not. The standard procedure was as follows: You were given some expression  $df = F_x dx + F_y dy + F_z dz$ , and asked to determine if  $df$  was an exact differential or not.

The way to determine this was to check if  $F_x = \partial f/\partial x$ ,  $F_y = \partial f/\partial y$ , and  $F_z = \partial f/\partial z$ .

The reason why this notion of an exact differential and the physical definition we gave above are equivalent is that  $df$  is an exact differential if and only if  $f$  is a state function. By  $f$  being a state function, we mean that the change in  $f$  in moving from  $\vec{x}_1 = (x_1, y_1, z_1)$  to  $\vec{x}_2 = (x_2, y_2, z_2)$  is independent of the path from  $\vec{x}_1$  to  $\vec{x}_2$ . Therefore, if  $g_1(t) = (g_{1x}(t), g_{1y}(t), g_{1z}(t))$  and  $g_2(t) = (g_{2x}(t), g_{2y}(t), g_{2z}(t))$  are two paths for which  $g_1(0) = g_2(0) = \vec{x}_1$  and  $g_1(1) = g_2(1) = \vec{x}_2$ , then,

$$\begin{aligned} f(\vec{x}_2) - f(\vec{x}_1) &= \int_0^1 (\vec{F}(t) \cdot g_1'(t)) dt \\ &= \int_0^1 (\vec{F}(t) \cdot g_2'(t)) dt \end{aligned} \quad (8)$$

where  $\vec{F} = (F_x, F_y, F_z)$ .

## V. SPECIFIC STATE FUNCTIONS

In this section we will consider some state functions that may be constructed from the thermodynamic variables we have seen so far.

### A. Enthalpy

One rule regarding state functions is that the sum, product, quotient, etc. of any two state functions is a state function. One very important state function is the *enthalpy*, denoted  $H$ . Enthalpy is defined very simply as follows:

$$H = U + PV \quad (9)$$

Why is enthalpy important? Well, in studying thermodynamic changes which occur to systems (for example, a chemical reaction), we often consider the change with one of the thermodynamic variables  $T$ ,  $P$ ,  $V$  fixed. A process may be kept at fixed  $T$  if the system is placed in a large thermal bath, to keep the system at constant temperature. A process may be kept at constant pressure if one wall of the container is movable (like our piston example), so that it may expand and contract to equalize any pressure changes. A process may be kept at constant volume with a closed container with immovable walls.

For a process that occurs at constant volume, the first law reads,

$$dU = \delta Q \quad (10)$$

so that  $\Delta U = Q$ . Therefore, *for a process that occurs at constant volume, the change in internal energy of a system is equal to the heat added to the system.*

Now, for a process that occurs at constant pressure, the first law reads,

$$\begin{aligned} dU &= \delta Q - PdV \\ \Rightarrow \delta Q &= dU + PdV \\ &= d(U + PV) = dH \end{aligned} \quad (11)$$

where the equality  $PdV = d(PV)$  because  $P$  is constant.

Integrating, we get  $\Delta H = Q$ . Therefore, *for a process that occurs at constant pressure, the change in enthalpy of a system is equal to the heat added to the system.*

### B. Heat capacity

When heat is added to a system, the temperature will in general change. The *heat capacity* is a measure of how strongly the temperature of a system is affected by heat flows. There are many ways to define heat capacities, depending on the circumstances under which the heat is transferred. We consider two types of heat capacity:

1. The *constant volume* heat capacity, denoted  $C_V$ : This is the amount of heat added to the system per unit temperature change, when the heat is transferred at constant volume. We have,  $C_V = (\delta Q/\partial T)_V = (\partial U/\partial T)_V$ , since  $dU = \delta Q$  for a constant volume process.
2. The *constant pressure* heat capacity, denoted  $C_P$ : This is the amount of heat added to the system per unit temperature change, when the heat is transferred at constant pressure. We have,  $C_P = (\delta Q/\partial T)_P = (\partial H/\partial T)_P$ .

For an ideal gas, it may be shown that  $U$  depends only on the temperature  $T$  (this is essentially due to the fact that the energy of an ideal gas is simply the sum of the kinetic energies of the individual gas particles).

Therefore,  $(\partial H/\partial T)_P = dU/dT + P(\partial V/\partial T)_P = C_V + nR$ , so  $C_P = C_V + nR$  for an ideal gas. If we let  $\bar{C}_V$ ,  $\bar{C}_P$  denote the constant volume and constant pressure heat capacities per mole of gas, then we have,

$$\bar{C}_P = \bar{C}_V + R \quad (12)$$

## VI. THE FIRST LAW APPLIED TO CHEMICAL REACTIONS

A chemical reaction is a transformation of one set of chemicals into another. A group of chemicals, called the *reactants*, interact and transform into another set of chemicals called the *products*. An example of a chemical reaction is,



A chemical reaction is *exothermic* if it gives off heat, and *endothermic* if it requires a net heat input for it

to progress. The exothermicity or endothermicity of a chemical reaction is measured by placing it in a container, and allowing the reaction to proceed at constant temperature, by removing or adding heat as needed (this can be done by placing the system in a heat bath).

If the reaction occurs at constant volume, then we have,

$$\Delta U = Q \quad (14)$$

If the reaction is exothermic, it will give off heat, so that  $Q$  is negative.

If the reaction occurs at constant pressure, then we have,

$$\Delta H = Q \quad (15)$$

We can define a standard  $\Delta U$  and  $\Delta H$  of a chemical reaction. For  $\Delta U$ , it is the total heat added to the system when the reaction goes to completion at a given temperature, fixed volume, with a prespecified initial number of moles of reactants (these must be in the appropriate stoichiometric ratios so that everything can react).

For  $\Delta H$ , it is the total heat added to the system when the reaction goes to completion at a given temperature, pressure, and with a prespecified initial number of moles of reactants.

Typically, we assume that we start with one mole of one of the reactants or finish with one mole of one of the products when defining  $\Delta U_{rxn}$  and  $\Delta H_{rxn}$ . This must be specified, however.