Lecture 2: Fundamental Principles and Equations for a Closed System, Part 1

Ref: (1) Lupis / Ch01, (2) Tester, Ch03&04.

1. THE FIRST LAW OF THERMODYNAMICS FOR CLOSED SYSTEM

1.1 Enunciation of the First Law

In its simple form, the first law states: "In any process, the energy is conserved."

The mathematical translation of this principle is: For the amount heat Q and work W absorbed into the system, the total amount of energy E change in (or absorbed by) the system is

$$dE = \delta Q + \delta W \qquad (1.1b)$$

or, for a finite process

$$\Delta E = Q + W \qquad (1.1b)$$

Here Q and W are both path dependent functions.

For composite systems with external force fields, the total energy E has three major components:

(1) *kinetic energy*, E_{KE}, associated with the motion of the system,

(2) *potential energy*, E_{PE}, associated with the relative position of the system, and

(3) *internal energy*, U, associated with the energy contained in the molecules comprising the system.

For simple systems with no external force fields acted upon the system, the total energy term in eq(1.1) can be replaced by the internal energy. The first law then transforms into:

$$dU = \delta Q + \delta W \qquad (1.2)$$

The applications of the first law are merely accounting processes. But its significance is not immediately apparent since dE cannot be measured directly. Only when the heat and work interactions are measured in terms of thermodynamic variables (m or n, T, P, V, etc.), we obtain the full utility of the First Law.

Almost all engineering applications of the First Law fall within two categories:

(1) for given or measured interactions at the boundaries, what are the corresponding changes in the properties of the system? and

(2) for given changes in the properties, what interactions may occur at the boundaries?

1.1.1 *Work interactions*

The work term includes all non-thermal interactions.

According to mechanics, the mechanical work, W, associated with the movement of a rigid body is defined by the scalar product of the net force and displacement vectors

$$\delta W = (\textstyle\sum \boldsymbol{F}).d\boldsymbol{x} \qquad (1.3a)$$

The force against which the work is done can be either a *boundary force*, $\mathbf{F}_S$, (acting on the boundary of the system) or a *body force*, $\mathbf{F}_b$ (associated with the external fields, e.g., gravitational, inertial, coulombic, etc.). For a rigid body acted upon by both boundary and body forces, Newton's Second Law of Motion states that

$$\textstyle\sum F_s + \sum F_b = 0 \qquad (1.3b)$$

The most common work term in thermodynamics is the so-called *mechanical work* as expressed by "the work done against external pressure",

$$\delta W_{rev} = -P_{ext}d\bar{V} = -Pd\bar{V} \qquad (1.4)$$

1.1.2 *Heat interactions*

Heat is a thermodynamic quantity and is recognisable only by its effect on material substance.

Using First Law, heat is the energy difference between two states an adiabatic process, which can be determined by measuring the work.

$$\Delta E = 0 + W = W_{adiabatic} \qquad (1.5a)$$

Now, for any process (adiabatic or non-adiabatic) within the same initial and final states, the energy difference will be the same as that found for the adiabatic process (as energy is a state function).

If the process is not adiabatic, the heat as the difference of the total energy change and the actual work performed.

$$Q = \Delta E - W = W_{adiabatic} - W_{actual} \qquad (1.5b)$$

A system must have at least one non-adiabatic or diathermal wall if it is to undergo a heat interaction. The converse is, however, not necessarily true. For example, if the temperatures of system and its surroundings are equal, there would be no heat interaction even though the system may have a diathermal wall.

1.2 State Function and Perfect Differentials

Regardless of the transformation process linking the two states 1 and 2, if the change in the property Z always remains

$$\Delta Z = Z_2 - Z_1 \qquad (1.6)$$

then Z is said to be a *state function*, and its differential dZ will be a *perfect differential*. Mathematically, if Z depends on the variables x and y, and it is possible to write

$$dZ = M(x, y)dx + N(x, y)dy \qquad (1.7a)$$

where

$$M(x, y) = \left(\frac{\partial Z}{\partial x}\right)_y \quad \text{and} \quad N(x, y) = \left(\frac{\partial Z}{\partial y}\right)_x \qquad (1.7b)$$

then the necessary and sufficient condition for dZ to be a perfect differential (regardless of any path chosen between the two states) is:

$$\left(\frac{\partial Z}{\partial y}\right)_x = \left(\frac{\partial Z}{\partial x}\right)_y \qquad (1.8)$$

which is the *Maxwell relation*.

If this test on M and N is not successful, then dZ is not a perfect differential and Z is not a state function.
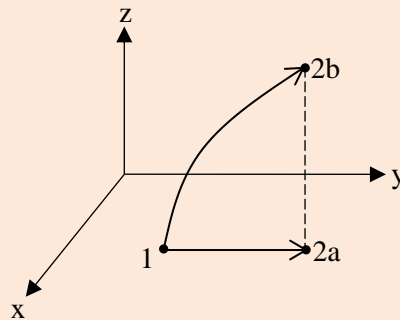
Also, Eq.(1.7a) cannot be integrated between two states 1 and 2 unless one specifies a certain path, and the change ΔZ will depend on that path.

Question

Is *hardness* a state function?

Answer

To answer this question, consider two properties A (x, y) and B (x, y, z) of a system, which change from state 1 to state 2.

If the states 1 and 2 are defined solely by the variables x and y, then $[A(x,y)]_{2a} = [A(x,y)]_{2b}$, which leads to $\Delta A_{1 \searrow 2a} = \Delta A_{1 \searrow 2b}$.

But since $[B(x,y,z)]_{2a} \neq [B(x,y,z)]_{2b}$, this lead to $\Delta B_{1 \searrow 2a} \neq \Delta B_{1 \searrow 2b}$.

Thus, A is a state function. Property B is often said to depend on the *history* of the system, which is resulted from an insufficient characterisation of the initial and final states.

Likewise, hardness is thus a state function. However, the number of variables necessary to fully characterise the system (e.g., density, distribution patterns of dislocation, vacancy, grain boundary, etc.) may often be too large to determine the existence of a perfect differential.

1.3 Applications of the First Law for Closed Systems

Applications of the first law of thermodynamics are illustrated here by two examples. In both cases, ideal gases have been chosen as the system.

An ideal gas is defined as one that obeys the ideal gas law,

$$P\bar{V} = nRT \qquad (1.9)$$

and whose total internal energy is a function only of n and T, that is, $\bar{U} = \bar{U}(n, T)$, and

$$\bar{U} = nU_0 + n \int \left(\frac{dU}{dT}\right) dT \qquad (1.10)$$

Here U_0 is a reference energy per mole (or mass) of material at $T = T_0$.

It is obvious that in dealing with ideal gases, there is a great simplification since only the variables n and T need to be considered. For non-ideal gases (and liquids or solids), $\bar{U}$ would have to be expressed as a function of n plus two other independent variable properties.

In presenting numerical examples where only ideal gases are considered, eq(1.9) is used to relate the pressure-temperature-volume variables. To employ eq(1.10), we defined heat capacity, C, to relate heat input to temperature:

$$C = \frac{\delta Q}{dT} \qquad (1.11a)$$

Since δq is not a perfect differential, C is a process variable and depends on the path of transformation.

$$C_P = \left(\frac{\delta Q}{dT}\right)_P \qquad (1.11b)$$

$$C_V = \left(\frac{\delta Q}{dT}\right)_V \qquad (1.11c)$$

$$C_P - C_V = \frac{TV\alpha^2}{\beta} \qquad (1.11d)$$

If the work of the system is done only against external pressure then, using first law,

$$d\bar{E} = \delta Q - PdV$$

$$d\bar{E}_V = \delta Q_V = C_V dT \qquad (1.12a)$$

and, using the definition of enthalpy

$$d\bar{H} = \delta Q + \bar{V}dP$$

$$d\bar{H}_P = \delta Q_P = C_P dT \qquad (1.12b)$$

The definition of C_P and C_V are, however, not limited to ideal gases, but applies in all cases.

The temperature dependence of the C_P of a substance is often expressed by an equation of the form

$$C_P = a + bT + cT^{-2} \qquad (1.13)$$

where a, b and c are constants.

Example 1.1

Two well-insulated cylinders are placed as shown in the figure below. The pistons in both cylinders are of identical construction. The clearances between piston and walls are also made identical in both cylinders. The pistons and the connecting rod are metallic. Cylinder A is filled with gaseous helium at 2 bar and cylinder B is filled with gaseous helium at 1 bar. The temperature is 300 K and the length L is 10 cm. Both pistons are only slightly lubricated. The stops are removed. After all oscillations have ceased and the system is at rest, the pressures in both cylinders are, for all practical purposes, identical.

Assuming that the gases are ideal with a constant C_V and, for simplicity, assuming that the masses of cylinders and pistons are negligible (i.e., any energy changes of pistons and cylinders can be neglected), what are the final temperatures?
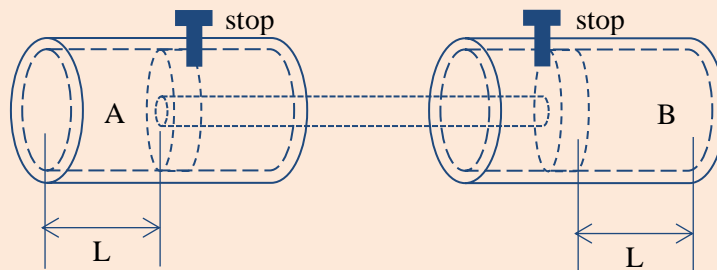
Solution

Since mass and initial temperature is known for the gas in each compartment, the final temperature can be calculated for each compartment, if the final energy – or energy change – of each compartment is determined first.

Thus, using eq(1.9), (1.10) and (1.12a) for each simple system (for which $\bar{E}$ is replaced with $\bar{U}$),

$$n_A = \frac{P_A\bar{V}_{Ai}}{RT_{Ai}} \qquad (1.14)$$

$$n_B = \frac{P_B \bar{V}_{Bi}}{R T_{Bi}} \qquad (1.15)$$

$$T_{Af} = T_{Ai} + \frac{\bar{U}_{Af} - \bar{U}_{Ai}}{n_A C_V} \qquad (1.16)$$

$$T_{Bf} = T_{Bi} + \frac{\bar{U}_{Bf} - \bar{U}_{Bi}}{n_B C_V} \qquad (1.17)$$

where $\bar{U}_{Af}$ and $\bar{U}_{Bf}$ are the only unknowns ($\bar{U}_{Ai}$ and $\bar{U}_{Bi}$ can be chosen at will because U_0 in eq(1.10) is an arbitrary constant).

Since the pistons and shaft have been assumed to be good conductors of heat, the final temperatures of compartments A and B will be equal:

$$T_{Af} = T_{Bf} \qquad (1.18)$$

Now, the composite system (A+B) is equivalent to an isolated system. Thus, the overall changes in the total internal energy of this composite system will be zero, i.e.,

$$\Delta \bar{U}_A = -\Delta \bar{U}_B \qquad (1.19)$$

Combining eq(1.19) with eqs(1.16) and (1.17), and making use of eq(1.18), we obtain

$$T_f = \frac{n_A T_{Ai} + n_B T_{Bi}}{n_A + n_B} \qquad (1.20)$$

Now, for this special case where $T_{Ai} = T_{Bi} = T_i$, we have

$$T_f = T_i = 300\ K$$

Let us now use the hindsight to re-evaluate the problem.

We had a qualitative feeling for the path that the frictional work is involved, but we could not describe the path quantitatively because we did not know the coefficient of friction of either piston-cylinder. Nevertheless, we were able to determine the final conditions and, therefore, we did not have to describe the path to find the solution.

Such a situation would be expected if the end state were independent of the path. This is obviously the case in the present example: since the composite system A+B is an isolated simple system, there is only one state to which it can go, and that is the one for which $\bar{U} = \bar{U}_{Ai} + \bar{U}_{Bi}$ and $T = T_{Af} = T_{Bf}$.

For an ideal gas, $\bar{U}$ is a unique function of n and T only, and thus the final temperature can be determined. If the gas were not ideal, $\bar{U}$ would also depend on $\bar{V}$ (or P). But, since the final energy, volume, and mass are known, the final temperature could still be determined.

Example 1.2

Consider the situation described in Example 1.1, but with well-insulated pistons and connecting rods of low thermal conductivity. What are the final temperatures after the oscillations have ceased and the pressures have equalised?

Solution

The composite A+B system is no longer a simple system because it contains an internal adiabatic wall. Therefore, the final composite system can no longer be described by a single equilibrium state; instead, the final conditions will depend on the path of the process.

Now with the exception of eq(1.18), eqs.(1.14) to (1.17) and eq(1.19) are still valid. Combining eqs.(1.16) and (1.17) with eq(1.19) results in

$$n_A C_V \left(T_{Af} - T_{Ai} \right) + n_B C_V \left(T_{Bf} - T_{Bi} \right) = 0 \qquad (1.21)$$

which now gives us one equation with two unknowns, T_{Af} and T_{Bf}. To find other relationship between T_{Af} and T_{Bf}, we need to make some assumptions regarding the path.

If we have no information on the coefficient of friction, we are forced to use our engineering judgement to simplify the situation while obtaining a close approximation to the actual conditions. Let us assume that there is a friction only in compartment B. This will give us a lower bound for T_{Af} and the upper bound for T_{Bf}. We can then treat the case of friction only in compartment A, which will give us an upper bound for T_{Af}. In this manner, we can bracket the true solution.

If there is no friction in compartment A and if we assume that the process is quasi-static (i.e., no pressure or density gradients within the compartment), we can write the First Law for this simple system of gas in A as

$$d\bar{U}_A = +\delta W_A = -P_A d\bar{V}_A \qquad (1.22)$$

since

$$\delta W_{WA} = \delta Q_W = \delta Q_{AB} = 0$$

where W_{WA} is the work done by the wall of A, Q_W is the heat conducted through the wall, and Q_{AB} is the heat conducted from A to B through the piston.

Substituting for $\bar{U}_A$ in eq(1.22) from eq(1.16), and for $\bar{V}_A$ from eq(1.9), eq(1.22) becomes

$$n_A C_V dT_A = -n_A R \left(dT_A - \frac{T_A}{P_A} dP_A \right)$$

$$\left(\frac{C_V + R}{R} \right) \frac{dT_A}{T_A} = \frac{dP_A}{P_A}$$

Integrating between initial and final conditions, we obtain

$$\frac{T_{Af}}{T_{Ai}} = \left(\frac{P_{Af}}{P_{Ai}} \right)^{R/(C_V + R)} \qquad (1.23)$$

Equations (1.21) and (1.23) give us two equations in three unknowns, T_{Af}, T_{Bf}, and $P_{Af} = P_f$. The final pressure can be eliminated in the following manner. Since

$$\bar{V}_{Af} + \bar{V}_{Bf} = \bar{V}_{Ai} + \bar{V}_{Bi} = \bar{V}_T \qquad (1.24)$$

and $\bar{V}_T$ is known, substitution of eq(1.9) into Eq(1.24) gives

$$\bar{V}_T = \left(n_A T_{Af} + n_B T_{Bf} \right) \frac{R}{P_f} \qquad (1.25)$$

Equation (1.25) together with eqs(1.21) and (1.23) give us three equations in these unknowns. From eqs(1.25) and (1.21),

$$P_f = \frac{P_{Ai} \bar{V}_{Ai} + P_{Bi} \bar{V}_{Bi}}{\bar{V}_{Ai} + \bar{V}_{Bi}} = 1.5 \text{ bar}$$

From eq(1.23), with $C_V = 12.6$ J/mol-K,

$$T_{Af} = \left(\frac{1.5}{2} \right)^{0.4} = 267 \text{ K}$$

and from eq(1.21)

$$T_{Bf} = 366 \text{ K}$$

If it is assumed that there is friction only in compartment A, then we would have found

$$T_{Bf} = 353 \, K$$

Since in the actual case the friction is distributed between A and B, a better approximation might be $T_{Bf} = (366 + 353)/2 = 360$ K and, from eq(1.21), $T_{Af} = 270$ K.

The fact that the adiabatic wall in Example 1.2 prevents a direct solution to the problem in the absence of a complete description of the path is sometimes referred to as the "adiabatic dilemma." In fact, it is no dilemma at all, but results from the difference between heat and work interactions.
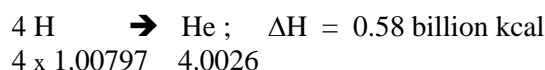
1.4 Standard States

Why does thermodynamics rarely deal with the absolute value of the energy or enthalpy?

It is possible, though, to assign a non-arbitrary value through the Einstein's relation between mass and energy, $E = mc^2$. Theoretically, the energy of a system is measurable by its mass by considering the fact that "the law of conservation of mass is only a consequence of the law of conservation of energy."

$$1 \text{ g mass} \equiv 9 \times 10^{20} \text{ erg} = 20 \text{ billion kcal.}$$

In true sense, unlike energy, mass is not conserved. For a nuclear reaction

$$\begin{array}{lll} 4 \text{ H} & \rightarrow \quad \text{He} \, ; & \Delta H = 0.58 \text{ billion kcal} \\ 4 \times 1.00797 & 4.0026 & \end{array}$$

about 0.02928 g of mass is converted into energy, thus releasing nearly 600 billion cal of energy. This is well above the thermodynamic range because typical chemical reactions do not involve more than a few kilocalories. So the corresponding changes in mass are thus well below the limits of detection.

So although it is then possible in thermodynamics to choose an arbitrary value for the energy or the enthalpy of an element, generally no such value is chosen because there is no need for it. Thus, the absolute values of energy or enthalpy remain arbitrary for the elements of our material world.

Since only changes in the enthalpy enter into calculations, it is convenient to choose *standard reference states*. Unless otherwise specified, "the standard state of a species corresponds to the most stable structure of that species at the specified temperature under 1 atm pressure." So, for instance, at room temperature, the standard states of iron, mercury and oxygen are, respectively, a bcc α-iron (ferrite), a liquid and a diatomic gas.

We must emphasize that, *it is possible* to identify a standard state that does not correspond to the most stable form of the species under consideration. For example, it may be convenient to choose a standard state of H_2O at 298 K that is a gas instead of the liquid, of an fcc austenite of iron rather than ferrite. Standard state may also correspond to a *virtual* state, that cannot be physically obtained but that can be defined theoretically and for which properties of interest can be calculated. Whatever we choose, we must recall that it corresponds to a fixed pressure, normally at 1 atm.

1.5 Heats of Reaction

For a general reaction

$$\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_k A_k = \nu_{k+1} A_{k+1} + \dots + \nu_r A_r \qquad or, \qquad \sum_{i=1}^{r} \nu_i A_i = 0 \qquad (1.28)$$

where the A_is represents reactants ($A_1, \dots A_k$) or products ($A_{k+1}, \dots A_r$) and the ν_i balance the reaction stoichiometrically (+ve for the products, -ve for the reactants), the *heat of reaction* is defined as

$$\Delta H = \sum_{i=1}^{r} \nu_i H_i \qquad (1.29)$$

where H_i is the enthalpy of the substance A_i. When A_i is not pure (e.g., when it is alloyed or a solution), H_i represents its partial molar enthalpy, $\bar{H}_i$.

When all substances A_i are in their standard states, Eq.(1.29) becomes

$$\Delta H^0 = \sum_{i=1}^{r} \nu_i H_i^0 \qquad (1.30)$$

ΔH or ΔH^0 represents the heat generated by the complete transformation of ν_i moles of reactants A_i (i = 1, ..., k) into ν_i moles of products A_i (i = k+1, ..., r) according to the reaction (1.28). In actuality, a reaction is rarely complete. Nevertheless, whether a reaction is complete or not, the heat generated may calculated as follows.

The increments dn_i in the number of moles of the substance A_i produced by the reaction are related to each other by the following relation

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \; .... \; = \frac{dn_r}{\nu_r} = d\lambda \qquad (1.31)$$

where λ is called the *progress variable* of the reaction. If is $d\lambda$ positive, reaction (1.28) proceeds forward; if $d\lambda$ is negative, the reaction proceeds backward.

The total enthalpy of the system containing n_1 moles of component A_1, n_2 moles of component A_2, ..., and n_r moles of component A_r is

$$H = \sum_{i=1}^{r} n_i H_i \qquad (1.32)$$

At constant T and P, the increase in the enthalpy due to the progress of the reaction is

$$dH = \sum_{i=1}^{r} H_i dn_i \qquad (1.32)$$

(since, for pure substances, H is independent of composition. Thus, $dH = Hdn + ndH = Hdn$).

Combining Eqs. (1.33) and (1.31) yields

$$dH = \sum_{i=1}^{r} H_i(\nu_i d\lambda_i) = \left(\sum_{i=1}^{r} \nu_i H_i \right) d\lambda_i = \Delta H \, d\lambda_i \qquad (1.34)$$

Thus, the increase in enthalpy of the system is the (algebraic) product of the heat of reaction ΔH and the extent of its progress.

Example 1.3

For a system containing 2 mol of calcium, 3 mole of graphite, and 1 mole of calcium carbide, find enthalpy change of the reaction: $Ca + 2C = CaC_2$, $\Delta H_{298}^0 = -15000$ cal.

Solution

	Ca	2C	=	CaC$_2$
Initial state (mol):	2	3		1
Final state (mol):	2-λ	3-2λ		1+λ

Since, according to the reaction stoichiometry, 2 mols of C are required for 1 mol of Ca and there are 2 mols of Ca but only 3 mols of C, the reaction will complete and proceed to the right. Consequently, $3-2\lambda = 0$ or, $\lambda = 1.5$, and the final state of the system contains 0.5 mol of Ca and 2.5 mol CaC$_2$.

Then, the enthalpy change of the reaction, $\Delta H = (\Delta H_{298}^0) \lambda = (-15000 \text{ cal}) \, 1.5 = 22500$ cal.

The ΔH of a reaction is a function of temperature, and to find its temperature dependence we note that

$$\left(\frac{\partial \Delta H}{\partial T} \right)_P = \left(\frac{\partial (\sum_{i=1}^{r} \nu_i H_i)}{\partial T} \right)_P = \sum_{i=1}^{r} \nu_i \left(\frac{\partial H_i}{\partial T} \right)_P = \sum_{i=1}^{r} \nu_i C_{P,i} = \Delta C_P \qquad (1.35)$$

The expression is known as the *Kirchhoff's law*. When all products and reactants are in their standard states, it becomes

$$\frac{d\Delta H^o}{dT} = \Delta C_P^o \qquad (1.36)$$

1.6 Heats of Formation

The standard heat of reaction corresponding to the formation of a substance from its elements in their standard states is defined as the standard heat of formation of that substance. For example, the standard heat of formation ΔH_f^o of CO gas corresponding to the reaction,

C (graphite) + ½ O_2 (gas) = CO (gas)
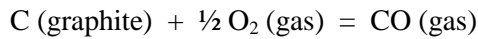
can be expressed as:

$$H_f^o(CO) = \Delta H^0 = H^o(CO) - H^o(C) - \frac{1}{2}H^o(O_2)$$

It is obvious that the standard heat of formation of an element in its standard state is zero.

Knowledge of the heats of formation simplifies the calculation of the heat of reactions ΔH of more complex reactions because they may be written as an algebraic sum of the heats of formation:

$$\Delta H^0 = \sum_{i=1}^{r} \nu_i H_{f,i}^0 \qquad (1.37)$$

and

$$\Delta H = \sum_{j=k+1}^{r} |\nu_j| H_{f,j}(\text{products}) - \sum_{i=1}^{r} |\nu_i| H_{f,i}(\text{reactants}) = \sum_{i=1}^{r} \nu_i H_{f,i} \qquad (1.38)$$

Equation (1.38) is the mathematical equivalent of the Hess's law.