

高等教育双语教学推荐教材

# 化工热力学

(英文版)

**Chemical Engineering Thermodynamics**

于志家 李香琴 兰忠 编



化学工业出版社

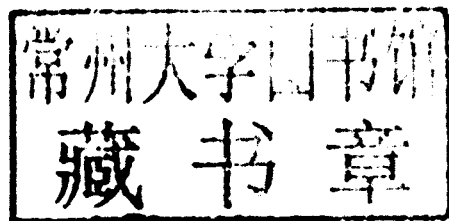
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· 北京 ·

本书应国内高校化工热力学课程双语教学的需要,吸取国内外最新教材的精华,参考国内多数高校执行的48学时安排与双语教学的需要与特点,精选教学内容,采用英文编写。

本书讲述并应用热力学基本原理,阐述流体的热力学性质及相平衡,对化工过程进行节能分析。原理阐述简练,例题与习题适量,注重利用热力学原理解决实际化工生产问题。

全书共分九章,主要内容有:导论,流体的 $p$ - $V$ - $T$ 关系,流体的热力学性质,混合物的热力学性质,溶液的热力学性质,流体相平衡,流动、压缩及膨胀过程热力学计算,蒸汽动力循环及制冷循环,化工过程的热力学分析。书中各章都配有例题及一定量的习题。习题设置注意知识点覆盖,并附有答案。

本书可作为高等学校化工类专业本科生的双语教学教科书与教学参考书。

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# 前言

进入 21 世纪,随着经济全球化和高等教育国际化的发展,高校教育必须按照国际合作、全球竞争的标准培养既具有宽厚扎实的基础知识和基本技能,又具有国际交流、合作与竞争能力的高素质复合型人才。教育要面向世界、面向未来,这是我国教育发展的必然要求。当代大学生要努力成为具有国际视野和竞争力的创新人才。这种需求决定了学生对外语学习的强烈需求,实用外语是他们走向国际舞台一显身手的重要工具。双语教学就在这种时代背景下应运而生。我国对高等学校的双语教学改革十分重视。教育部在 2001 年 4 号文件中提出,“本科教育要创造条件,使用英语等外语进行公共课和专业课教学”。自 2007 年,教育部面向全国所有本科院校,每年建设 100 门双语教学示范课程,旨在通过双语教学课程示范,推动双语教学改革,促进双语教学课程建设,提高高校双语教学水平。目前全国许多高校都开设了基础课、专业基础课与专业课不同层次的双语课,使双语教学在培养外向型高素质人才计划的实施中起到越来越重要的作用。然而,在双语教学中,教材建设却相对落后,阻碍了双语教学的快速推广。鉴于国内课程体系划分相对较细,国外原版教材在内容上并不是很适合,加之国外原版教材价格昂贵,购书经济负担较重,因而编写适合国情的实用英文教材是当前急待完成的任务。

化工热力学 (Chemical Engineering Thermodynamics) 是化学工程的重要分支和基础学科,化工热力学课程是化工类各专业的重要专业基础课。目前国内已有多所院校开设了化工热力学课程的中英文双语教学,所采用的教材多为化学工业出版社影印出版的 J. M. Smith 主编的《Introduction to Chemical Engineering Thermodynamics》,该书阐述由浅入深,较适宜我国学生学习,但内容需要优化调整,以更好地适应国内双语教学的需求。

本书力求加强基础,面向实用,引导思维,启发创新,便于自学。教材内容选取适度,便于不同水平的学生学习。

全书共分九章。内容基于读者已学完物理化学课程的热力学基础进行组织,编排次序注重课程内容更好的衔接。第一章是绪论,介绍热力学的发展及热力学第一、第二定律;第二章阐述流体的  $p$ - $V$ - $T$  关系;第三章介绍纯组分热力学性质的计算;第四章是混合物热力学性质的计算;第五章为溶液热力学基础;第六章是流体相平衡,重点阐述了汽-液平衡计算,对气-液与液-液平衡亦作了适当的介绍;第七章为流动过程热力学,介绍典型化工过程的流体输运、功能热转换与计算;第八章阐述流体的动力循环与制冷循环;第九章为化工过程的节能分析。前五章重点阐述化工热力学的基础理论,后四章着重体现了化工热力学理论与化工生产实践的结合。考虑到课程的学时限制,本教材略去了化学反应平衡内容,

请读者见谅。

本教材主要作为化学工程与工艺专业本科生的双语教学之用，也可作为化学、化工等专业教师、研究生和从事相关工作的工程技术人员的参考资料。

本教材的第一、第五、第六章由于志家编写，第二、第三、第四章由李香琴编写，第七、第八、第九章由兰忠编写；全书由于志家统稿。

在教材编写过程中得到了大连理工大学张乃文副教授、陈嘉宾教授、张艳老师与研究生姜营营、姜睿、徐威、温荣福、郑毅、赵小航、于得旭、王松、程惠远及本科生丛阳、杨筱恬、周昊等在内容、例题、习题、文档处理等方面提供的诸多帮助，得到了大连理工大学教材出版基金资助，得到化工与环境生命学部张述伟副部长等有关领导的大力支持，在此深表谢意。

由于时间与水平有限，错误之处在所难免。衷心希望双语教学的各位同仁与读者给予批评指正。

编者

于大连理工大学

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# Chapter 1

## Introduction

### 1.1 The Scope of Chemical Engineering Thermodynamics

The phenomenon of heating is one of the earliest natural phenomena recognized and used by human being. In ancient time, our ancestors happened to find that burned foods taste better, and they managed to keep and use fire in every day life as shown in Fig. 1.1, and even to make fire by scrubbing two pieces of wood as shown in Fig. 1.2. Making fire may be considered as the earliest human activity of energy transformation from work to heat. The invention of steam engine which could be equipped to a cart to make it auto-running stimulated the industrial civilization in the 19<sup>th</sup> century and eventually developed the modern high speed train, shown in Fig. 1.3 and Fig. 1.4. The science of thermodynamics was born and grown from the study of heat phenomenon and its applications in life activities. The 1<sup>st</sup> and 2<sup>nd</sup> laws of thermodynamics were developed, which described the conservation of energy and the efficiency of heat engine. These laws and relevant theories set up the fundamentals of thermodynamics. The application of the principles and laws of thermodynamics in chemical industry and chemical engineering gave the birth of the major branch of chemical engineering, say the chemical engineering thermodynamics with which chemical engineering science developed and huge modern chemical works were designed and constructed as shown in Fig. 1.5. Nowadays, the science of chemical engineering thermodynamics has been developed as one of the most strict and systematic subjects.



Fig. 1.1 The human practice of using fire in the ancient time



Fig. 1.2 The making of fire by scrubbing two pieces of wood

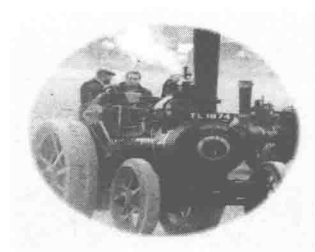


Fig. 1.3 The steam engine equipped cart in 19<sup>th</sup> century

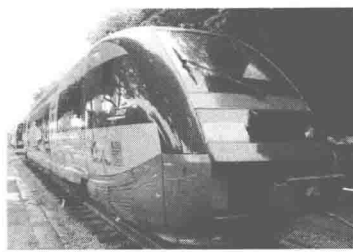


Fig. 1.4 A modern high speed train

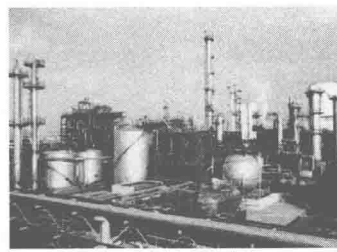


Fig. 1.5 A modern chemical works

Chemical engineers cope with a variety of problems in the design, the construction and the operation of chemical processes. Among them are the calculations of heat and work requirement and the determination of equilibrium conditions for phases and chemical reactions. A qualified practical chemical engineer must get a sound knowledge of thermodynamics.

Chemical engineering thermodynamics considers the requirement of the transfer of heat and energy for chemical processing, phase equilibrium for the separation of mixtures and chemical equilibrium for the conversion of raw materials to products. Fluid properties are essential to the practical application of thermodynamics. Thermodynamic analysis is a powerful tool for the optimization of a chemical plant. The above topics and the relative considerations will be the main contents of the textbook.

Thermodynamics is often characterized as a difficult subject. Abstractive concepts, strict mathematical deductions and complex systems make the subject quite hard to learn. Indeed, if one's approach is to memorize every equation developed in the course, the subject will be very difficult. Learners are encouraged to try to understand the concepts and develop the ability to apply the basic principles in a systematic way. Then they will find the subject is intuitive and fun.

## 1.2 System and Surroundings

In chemical engineering thermodynamics, the materials or a region under study is called the system, and all of the rest are its surroundings. System and surroundings are related with respect of mass and energy transfer with which systems can be classified into isolated, closed and open systems.

**Isolated system:** A system is referred as an isolated system when there is neither material nor energy transferred across the boundary between the system and its surroundings.

**Closed system:** A system is referred as a closed system when there is only energy transferred across the boundary between the system and its surroundings, but without any material or mass transfer.

**Open system:** A system is referred as an open system when there are both material and energy transferred across the boundary between the system and its surroundings.

## 1.3 The Chemical State and Fluid Properties

The chemical state is used to describe the macroscopic over view of fluids. Matter appears

in three states, say the solid state, liquid state and gas state, or three phases. A mixture may be in a homogeneous phase or in a heterogeneous phase. The state of a substance or mixture of substance can be determined by the values of the following properties:

- ① Mass;
- ② Composition (mole or mass fraction for each chemical species);
- ③ Phase (solid, liquid, gas);
- ④ Form (crystalline modification — applied only to solid);
- ⑤ Temperature;
- ⑥ Pressure.

Once the state of a substance is fixed by giving values of these properties, all the other properties including volume, internal energy, enthalpy, entropy, Helmholtz energy, Gibbs energy, density and heat capacity get definite values. The state of a substance is independent of its position in a gravitational field and its velocity in most of chemical processing where the changes in potential energy and kinetic energy are negligible.

The equilibrium state plays a central rule in chemical engineering thermodynamics. The general characteristic of the equilibrium state are:

- ① It does not vary with time;
- ② The system is uniform (there are no internal temperature, pressure, velocity, or concentration gradients), or is composed of uniform subsystems;
- ③ All the flows of heat, mass or work between the system and its surroundings are zero;
- ④ The net rate of each chemical reaction is zero.

The state of a fluid can be described by some of the parameters such as temperature, pressure, volume, internal energy, enthalpy, entropy, Helmholtz energy and Gibbs energy, which are generally named as properties of the system. Properties can be classified into two types, the measurable properties such as temperature, pressure and volume and the properties which can not be measured directly such as the others. With another consideration, properties can be intensive which are unrelated with the mass of the system or extensive which are proportional to the mass of the system. Temperature  $T$ , pressure  $p$  and density  $\rho$  are intensive; and volume  $V$ , internal energy  $U$ , enthalpy  $H$ , entropy  $S$ , Helmholtz energy  $A$ , and Gibbs energy  $G$  of a system are extensive. Any extensive property divided by the amount of the material (moles or mass) gives an intensive property. Then  $V_m$ ,  $U_m$ ,  $H_m$ ,  $S_m$ ,  $A_m$  and  $G_m$  are intensive properties.

## 1.4 The First Law of Thermodynamics

The first law of thermodynamics is about energy conversion and conservation.

Energy is the ability of a body for doing work. A moving body possesses kinetic energy, a high raised body possesses potential energy and a fluid possesses internal energy related to a reference state.

When a body of mass  $m$ , acted upon by a force  $F$ , is displaced a distance  $dl$  during a differential interval of time  $dt$ , the work done is given by:

$$dW = madl = m \frac{dv}{dt} dl = mvdv$$

This equation may be integrated for a finite change in velocity from  $v_1$  to  $v_2$ :

$$W = m \int_{v_1}^{v_2} v dv = \frac{1}{2} m v_2^2 - \frac{1}{2} m v_1^2 = \Delta \left( \frac{m v^2}{2} \right)$$

The amount of work done by a moving body equals the change in  $\left( \frac{m v^2}{2} \right)$  term of the body which was named as kinetic energy by Lord Kelvin in 1856:

$$E_K = \frac{1}{2} m v^2$$

If a body of mass  $m$  is raised from an initial elevation  $z_1$  to a final elevation  $z_2$ , an upward force at least equal to the weight of the body must be exerted on it, and this force must move through the distance  $z_2 - z_1$ . Because the weight of the body is the force of gravity on it, the minimum force required is given by Newton's law:

$$F = ma = mg$$

where  $g$  is the local acceleration of gravity. The minimum work required to raise the body is the product of this force and the change in elevation:

$$W = F(z_2 - z_1) = mg(z_2 - z_1) = \Delta(mgz)$$

Then the work done on a body in raising it is equal to the change in the quantity of  $mgz$ . Conversely, if a body is lowered against a resisting force equal to its weight, the work done by the body is equal to the change in the quantity of  $mgz$ . The quantity of  $mgz$  is defined as potential energy.

Kinetic energy and potential energy are called mechanical energy, and generally referred as external energy. Both show that the work done is equal to the change in a quantity describing the condition of the body in relation to its surroundings. In each case, for a rigid body, if the body falls from a high elevation to a lower one freely, its potential energy decreases, but at the same time, its kinetic energy increases with respect to the velocity change acquired. The total amount of mechanical energy conserves:

$$\Delta E_K + \Delta E_P = 0$$

Another kind of energy of fluid mostly considered is the internal energy relating with the microscopic energy of ceaseless motion of the system molecules, which can be depicted with Joule's experiments (1840—1878). In Joule's experiments, a known amount of water was placed in an insulated container and agitated with a rotating stirrer. It was found that a fixed amount of work was required per unit mass of water for every degree of temperature rise caused by the stirring, and that the original temperature of the water could be restored by the transfer of heat through simple contact with a cooler object. Thus Joule demonstrated that a quantitative relationship exists between work and heat and, therefore, that heat is a form of energy. Energy added to the water as work is later transferred from the fluid as heat. Where is this energy between its addition to and transfer from the water? A rational concept is that it is contained within the water in another form, called internal energy to distinguish it from the external energy owing to the macroscopic velocity and position.

Energy is the ability for doing work, which is commonly regarded as residing in a body. As discussed above, there are two kinds of energy, the one that can store in the system and are functions of state such as the kinetic energy, potential energy and inter-

nal energy, and the other is the energy in transit, never stored in a body or a system, and is function of process such as work and heat. The generality of the principle of conservation of energy in mechanics expended if we look upon work and heat themselves as other forms of energy. This is clearly permissible, because energy change is equal to the work done and heat added in producing them. This lead to the statement of the first law of thermodynamics:

Though energy assumes many forms, the total amount of energy is constant. Energy can be neither created nor destroyed. It can be converted from one form to other forms. When energy disappears in one form, it appears simultaneously in other forms.

The description was at first just a postulate, but all the observations of ordinary process support it. Hence, it has achieved the stature of the first law of thermodynamics.

#### 1.4.1 The first law of thermodynamics for controlled mass system

Isolated or closed systems are usually referred as the controlled mass system where there is no mass transfer between the systems and the surroundings. The first law of thermodynamics for a controlled mass system can be expressed by the following equation:

$$\Delta E = Q + W \quad (1.1)$$

where  $Q$  is the heat transferred from the surroundings to the system,  $W$  is the work done by the surroundings on the system and  $E$  is the total energy of the system including potential energy, kinetic energy, internal energy, surface energy, electrical energy, and magnetic energy etc. In chemical process, the change in surface energy, electrical energy, and magnetic energy of fluid can be ignored. Then, the first law of thermodynamics applied to controlled mass system can be written as:

$$\Delta U + \Delta E_k + \Delta E_p = Q + W \quad (1.2)$$

where  $\Delta U$ ,  $\Delta E_k$  and  $\Delta E_p$  are the changes in internal energy, kinetic energy and potential energy respectively.

For stationary control mass, there is no change in potential energy or kinetic energy. The above equation becomes

$$\Delta U = Q + W \quad (1.3)$$

Eq. (1.3) applies to processes involving finite changes in the internal energy of the system. For differential changes:

$$dU = dQ + dW \quad (1.4)$$

#### 1.4.2 The first law of thermodynamics for controlled volume system

The applications of Eq. (1.3) or Eq. (1.4) are for controlled mass system in which changes in potential energy and kinetic energy are negligible. But far more frequently we find continuous processes in chemical industries, through which feeds flow into and the products flow out of the system continuously. The process is catalogued as open system or controlled volume system. A typical controlled volume flow system can be schematically shown in Fig. 1.6. The feed is pumped into the reactor from the outside of the con-

control volume. The product is withdrawn from the control volume. There are four interactions between the control volume and the surroundings: the shaft work done by the pump, the heat added to the reactor, reactant entering, and product leaving. Now suppose that reactants and products enter and leave the control volume as fluid in pipes with cross-sectional area of  $A_1$  and  $A_2$ , respectively, as shown in Fig. 1.7. For a continuous process operated at steady state, at time 0, we select all the materials inside the control volume plus 1 kg of feed as the control mass, which is shown in Fig. 1.7(a). If the specific volume of the feed is  $V_1$ , then the distance  $l_1$  is equal to

$$l_1 = \frac{V_1}{A_1} \quad (1.5)$$

At time  $t$ , the feed has entered the control volume, and the equal mass of product of specific  $V_2$  has been pushed out of the control volume a distance

$$l_2 = \frac{V_2}{A_2} \quad (1.6)$$

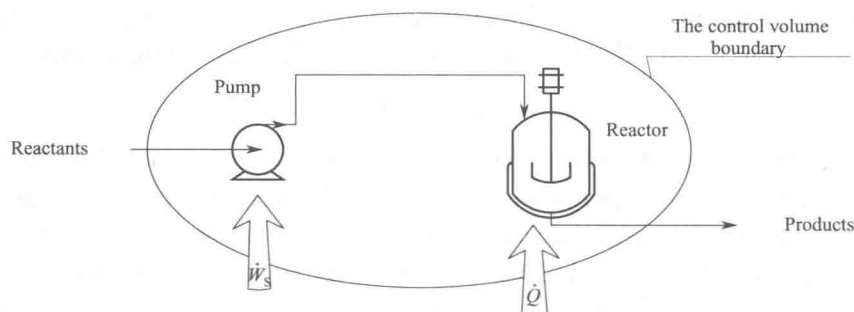


Fig. 1.6 Energy balance for a control volume

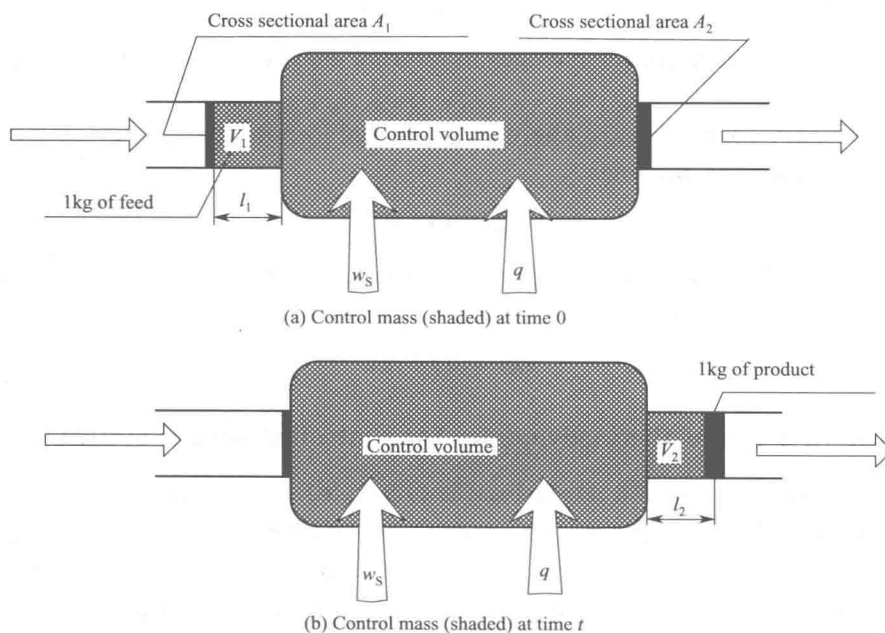


Fig. 1.7 Mass and energy flow across the control volume boundary

The control mass occupies a new location as shown in Fig. 1.7(b). Let  $w_s$  be the shaft work done by the surroundings to the system per unit mass of reactant, and  $q$  be the heat entering the control volume per unit mass of reactant. Besides  $w_s$ , there is work associated with pushing the reactant into the control volume ( $w_1$ ) and the work associated with the product leaving the control volume ( $w_2$ ). For the control mass, from Eq. (1.2),

$$\Delta u + \Delta(\text{k. e.}) + \Delta(\text{p. e.}) = q + w_s + w_1 + w_2 \quad (1.7)$$

All the quantities in Eq. (1.7) are written in lowercase as the reminder that they refer to unit mass of material passing through the control volume. And :

$$\text{k. e.} = \frac{1}{2}v^2, \text{ p. e.} = gz, w_1 = p_1 A_1 l_1 = p_1 V_1, w_2 = -p_2 A_2 l_2 = -p_2 V_2$$

Substitute the above expressions into Eq. (1.7), resulting in:

$$\Delta u + \frac{1}{2}\Delta v^2 + g\Delta z = q + w_s + p_1 V_1 - p_2 V_2 \quad (1.8)$$

where  $\Delta u = u_2 - u_1$  is the internal energy change of unit mass

$$(u_2 + p_2 V_2) - (u_1 + p_1 V_1) + \frac{1}{2}\Delta v^2 + g\Delta z = q + w_s \quad (1.9)$$

The group of  $(u + pV)$  is named as enthalpy and  $pV$  is generally referred to as the flow work. Therefore, Eq. (1.9) can be written simply as

$$\Delta h + \frac{1}{2}\Delta v^2 + g\Delta z = q + w_s$$

(control volume, steady state, unit mass of material) (1.10)

where  $\Delta h = h_2 - h_1 = h_{\text{product}} - h_{\text{reactant}}$ . If the process involves multi-streams of mass, heat and shaft work, Eq. (1.10) can be rewritten in terms of flow rate:

$$\sum_i F_i \left( h_i + \frac{1}{2}v_i^2 + g z_i \right) + \sum_i \dot{Q}_i + \sum_i \dot{W}_{si} = 0$$

(control volume, steady state) (1.11)

For unsteady state, the accumulation of energy in the control volume should be considered:

$$\frac{dE}{dt} = \sum_i F_i \left( h_i + \frac{1}{2}v_i^2 + g z_i \right) + \sum_i \dot{Q}_i + \sum_i \dot{W}_{si} \quad (\text{control volume}) \quad (1.12)$$

where  $F_i$ ,  $\dot{Q}_i$  and  $\dot{W}_{si}$  are the mass flow rate of stream  $i$ , the heat transfer rate of the  $i^{\text{th}}$  heat transfer facility and the shaft work rate added to the control volume for the  $i^{\text{th}}$  work transportation, respectively. For any one of the 3 terms, when it flows into the control volume, it is signed “+” or “-” while flows out of the control volume;  $h_i$ ,  $v_i$  and  $z_i$  are the specific enthalpy, flow velocity and horizontal height of stream  $i$ . Eq. (1.12) is the general form of the 1<sup>st</sup> law of thermodynamics for a control volume system. For most chemical processes, the changes in kinetic energy and potential energy are much smaller than that of enthalpy or internal energy changes. So Eq. (1.12) can be reduced to:

$$\frac{dE}{dt} = \sum_i F_i h_i + \sum_i \dot{Q}_i + \sum_i \dot{W}_{si} \quad (1.13)$$

And for steady continuous flow,

$$\sum_i F_i h_i + \sum_i \dot{Q}_i + \sum_i \dot{W}_{si} = 0 \quad (1.14)$$

Eq. (1.13) and Eq. (1.14) can be used either on mass basis or on mole basis. If  $F_i$  is



mass flow rate, the  $h_i$  must be specific enthalpy of stream  $i$ ; and if  $F_i$  is mole flow rate, the  $h_i$  must be mole enthalpy of stream  $i$ . In accordance with the later discussions,  $H_{mi}$  is preferred instead of  $h_i$ , then gives:

$$\sum_i F_i H_{mi} + \sum_i \dot{Q}_i + \sum_i \dot{W}_{si} = 0 \quad (1.15)$$

### ► Example 1.1

An insulated and electrically heated tank (Fig. 1.8) containing 190 kg of liquid water at 60°C is serving with hot water when a power outage occurs. If water is fed and withdrawn from the tank at a steady rate of  $F_1 = F_2 = 0.2 \text{ kg} \cdot \text{s}^{-1}$ , how long will it take for the temperature of the water in the tank to drop from 60°C to 35°C? Assume cold water enters the tank at 10°C, and negligible heat losses from the tank. For liquid water  $C_v = C_p = C$ , independent of  $T$  and  $p$ .

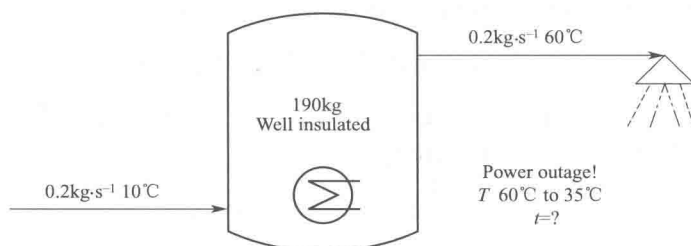


Fig. 1.8 An insulated, electrically heated hot water facility

### Solution:

Here, after the power outage,  $\dot{Q} = \dot{W}_s = 0$ . Additionally, assume perfect mixing of the contents of the tank; this implies that the properties of the water leaving the tank are the same of those of the water in the tank. With the mass flowrate into the tank equal to the mass flowrate out,  $m$  is constant; moreover, the differences between inlet and outlet kinetic and potential energies can be neglected. Eq. (1.13) is therefore written as:

$$m \frac{dE}{dt} = F_1 h_1 - F_2 h_2$$

With  $C_v = C_p = C$ ,

$$\frac{dE}{dt} = C \frac{dT}{dt} \quad \text{and} \quad h_2 - h_1 = C(T_2 - T_1)$$

The energy balance then becomes, on rearrangement,

$$dt = -\frac{190}{0.2} \times \frac{dT_2}{T_2 - T_1}$$

Integration from  $t=0$  (where  $T=T_0$ ) to arbitrary time  $t$  yield:

$$t = -\frac{190}{0.2} \times \ln\left(\frac{T_2 - T_1}{T_0 - T_1}\right)$$

Substitution of numerical values into this equation gives, for the conditions of this problem,

$$t = -\frac{190}{0.2} \times \ln\left(\frac{35-10}{60-10}\right) = 658.5 \text{ s} = 11 \text{ min}$$

Thus, it takes about 11 minutes for the water temperature in the tank to drop from 60°C to 35°C.