

Introduction to Physical Chemistry – Lecture 5

I. LECTURE OVERVIEW

In this lecture, we will consider energy and heat flows under various conditions. We will also define the concept of *reversibility*, which will be important later, when we consider entropy.

II. THE CONCEPT OF REVERSIBILITY

A central concept in thermodynamics is the notion of *reversibility*. A reversible process is one that is thermodynamically allowed in both directions. For example (see Figure 1), consider the flow of heat from a region of high temperature to a region of low temperature. This is an irreversible process, because heat never flows from a region of low temperature to a region of high temperature (such an occurrence would violate what is known as the Second Law of Thermodynamics, which we will discuss later).

However, heat flow between regions of identical temperature can happen in both directions, because there is no preferred flow direction from one region to another. Therefore, a transfer of an amount Q of heat energy from one region to another, when both regions have the same temperature, can also occur in the reverse direction.

Another example is PV -work. If the pressure of the gas inside the container is greater than the external pressure on the piston, then the gas will push the piston outward until the gas pressure becomes equal to the external counterpressure. Again, this process is irreversible, because the reverse process is not possible when the gas pressure is greater than the external pressure. However, if the external pressure exerted on the face of the piston is continuously adjusted to be equal to the gas pressure, then the process whereby the gas pushes the piston outward is a reversible one, because there is no preferred direction for the piston to move.

Finally, our last example involves phase transitions. Consider, for example, the melting of ice at 1 atm pressure. Below 0°C , the freezing of liquid water to ice is an irreversible process, since we will never see ice below 0°C melt into water. Conversely, the melting of ice to liquid water above 0°C is an irreversible process, since we will never see water freeze above 0°C . At exactly 0°C , the melting of ice and the freezing of water are both reversible, because here we have an equilibrium between the two phases.

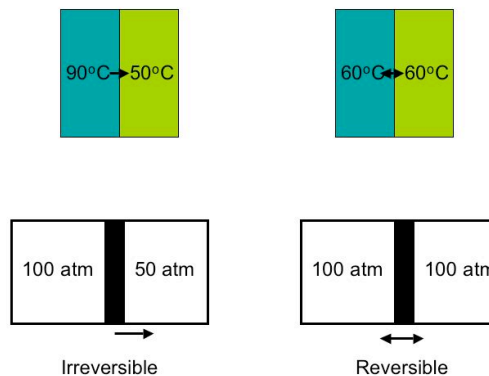


FIG. 1: Examples of reversible and irreversible processes.

III. CALCULATING THERMODYNAMIC CHANGES OF STATE

In this section, we will compute changes in various thermodynamic variables given processes that occur under various conditions. In all examples for this section, we will consider an ideal gas container in a box with a movable wall.

A. Isothermal expansion/compression

The first example we consider is that of an isothermal expansion or compression. In this case, an ideal gas at constant temperature pushes against the movable wall (i.e. piston). Constant temperature is maintained by placing the system in a thermal bath at the given temperature, to prevent any changes in the temperature of the system.

So, suppose a gas with initial pressure P , temperature T , volume V_1 , and mole number n undergoes an isothermal expansion from volume V_1 to volume V_2 . We wish to compute Q , W , and ΔU for this process.

First of all, we know that for an ideal gas, U only depends on T , hence $dU = 0$. Since the First Law reads $dU = \delta Q - \delta W$, we have $\delta Q = \delta W = PdV$ for an isothermal process. For an ideal gas, $P = nRT/V$, hence,

$$\begin{aligned}\delta Q = \delta W &= \frac{nRT}{V}dV \Rightarrow \\ Q = W &= \int_{V_1}^{V_2} \frac{nRT}{V}dV = nRT \ln \frac{V_2}{V_1}\end{aligned}\quad (1)$$

Since this expression is correct whether or not $V_2 > V_1$ or vice versa, this formula is also valid for an isothermal compression.

B. Adiabatic expansion/compression

An *adiabatic* process is one where no heat is added or removed from the system. In this case $\delta Q = 0$ throughout the process, so we have $dU = -\delta W = -PdV$. For an ideal gas, we have $\delta U = C_V dT$. Therefore, if T_1 and T_2 denote the start and end temperatures of the gas during the expansion/compression process, and if V_1 and V_2 denote the start and end volumes, then

$$\begin{aligned}
 C_V dT &= -\frac{nRT}{V} dV \Rightarrow \\
 C_V \frac{dT}{T} &= -nR \frac{dV}{V} \Rightarrow \\
 C_V \int_{T_1}^{T_2} \frac{dT}{T} &= -nR \int_{V_1}^{V_2} \frac{dV}{V} \Rightarrow \\
 C_V \ln \frac{T_2}{T_1} &= -nR \ln \frac{V_2}{V_1} \Rightarrow \\
 \ln \frac{T_2}{T_1} &= \frac{nR}{C_V} \ln \frac{V_1}{V_2} \Rightarrow \\
 \frac{T_2}{T_1} &= \left(\frac{V_1}{V_2}\right)^{nR/C_V} \Rightarrow \\
 \frac{T_2}{T_1} &= \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{R/\bar{C}_V} \quad (2)
 \end{aligned}$$

where \bar{V} denotes the molar volume of the gas (equivalent to V_m).

Note that if $\bar{V}_1 < \bar{V}_2$, then $T_2 < T_1$, so that a gas cools as it adiabatically expands. If $\bar{V}_1 > \bar{V}_2$, then $T_2 > T_1$, so that a gas heats up as it adiabatically expands.

We can relate temperature to pressure, and pressure to volume as well, for a gas that undergoes adiabatic expansion or compression. Using $P\bar{V} = RT$, we have,

$$\begin{aligned}
 \frac{T_2}{T_1} &= \left(\frac{RT_1 P_2}{RT_2 P_1}\right)^{R/\bar{C}_V} \Rightarrow \\
 \left(\frac{T_2}{T_1}\right)^{1+R/\bar{C}_V} &= \left(\frac{P_2}{P_1}\right)^{R/\bar{C}_V} \Rightarrow \\
 \left(\frac{T_2}{T_1}\right)^{\bar{C}_P/\bar{C}_V} &= \left(\frac{P_2}{P_1}\right)^{R/\bar{C}_V} \Rightarrow \\
 \frac{T_2}{T_1} &= \left(\frac{P_2}{P_1}\right)^{R/\bar{C}_P} \quad (3)
 \end{aligned}$$

and so as a gas is adiabatically compressed to higher pressures it heats up.

Finally, we can obtain the relationship between P and \bar{V} , using the ideal gas relation. We have,

$$\begin{aligned}
 \frac{P_2 \bar{V}_2}{P_1 \bar{V}_1} &= \left(\frac{P_2}{P_1}\right)^{R/\bar{C}_P} \Rightarrow \\
 \frac{\bar{V}_2}{\bar{V}_1} &= \left(\frac{P_2}{P_1}\right)^{(R-\bar{C}_P)/\bar{C}_P} \Rightarrow \\
 \frac{\bar{V}_2}{\bar{V}_1} &= \left(\frac{P_2}{P_1}\right)^{-\bar{C}_V/\bar{C}_P} \Rightarrow \\
 \frac{P_2}{P_1} &= \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\bar{C}_P/\bar{C}_V} \quad (4)
 \end{aligned}$$

The quantity \bar{C}_P/\bar{C}_V is usually denoted by γ .

We summarize the results for the adiabatic expansion/compression of an ideal gas:

1. $\frac{T_2}{T_1} = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{R/\bar{C}_V}$, so that a gas heats up as it is compressed adiabatically, and cools as it expands adiabatically. This makes sense, since, as a gas is compressed, work is being done on it, and so the internal energy increases. As a gas expands, it does work on the surroundings, hence the internal energy decreases.
2. $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/\bar{C}_P}$, which simply states that the temperature of the gas increases/decreases as the pressure of the gas increases/decreases to due adiabatic compression/expansion.
3. $\frac{P_2}{P_1} = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^\gamma$, so that the gas pressure increases/decreases as it is adiabatically compressed/expanded.

C. Isovolumetric changes of state

We now consider processes for which $dV = 0$, i.e., *isovolumetric* processes. In this case, $dW = 0$, so that the first law reads $dU = \delta Q$. Therefore, for an ideal gas, $C_V dT = \delta Q \Rightarrow C_V \Delta T = Q$. So, the total heat added to the system is simply given by the *constant volume* heat capacity times the change in temperature.

D. Isobaric changes of state

An *isobaric* process is one that occurs at constant pressure. The first law reads $dU = \delta Q - PdV \Rightarrow \delta Q = dU + PdV = d(U + PV) = dH$. Therefore, for an ideal gas, $C_P dT = \delta Q \Rightarrow C_P \Delta T = (C_V + nR)\Delta T = Q$. So, the total heat added to the system is given by the *constant pressure* heat capacity times the change in temperature.

IV. CHEMICALLY REACTING SYSTEMS: THE BOMB CALORIMETER

As an application of the First Law to chemically reacting systems, we consider a device called a *bomb calorimeter* (see Figure 2). A bomb calorimeter measures the energy released in a chemical reaction by allowing it to proceed to completion under isovolumetric, adiabatic conditions. By measuring the temperature change from the beginning and end of the reaction, it is possible to measure ΔU for the reaction. We illustrate how:

Consider some chemical reaction $r_1 R_1 + r_2 R_2 + \dots + r_N R_N \rightarrow p_1 P_1 + p_2 P_2 + \dots + p_M P_M$, where R_i denotes reactant i , and P_i denotes product i .

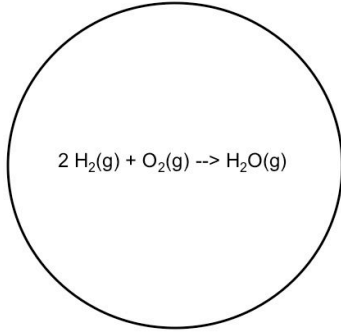


FIG. 2: Illustration of a bomb calorimeter.

Suppose, in a container of volume V , and initial pressure P_1 and temperature T_1 , we place nr_i moles of reactant R_i for each i , and allow the reaction to proceed to completion. Then, at the end of the reaction, we will have np_1 moles of P_1 , np_2 moles of P_2 , \dots , np_M moles of P_M inside the container. The final temperature and pressure will also be T_2 and P_2 respectively.

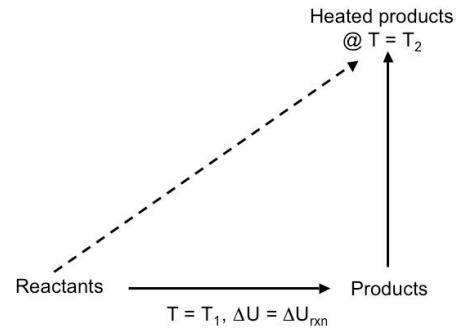
The question is, what is ΔU for the reaction? To compute this, note from the First Law that since the volume of the container does not change, $\delta W = 0$, and since the process is adiabatic, $\delta Q = 0$. Therefore, $dU = 0$, hence for the whole reaction we have $\Delta U = 0$. Since U is a state function, it is independent of path, and hence we can compute it along any convenient path desired.

If we let $\Delta\bar{U}_{rxn}$ denote the ΔU associated with the reaction when $n = 1$ (that is, when r_i moles of reactant i are present), then $\Delta U_{rxn} = n\Delta\bar{U}_{rxn}$.

So, the path we pick is the following: Let the reaction go to completion at the temperature T_1 , which releases an amount of energy $n\Delta\bar{U}_{rxn}(T_1)$ (where we indicate that the energy of the reaction is temperature-dependent. Strictly speaking, there will in general be a pressure-dependence as well, but this issue unnecessarily complicates the situation for now. For ideal gases, we can safely assume that the energy of a reaction only depends on temperature).

The released energy $-n\Delta\bar{U}_{rxn}(T_1)$ then goes into changing the temperature of the system from T_1 to T_2 (there is a negative sign because, if the internal energy change associated with the reaction is negative, this means that the products have a lower internal energy than the reactants. The energy difference is given off as heat, hence there is a positive amount of heat energy released into the container). If we are working with an ideal gas, and if we assume that the heat capacities are temperature-independent, then the total energy required to raise the temperature of the final mixture from T_1 to T_2 is given by, $n(p_1\bar{C}_{V,P_1} + \dots + p_M\bar{C}_{V,P_M})(T_2 - T_1)$.

So, summing the internal energy changes from the reaction itself and the subsequent heating of the final prod-

FIG. 3: Illustration of the path taken in computing $\Delta\bar{U}_{rxn}$.

uct mixture, we have,

$$\begin{aligned} 0 = \Delta U &= n\Delta\bar{U}_{rxn}(T_1) \\ &+ n(p_1\bar{C}_{V,P_1} + \dots + p_M\bar{C}_{V,P_M})(T_2 - T_1) \\ \Rightarrow \Delta\bar{U}_{rxn}(T_1) &= -(p_1\bar{C}_{V,P_1} + \dots + p_M\bar{C}_{V,P_M})(T_2 - T_1) \end{aligned}$$

There may be a point of confusion that should be cleared up. When the reactants react, the change in internal energy of the reaction mixture is the negative of the energy released as a result of the reaction, for this energy is released as heat to the surroundings, and hence the system itself has lost internal energy. If the reaction occurs under isothermal conditions, then this released heat energy will manifest itself as heat output to the environment. The way we have written the First Law, this gives a negative Q for the reaction process, so that $\Delta U = Q$. In the case of the bomb calorimeter, the released heat is trapped inside the container, so it has nothing else to do except heat the final product mixture. Since no heat escapes out into the environment, we have $\Delta U = 0$ for the whole process. However, we see that $\Delta U = \Delta U_{rxn} + Q_{heating}$. As we have seen above, $\Delta U_{rxn} = n\Delta\bar{U}_{rxn}(T_1)$, and $Q_{heating} = (p_1\bar{C}_{V,P_1} + \dots + p_M\bar{C}_{V,P_M})(T_2 - T_1)$.

So, by measuring the temperature change in a bomb calorimeter, we can determine ΔU for a reaction.

It should be noted that the bomb calorimeter can be designed so that the reactions occur at constant *pressure*, rather than constant volume. In this case, if we rework our derivation, we see that $\Delta H = 0$ inside the constant pressure bomb calorimeter. We then get that,

$$\Delta\bar{H}_{rxn}(T_1, P) = -(p_1\bar{C}_{P,P_1} + \dots + p_M\bar{C}_{P,P_M})(T_2 - T_1) \quad (6)$$