

With CD-ROM for
Computer-Aided Learning

CHEMICAL
THERMODYNAMICS
FOR METALS
AND MATERIALS

HAE-GEON LEE

Imperial College Press

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ICP

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To
Myoung-Hi
and
Hanna, Rebecca and Chris

PREFACE

This book with CD-ROM presents classical thermodynamics with an emphasis on chemical aspects. It is written primarily for students and graduate engineers of metals and materials. Since its treatment of the subject is sufficiently general, students in related fields such as physical chemistry and chemical engineering can also use it.

As thermodynamics is a key discipline in most science and engineering fields, a great number of books, each claiming originality in presentation and approach, have been published on the subject. However, thermodynamics is still a confusing subject for uninitiated students and an “easy to forget” one for graduate engineers.

After many years of experience both teaching thermodynamics at university and actually practising it in industry, I have concluded that the most effective way of presenting thermodynamics is to simulate the method that a lecturer would employ in class. When teaching, the lecturer may write important equations and concepts on the board, draw underlines, circle or place tick marks to emphasise important points, draw arrows to indicate relationships, use coloured chalk for visual effect, and erase some parts to write new lines. He/she may even repeat some parts to stress their importance. A book written on paper alone cannot properly simulate the techniques mentioned above.

This package consists of a book and a computer-aided learning package, and is both unique and beneficial in that it simulates the classroom interaction much more closely due to its employment of multimedia capabilities. Unlike the passive presentation found in most textbooks, this package provides the user with an interactive learning environment. Fast topic selection, free repetition and cross-referencing by toggling between sections or even other packages are just some of the advantages this package has. This approach is in many important respects better than those adopted by other available books on the subject.

This package provides a comprehensive treatment of all the important topics of thermodynamics. It is comprised of a number of smaller sections, each of which deals with a specific topic of thermodynamics. Each section is divided into three parts:

Text : This part covers the fundamental concepts of thermodynamics.

Examples : This part presents extended concepts through questions and answers.

Exercises : This part develops skills necessary to deal with numeric problems.

This book is intended for use primarily at the undergraduate level, but will also be useful to the practising graduate engineers in industry.

Having been evolved from my teaching materials, this book unavoidably includes a blending of knowledge of many other authors with that of my own. I acknowledge their contributions. I am indebted to my teacher, Professor Y.K. Rao for introducing me to the

world of thermodynamics. I am particularly grateful to my former colleague Professor Peter Hayes at The University of Queensland, Australia, for making many useful comments and giving me constant encouragement.

I want to acknowledge the major effort expended by many of my students: Y. B. Kang, T. I. Kim, C. H. Park and S. S. Lee for helping me to design this electronic book and H. J. Kong for helping to typeset the manuscript.

I am also pleased to acknowledge the financial support from The Commonwealth Government of Australia and Pohang University of Science and Technology, Korea.

Finally, I am deeply thankful to my wife and children for the love and encouragement they have given to me.

Hae-Geon Lee

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CHAPTER 1

FUNDAMENTAL PRINCIPLES AND FUNCTIONS

1.1. First Law of Thermodynamics

1.1.1. Heat, Work and Internal Energy

The First Law of Thermodynamics is really a statement of the Principle of Conservation of Energy:

Energy can neither be created, nor destroyed.

Energy can be transported or converted from one form to another, but cannot be either created or destroyed.

Chemical and/or physical changes are accompanied by changes in energy.

The types of energy commonly encountered include:

Heat energy

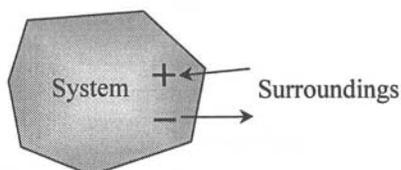
Work or mechanical energy

Electrical energy

Chemical energy

Heat (q)

Heat flows by virtue of a temperature difference. Heat will flow until temperature gradients disappear. When heat flows, energy is transferred. The sign convention is that heat is *positive* when it flows to the system from the surroundings and *negative* when it flows from the system to the surroundings.



System is defined as a portion of the universe that is chosen for thermodynamic discussion and the *surroundings* is the remainder of the universe.

Work (w)

Work is the transfer of energy by interaction between the system and the surroundings. There are many types of work:

Mechanical work

Electrical work

Magnetic work

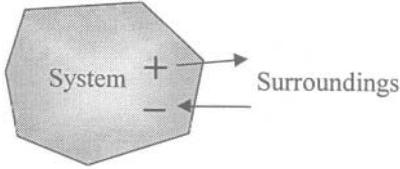
Surface tension

For now, we will be dealing mainly with mechanical work.

The system can do work on the surroundings. The surroundings can also do work on the system. The sign convention employed in this text:

If the system does work on the surroundings, then work (w) is *positive*.

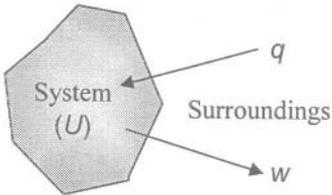
If the surroundings does work on the system, then work (w) is *negative*.



Some texts adopt different sign convention: i.e., w is positive when work is done on the system.

Internal Energy (U)

Energy contained in the system is called the internal energy.



- If heat (q) is supplied to the system, the internal energy of the system (U) will increase.
- If the system does work (w) to the surroundings, energy will be expended and hence the internal energy (U) of the system will decrease.

Net change in the internal energy (ΔU) is then

$$\Delta U = q - w$$

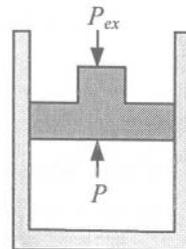
This principle is referred to as the *First Law of Thermodynamics*: Energy may be converted from one form to another, but it cannot be created or destroyed.

Example 1

Work can be expressed in terms of a force and the displacement of its point of action. If the gas inside the cylinder shown expands and pushes the piston against the external pressure P_{ex} , can the force (F) exerted by the gas on the piston be represented by the following equation?

$$F = AP_{ex}$$

where A is the cross sectional area of the piston.



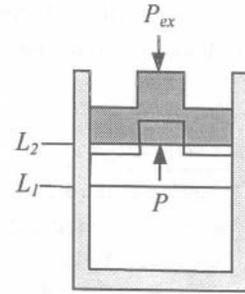
As *force = area x pressure*, the expression is correct. If the gas expands against the external pressure P_{ex} from L_1 to L_2 in the figure, the work done by the system (i.e., the gas) is

$$w = \int_{L_1}^{L_2} AP_{ex} dL = \int_{V_1}^{V_2} P_{ex} dV$$

If the external pressure is continuously adjusted so that it is kept the same as the internal pressure P ,

$$w = \int_{V_1}^{V_2} P dV$$

Work under these conditions is called *reversible work*.



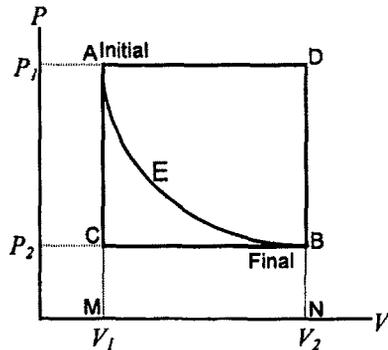
More about reversible work

Work is a mode of energy transfer which occurs due to the existence of imbalance of forces between the system and the surroundings. When the forces are *infinitesimally* unbalanced throughout the process in which energy is transferred as work, then the process is said to be reversible.

Example 2

A system can change from one state to another in many different ways. Suppose a system changes from the initial state (A) in the figure to the final state (B). Determine the work done by the system for each of the following paths:

- Path 1 : A→C→B
- Path 2 : A→E→B
- Path 3 : A→D→B



Recall that

$$w = \int_{V_1}^{V_2} P dV$$

Path 1: Initially the pressure is decreased from P_1 to P_2 (i.e., A→C) at the constant volume V_1 by decreasing the temperature. In this process no work has been done as there was no volume change. Next, the volume of the system expands from V_1 to V_2 (i.e., C→B) at the constant pressure P_2 . The amount of work done in this process is represented by the area CBNM. This is the total work done if the system follows the path 1.

Path 2: If the system follows the path A→E→B, work done by the system is represented by the area AEBNM.

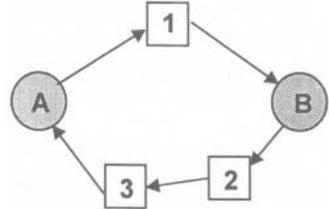
Path 3: Similarly, the amount of work done by the system is given by the area ADN M.

The amount of work done by the system depends on the path taken, and hence cannot be evaluated without a knowledge of the path.

Example 3

Suppose that a substance can exist in several different states as shown in the figure. The substance in state A undergoes a change to state B via state 1, and then comes back to state A via states 2 and 3.

Is the gain of internal energy in the forward process (A→B) different from the loss in the backward process (B→A)?



No. It should be the same. If different, the system will return to the initial state A with a net gain of internal energy. In other words, if different, the system will gain even more energy by repeating the process from nowhere. This is contrary to the First Law of Thermodynamics. Therefore the internal energy gained in the forward process must be equal to that lost in the return process.

We have seen here that internal energy (U) differs from heat (q) and work (w) in that it depends only on the state of the system, not on the path it takes. Functions which depend only on the initial and final states and not on path are called *state functions*.

Example 4

Which of the following thermodynamic terms are state functions?

Temperature (T), Pressure (P), Heat (q), Work (w), Volume (V)

State functions : T, P, V Non-state functions : q, w

State functions which depend on the mass of material are called *extensive properties* (e.g., U, V). On the other hand some state functions are independent of the amount of materials. These are called *intensive properties* (e.g., P, T).

- Thermodynamics is largely concerned with the relations between state functions which characterise systems:
- A state function can be integrated between the initial (A) and final (B) states, being independent of integration path.

$$\text{(Example)} \quad \Delta U = \int_A^B dU$$

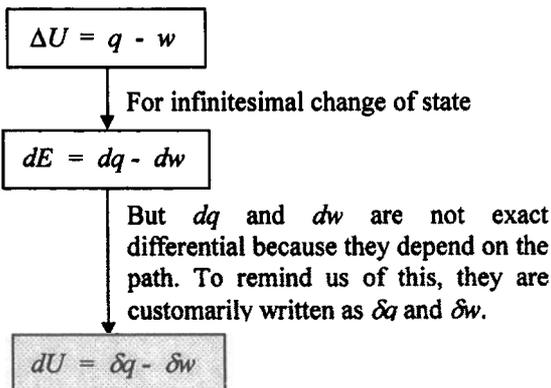
- An exact differential can be written in terms of partial derivatives. For instance, as $U = f(T, V)$,

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

- The order of differentiation of a state function is immaterial.

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right)_V \right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right]_V$$

- The First Law of Thermodynamics may be summarised by the following equation :

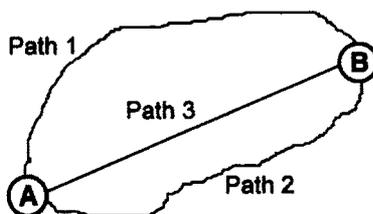


More about q and w

“Heat” and “work” are defined only for processes: heat and work are modes of energy transfer. A system cannot possess either heat or work. There is no function of state that can represent heat or work.

Exercises

1. Calculate the work done by one mole of an ideal gas when it isothermally expands from 1m^3 to 10m^3 at 300K .
2. A system moves from state A to state B as shown in the figure. When the system takes path 1, $1,500\text{ J}$ of heat flow into the system and 200 J of work done by the system.
 - a) Calculate the change of the internal energy.
 - b) If the system takes path 2, 100 J of work is done by the system. How much heat flows into the system?
 - c) Now the system returns from state B to state A via path 3. 100 J of work is done on the system. Calculate the heat flow.



1.1.2 Enthalpy and Heat Capacity

Enthalpy (H)

If a process takes place at *constant volume*,

$$w = P\Delta V = 0$$

From the first law of thermodynamics,

$$\Delta U = q - w = q$$

Therefore, the increase or decrease in internal energy of the system is equal to the heat absorbed or released, respectively, at constant volume. If a process is carried out at a *constant pressure* rather than at a constant volume, then the work done by the system as a result of the volume change is

$$w = \int_1^2 PdV = P \int_1^2 dV = P(V_2 - V_1)$$

From the first law of thermodynamics,

$$\Delta U = q - w$$

$U_2 - U_1$ $P(V_2 - V_1)$

Rearrangement yields

$$(U_2 + PV_2) - (U_1 + PV_1) = q$$

The function $U + PV$ occurs frequently in chemical thermodynamics and hence it is given a special name, *enthalpy* and the symbol H .

$$H = U + PV$$

Then

$$\Delta H = H_2 - H_1 = q$$

For a system at constant pressure, therefore,

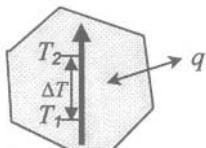
assuming PV work only.

Increase in enthalpy = Heat absorbed Decrease in enthalpy = Heat released	→	$\Delta H = q$
--	---	----------------

For changes at other than constant pressure, ΔH still has a definite value, but $\Delta H \neq q$.

Heat Capacity (C)

The heat capacity of a system is defined as the amount of heat, q , required to raise the temperature of the system by ΔT . Thus,



$$C = \frac{q}{\Delta T} \quad \text{where } C \text{ is the heat capacity.}$$

For an infinitesimal change in T ,

$$C = \frac{dq}{dT}$$

Heat capacity is the measure of the capacity of a system to take in energy as heat.

Recall that heat q is not a state function, so that the change in q depends on the other variable, for instance, V or P , in addition to T . Therefore,

at constant volume,

$$\delta q = dU \longrightarrow C_V = \frac{dU}{dT}$$

and,

at constant pressure,

$$\delta q = dH \longrightarrow C_P = \frac{dH}{dT}$$

where C_V is the heat capacity at constant volume, and C_P is the heat capacity at constant pressure. The variation with temperature of the heat capacity, C_P , for a substance is often given by an expression of the form :

$$C_P = a + bT + cT^{-2}$$

where a , b and c are constants to be determined empirically.

Some examples,

$$C_{P, Al_2O_3} = 106.6 + 17.8 \times 10^{-3} T - 28.5 \times 10^5 T^{-2}, \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_{P, CO_2(g)} = 44.1 + 9.04 \times 10^{-3} T - 8.54 \times 10^5 T^{-2}, \text{ J mol}^{-1} \text{ K}^{-1}$$

Example 1

- 1) Prove the following statements :
 - a) ΔU and ΔH are usually very similar to each other for processes involving solids or liquids.
 - b) If gases are involved in a process, these may be significantly different.
- 2) If a reaction involves an increase of 1 mole of gases in the system, calculate the difference $\Delta H - \Delta U$ at 298K.

- 1) PV work of condensed phases is normally negligibly small :

$$\Delta H = \Delta U + \Delta(PV) \cong \Delta U.$$

If gases are involved in a process,

$$\begin{array}{c} \boxed{\Delta H = \Delta U + \Delta(PV)} \\ \downarrow PV = nRT \text{ for a perfect gas} \\ \boxed{\Delta H = \Delta U + \Delta(n)RT} \end{array}$$

Therefore, if there is a change in the total number of moles of the gas phase, ΔH may be significantly different from ΔU .

- 2) $\Delta H - \Delta U = \Delta(n)RT = (1)(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298\text{K}) = 2.48 \text{ kJ mol}^{-1}$

Example 2

- 1) Prove the following statements :
 - a) For condensed phases, i.e., solids or liquids, C_V and C_P are quite similar in magnitude.
 - b) C_V and C_P are significantly different for ideal gases.
- 2) C_P and C_V for argon gas are as follows:

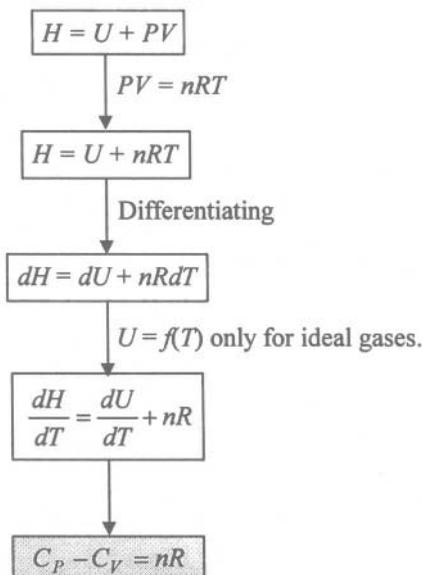
$$C_P = 20.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_V = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$$
 Calculate $C_P - C_V$.

- 1) a) For condensed phases,

$$\begin{array}{c} \boxed{\Delta H = \Delta U + \Delta(PV) \cong \Delta U} \\ \downarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P \\ \boxed{C_P = C_V} \end{array}$$

b) For ideal gases,

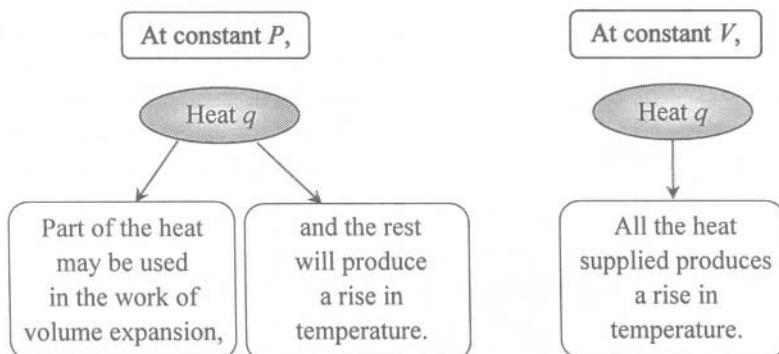


- 2) $C_p - C_v = 20.8 - 12.5 = 8.3 \text{ J mol}^{-1}\text{K}^{-1}$: This value is very close to the gas constant R , which verifies the relationship $C_p - C_v = nR$.

Example 3

Substances usually expand with increase in temperature at constant pressure. Is C_p usually larger than C_v ?

When heat is supplied to a substance,



Therefore, C_p is larger than C_v .

More rigorous analysis:

