CHAPTER 1

PHYSICAL CHEMISTRY

Physical chemistry is concerned with the study of the physical properties and structure of matter using the laws of chemical interaction. Generally, the purpose of physical chemistry is threefold:

- to collect the appropriate data required to define the properties of matter
- to establish the energy relations in physical and chemical transformations
- to predict the extent and rate of the transformation taking place and identify its controlling factors

For our concern as engineers, the principles of physical chemistry could lead to an understanding of such concepts as the identification of compositions in aqueous solutions, the effects of additives on water purification, the extent and prevention of corrosion in piping, and so on. There are two common approaches to understanding physical chemistry. The first is the **synthetic approach**, which begins with the study of the structure and behavior of matter from subatomic particles, electrons, and nuclei, to atoms and molecules, and then proceeds to their states of aggregation and subsequent chemical reactions. The other is the **analytical approach**, which begins with the investigation of large objects, such as biosystems and bodies of water, and works its way back to atoms and particles. The analytical approach will be used in this book. In this chapter, we will discuss the subjects of gas-liquid-solid phase behavior, thermodynamics, and kinetics. At the end we will discuss some of the commonly used units and conventions.

1.1 GAS-LIQUID-SOLID

All matter exists in one of three states of aggregation: gaseous, liquid, or solid. The particular state of a substance is determined by the pressure and temperature under which it exists. Because the gaseous phase is the most random form of the three states, we can easily understand liquid and solid state behavior by fully comprehending the gaseous state. Thus, our attention will be focused here on the gaseous phase.

There are several basic laws or generalizations that are important to the study of gases. The first one is **Boyle's Law**: The volume of any definite quantity of gas at constant temperature varies inversely with the pressure on the gas. Expressed mathematically

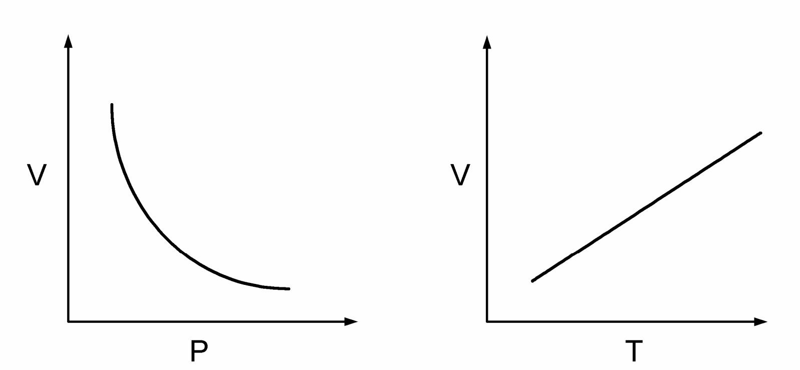

Figure 1-1. Illustration of Boyle's Law and Charles's Law.

$$V = \frac{K_1}{P} \quad \text{(T = constant)} \qquad [1\text{-}1]$$

If V is plotted versus P at a constant temperature, it will exhibit a hyperbolic characteristic curve, as shown in Figure 1-1.

Charles's or **Gay-Lussac's Law** states that the volume of a definite quantity of gas at constant pressure is directly proportional to the absolute temperature (Fig. 1-1), or

$$V = K_2 T \quad (P = \text{constant}) \qquad [1\text{-}2]$$

To obtain a simultaneous variation of the volume with pressure and temperature, we proceed as follows:

$$V = f(P, T)$$

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \qquad [1\text{-}3]$$

From Equation [1-1] by differentiation, we get

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{K_1}{P^2} = -\frac{PV}{P^2} = -\frac{V}{P} \qquad [1\text{-}4]$$

Similarly, from Equation [1-2] we get

$$\left(\frac{\partial V}{\partial T}\right)_P = K_2 = \frac{V}{T} \qquad [1\text{-}5]$$

Combining Equations. [1-4] and [1-5] into Equation [1-3]

$$\mathrm{d}V = - V/P\, \mathrm{d}P + V/T\, \mathrm{d}T$$

or

$$\mathrm{d}V/V + \mathrm{d}P/P = \mathrm{d}T/T$$

$$\ln V + \ln P = \ln T + \ln C$$

$$PV = \text{constant} \times T$$

$$PV = RT \quad \text{or} \quad PV = nRT \qquad [1\text{-}6]$$

Equation [1-6] is the **ideal gas equation**, where R is a universal constant for all ideal gases. In general, $R=Nk$ where N is Avogadro's number and k is Boltzmann's constant in terms of individual molecules. The value of R can be found from the fact that 1 mole of any ideal gas at **standard conditions** — that is, at 0°C and 1 atmosphere of pressure — occupies a volume of 22.414 liters. Therefore,

$$R = \frac{PV}{nT} = \frac{(1\,\text{atm})(22.414\,\text{L})}{(1\,\text{mole})(273.16\,\text{K})}$$

$$= 0.082 \text{ liter-atm/K/mole}$$

R can be expressed in any set of units representing work or energy. As an exercise, the following can be derived:

$$R = 8.314 \text{ joule/degreeK/mole}$$

$$= 1.987 \text{ cal/degreeK/mole}$$

As stated above, k is Boltzmann's constant in terms of individual molecules. In this instance, k can be easily computed out as

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

if the Avogadro's number

$$N = 6.02 \times 10^{23}\text{/mole}$$

As shown in Equation [1-3], V is considered a function of T and P. The partial derivatives in the equation have definite physical meanings and are measurable quantities. There are three commonly tabulated properties:

- compressibility coefficient

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad [1\text{-}6a]$$

- expansion coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad [1\text{-}6b]$$

- pressure coefficient

$$\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \qquad [1\text{-}6c]$$

If a gas obeys the ideal gas law, it can be easily found that

$$\alpha = \kappa\beta P \qquad [1\text{-}6d]$$

[Example 1-1] Thermometers are frequently broken in the laboratory by overheating. If a thermometer is exactly filled with mercury at 50°C, what pressure will be developed within the thermometer if it is heated to 52°C? (For mercury, the expansion coefficient is 1.8×10^{-4} per degree and the compressibility coefficient is 3.9×10^{-6} per atm.)

$$V = f(P,T)$$

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P$$

V = constant, $dV = 0$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\alpha}{\kappa}$$

For Hg, $\alpha = 1.8 \times 10^{-4}$ degree^{-1}, $\kappa = 3.9 \times 10^{-6}$ degree^{-1}. Thus,

$$\left(\frac{\partial P}{\partial T}\right)_V = 46 \text{ atm/degree}$$

1.2 THERMODYNAMICS

Thermodynamics is the study of the energy accompanying physical and chemical processes and the transformation of energy from one form to another. The two most important words in thermodynamics are **heat** and **work**, which are related forms of energy. Heat energy can do work, and work energy can generate heat. In dealing with thermodynamic problems, the term **"system"** is frequently employed. A system is defined as any parts of the world selected for study. In turn, the portion of the universe excluded from the system is called the surroundings or environment. A **boundary** (real or imaginary) separates the system from the surroundings. An **open system** can exchange both matter and energy with its surroundings, while an **isolated system** cannot. **A closed system** can exchange energy, but it cannot change matter. As an example, Figure 1-2 gives a general representation of a natural water system treated as an open system.

1.2.1 Temperature, Heat, and Work

The **zeroth law of thermodynamics** can be stated as: systems in thermal equilibrium have the same temperature. If two systems are in thermal equilibrium with a third system, then they all are in equilibrium with each other, and they all have the same temperature. Heat is a form of energy that passes from one body to another solely as a result of temperature difference. If the temperature of a system is kept constant, $dT = 0$, it is said to be under **isothermal conditions**. An **adiabatic process** is one for which there is no heat transfer between it and its surroundings, $dq = 0$. The basic unit of heat is the **calorie**, defined as the heat required to raise the temperature of one gram of water by one Celsius degree. In engineering practices, it is common to measure heat in **Btu**, which is the heat required to raise one pound of water by one Fahrenheit degree. The unit Btu equals 252 calories.

It is possible to have a system of methods to transfer energy to a system as work. **Mechanical**, or **pressure-volume work** is the most familiar. For a closed system, it is equivalent to the pressure times the change in volume:

$$dw = P dV \qquad [1\text{-}7]$$

Since heat and work are both forms of energy, they can be equated.

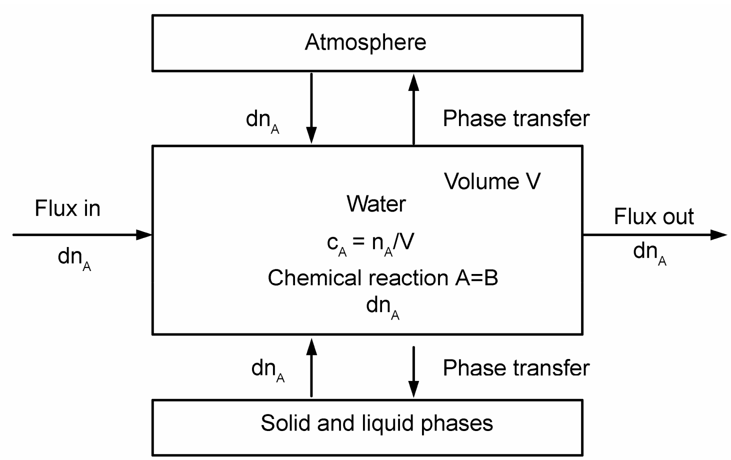

Figure 1-2. General representation of natural water systems is treated as an open system. The system receives fluxes of matter from the surroundings and undergoes chemical changes symbolized by the reaction A=B. The time invariant condition is represented by $dC_A/dt=0$. (Stumm and Morgan)

1.2.2 The First Law of Thermodynamics

The **first law of thermodynamics**, or the **law of conservation of energy**, states that energy can be neither created nor destroyed. The mathematical statement of the first law could be written as

$$\Delta E = q - w \qquad [1\text{-}8]$$

where

ΔE = change in internal energy of the system

q = heat flowing into the system

w = work done by the system

By convention, q has a positive value if heat is absorbed by the system, and a negative vatlue otherwise. If the system does work on the surroundings, w has a positive value, as shown in Figure 1-3.

In chemical systems, expansion work is usually the work performed. For a special case, if the volume of the system remains constant, then no expansion work can be done (i.e., $w = 0$). For this case

$$\Delta E = q_v \quad (V = \text{constant}) \tag{1-9}$$

Most chemical systems that engineers encounter, however, are open to the atmosphere and consequently operate under constant pressure rather than constant volume. For such systems, another property, **enthalpy**, is handier to use. The enthalpy, H, of a system is defined as follows:

$$H = E + PV \tag{1-10}$$

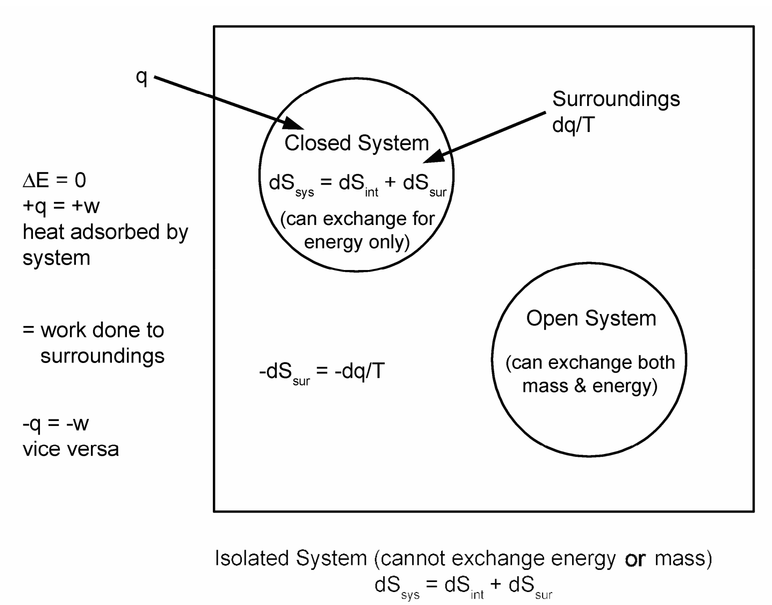

Figure 1-3. Illustration of a closed system, surroundings, and an isolated system or "universe" of a system plus surroundings. Heat transferred to the system, q, is positive, and that lost from the surroundings is $-q$. The entropy change of the system, dS_{sys}, is the sum of an internal change dS_{int} and a flow from the surroundings dS_{sur}.

Assuming that a chemical reaction takes place at a constant pressure and temperature, the change in the internal energy of the system would be

$$\Delta E = E_2 - E_1 = q_p - w = q_p - P\mathrm{d}V = q_p - P(V_2 - V_1)$$

where q_p is the heat absorbed at constant pressure. By rearranging the terms, then

$$(E_2 + PV_2) - (E_1 + PV_1) = q_p = H_2 - H_1$$

or

$$\Delta H = q_p \quad \text{(Constant } T, P\text{)} \qquad [1\text{-}11]$$

It is a universal practice to designate ΔH as **heat of reaction**. Chemical changes that are accompanied by the absorption of heat, which makes ΔH positive, are called **endothermic reactions**. **Exothermic reactions** are those with a negative ΔH value. The heat of reaction for a chemical reaction can be easily calculated from standard enthalpies, usually available in handbooks, of the species involved. Calculation of the heat of combustion of methane gas is illustrated in the following example:

	CH4(g) +	2O2(g)	→	CO2(g) +	2H2O(l)
ΔH^0_{298}	-17.89	0		-94.05	2(-68.32)

Hence, H^0_{298} for combustion = (-94.05) + 2(-68.32) - (-17.89) – 0

= -212.80 Kcal/mole of methane

1.2.3 The Second Law of Thermodynamics and Entropy Pollution

The first law, stating that energy must be conserved in all ordinary processes, imposes no direction on energy transformations. However, certain restrictions do exist. For example, heat always flows from a higher temperature level to a lower one and never in the reverse direction. Also, the efficiency of transformation from one form of work to another, such as from mechanical to electrical in an electrical generator, can be made to approach 100%. The transformation of heat (thermal energy) into work is especially inefficient, the highest efficiency being 45% for a modern turbine, as shown in Table 1-1. This inefficiency indicates that various forms of energy have different qualities. In this sense, work can be termed as energy of a higher quality than heat.

The concept of **entropy** was developed to serve as a general criterion of spontaneity for physical and chemical changes, or for direction of energy transformation. For the given state of a system, entropy, S, can be defined quantitatively as

$$S = k \ln \Omega \qquad [1\text{-}12]$$

where

k = Boltzmann's constant

Ω = the thermodynamic probability, defined as the number of ways that the particles of the system can be arranged among the energy levels accessible to them.

In most textbooks, entropy is defined by the following differential equation:

$$\mathrm{d}S = \mathrm{d}q_{rev} / T \qquad [1\text{-}13]$$

where the quantity q_{rev} is the amount of heat that the system absorbs if a chemical change is brought about in a reversible manner. If a spontaneous change occurs in a system, it will always be found that the total entropy change, including everything involved, is a positive value. A calculation of entropy change can help us determine whether a chemical or physical transformation could occur. If $S > 0$, the change will occur spontaneously; if $S < 0$, the change usually occurs in the reverse direction; and if $S = 0$, the system is at equilibrium. In general, the **second law of thermodynamics** states that all processes in nature tend to occur only with an increase in entropy and that the direction of change is always such as to lead to the entropy increase.

The first law tells us that the energy of the universe is constant, while the second law indicates that energy has different qualities and the entropy of the universe tends toward a maximum. Table 1-2 lists the quality of various forms of energy in terms of entropy — the higher the entropy per unit energy, the lower the quality of the energy. Those forms, having small amounts of entropy per unit energy, tend to transform into others with higher values, thereby producing greater quantities of entropy.

Table 1-1. Efficiency of Energy Converters

Type	Efficiency	Type of Conversion	
		From	To
Electric generator - Electric motor	99	Mechanical	Electrical
Low	62	Electrical	Mechanical
High	92	Electrical	Mechanical
Dry cell battery	90	Chemical	Electrical
Large steam boiler	88	Chemical	Thermal
Home furnace - Gas	85	Chemical	Thermal
Home furnace - Oil	65	Chemical	Thermal
Storage battery (lead acid)	72	Electrical	Chemical
		Chemical	Electrical
Fuel cell	60	Chemical	Electrical
Man on bicycle	50	Chemical	Mechanical
Liquid fuel rocket (H_2)	47	Chemical	Thermal
Turbine - Steam	45	Thermal	Mechanical
Turbine - Gas (aircraft or industrial)	35	Chemical	Thermal
Electric Power plant - Fossil fueled	40	Chemical	Thermal
Nuclear fueled	32	Nuclear	Thermal
		Thermal	Mechanical
		Mechanical	Electrical
Internal combustion engine - Diesel	37	Chemical	Thermal
Otto cycle (automobile)	25	Thermal	Mechanical
Wankel (rotary)	18		
Lasers	30-10	Electrical	Radiant
Lamps - High intensity	32	Electrical	Radiant
Lamps - Fluorescent	20	Electrical	Radiant
Lamps - Incandescent	4	Electrical	Radiant
Unaided walking man	12	Chemical	Mechanical
Solar cell	10-15	Radiant	Electrical
Steam locomotive	8	Chemical	Thermal
		Thermal	Mechanical
Thermocouple	6	Thermal	Electrical

Source: Much of the data of this table was obtained from C.M. Summers, Sci. Amer., 224(3), 155 (Sept. 1971).

Table 1-2. Quality of Various Forms of Energy

Form of Energy	Entropy Per Unit Energy
Gravitational	0
Nuclear	10^{-4}
Thermal	
Stars (106 K)	10^{-3}
Earth (102 K)	10^{2}
Chemical	1-10
Radiant	
Sunlight (visible)	1-10
Cosmic microwave	10^{4}

Source: Data adapted from F.J. Dyson, Sci.Amer., 224(3), 50-59 (Sept. 1971)

Therefore, any energy crisis is not the result of a lack of energy, because energy cannot be created or destroyed. Instead, it has resulted from the production of entropy associated with the conversion of high-grade energy sources into lower-grade ones. The production of entropy has been referred to as **entropy pollution,** because it is a kind of measure of the extent to which the universe has been irreversibly degraded. Table 1-3 gives the major energy resources available at the surface of the earth; each resource will be discussed further in later chapters.

1.2.4 Free Energy

To use entropy change as a criterion of spontaneous change requires taking both the system and all its surroundings into consideration. Usually, it is more convenient to limit our attention to the system only. This concentration can be accomplished in the following way:

$$\begin{aligned}\Delta S_{universe} &= \Delta S_{system} + \Delta S_{surrounding} \\ &= \Delta S_{system} + \frac{q_{surrounding}}{T} \\ &\geq 0\end{aligned} \qquad [1\text{-}14]$$

Table 1-3. Estimated Energy Resources*

Type	Total World Supply [a]	Economically Available (at No More Than Double Current Costs) World	U.S.
	Depletable supplies		(10^{21} J)
Fossil (chemical)			
Tar sands	2.1	-----	-----
Natural gas	3.8	2.2 - 3.8	0.6 - 1.1
Petroleum	6.0	3.2 - 6.0	0.6 - 1.1
Oil shale	13.3	-----	-----
Coal and lignite	185.0	21.1 - 31.5	5.0 - 7.2
Total Fossil	210.2	26.5 - 41.3	6.2 - 9.4
Nuclear			
Ordinary fission	2×10^4 [b]	14.0	1.4
Breeder fission	6×10^6 [b]	4000.0	400.0
Fusion (D-T)	215	-----	-----
Fusion (D-D)	1×10^{10}	-----	-----
	Continuous supplies		(10^{21} J/ year)
Solar	899	-----	50.0 [c]
Tidal	0.094	-----	0.009
Geothermal	0.010	-----	0.001

a Total supply including amount consumed to date.

b Estimated from total quantity of uranium and thorium within 1 mile of land surface assume 1% to be able for mining (Int. At. Energy Ag. Bull., 14(4), 11, 1972).

c Total supply is listed because no cost figures are available.

* Source: Data adapted from C. Starr, Sci. Amer., 224(3), 43, (Sept. 1971).

Because,

$$\Delta H = q_{system} = -q_{surroundings}$$

$$\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H_{system}}{T} \geq 0 \qquad [1\text{-}15]$$

Multiplying both sides by $-T$

$$-T\Delta S_{universe} = \Delta H_{system} - T\Delta S_{system} = \Delta G_{system} \leq 0 \qquad [1\text{-}16]$$

ΔG_{system} is defined by Equation [1-16] and is known as the change in **Gibbs free energy** of the system. So, if $\Delta G < 0$, the reaction will go spontaneously; if $\Delta G = 0$, the system is in equilibrium. ΔG is also defined as

$$G = H - TS \qquad [1\text{-}17]$$

At constant T and P

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= \Delta E + P\Delta V - T\Delta S \\ &= q - w + P\Delta V - T\Delta S\end{aligned} \qquad [1\text{-}18]$$

If the system change is brought about reversibly, then q becomes q_{rev} and w becomes w_{max}, and the maximum quality of work that can be obtained is

$$\Delta G = q_{rev} - w_{max} + P\Delta V - q_{rev}$$

and

$$-\Delta G = w_{max} - P\Delta V$$

$P\Delta V$ gives the portion of the work that must be wasted; therefore, the $-\Delta G$ indicates the useful work available for the system change.

$$-\Delta G = w_{useful} \quad \text{(constant } T, P\text{)} \qquad [1\text{-}19]$$

In principle, any spontaneous process can be made to do useful work as shown in Equation [1-19]. To find the relationship between the free energy and **equilibrium constant**, we proceed as follows:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P \qquad [1\text{-}20]$$

At constant temperature

$$\mathrm{d}G = V\mathrm{d}P = RT(\mathrm{d}P/P) = RT\,\mathrm{d}(\ln P) \qquad [1\text{-}21]$$

To give a reference point for the free energy as G^o at 25°C and 1 atmosphere,

$$G - G^o = RT \ln(P/P^o) = RT \ln\alpha \quad [1\text{-}22]$$

where $\alpha \propto P \propto$ concentration
where α is the activity. Consider the following reaction:

$$aA + bB \rightarrow cC + dD$$

$$\Delta G = \Sigma G_{products} - \Sigma G_{reactants} \quad [1\text{-}23]$$

$$\text{also } Gi = Gi^\circ + RT\, ln\, \alpha i$$

The free energy of this reaction is given by the following equation by substituting Equation [1-22] into Equation [1-23]:

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}\right)$$

As the reaction proceeds to a state of equilibrium, ΔG will be zero, and thus

$$\Delta G^\circ = -RT \ln\left(\frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}\right)_{\text{equilibrium}} \quad [1\text{-}24]$$
$$= -RT \ln K$$

where K is the **equilibrium constant**. Values for the standard free energies of various substances can be found from engineering or chemistry handbooks. By calculating the standard free energy change for the reaction, K is easily determined from the preceding equation.

1.2.5 Thermodynamic Properties

Thermodynamic systems may consist of one or more parts called **phases**, in which they are physically and chemically homogeneous. Thermodynamic systems are characterized by a small number of properties. The properties may be divided into two types: extensive and intensive. **Extensive properties** are additive; that is, they depend on the amount of substances present. Examples of such properties are total mass, volume, and energy. On the other hand, **intensive properties** are those whose values are independent of the total amount, but which depend on the concentration of the substance(s) in a system. Examples of intensive properties are pressure, temperature, molar volume, and chemical potential. Figure 1-4 illustrates a simplified model for the thermodynamic description of natural water systems. P and T are intensive variables, and the mole numbers, n_i, in each phase are extensive variables that together determine the volume, mass, composition, and other properties of the system.

Various forms of thermodynamic work are available. Basically, they can all be expressed as an intensive property times an extensive variation, as shown in Table 1-4.

Many thermodynamic properties and their relationships have been derived, making it a difficult task to memorize them all. To solve the problem, a handy scheme has been devised for memorizing important thermodynamic relations. A detailed description of the scheme based on Yen is given in Figure 1-5.

There are many thermodynamic functions that can be derived from the code sentence. "**T**he **G**ibbs **P**otential **H**as **S**hown **E**ndless **V**aluable **A**pplications" for the functions of $T, G, P, H, S, E, V,$ and A. This is actually based on the principle of symmetry of thermodynamic potentials; e.g., Jacobian. In order to obtain dE as a function of appropriate independent variables, look at the two diagonal lines toward the base E, taking the signs

$$dE = -PdV + TdS$$

Similarly

$$dG = VdP - SdT$$

$$dH = VdP + TdS$$

$$dA = -PdV - SdT \quad [1\text{-}24a]$$

Again for triangular relationship, for example, ΔSVT

$$\left(\frac{\partial E}{\partial S}\right)_V = T$$

the variable V is situated at the right angle while the independent variable and answer are at the other apexes.

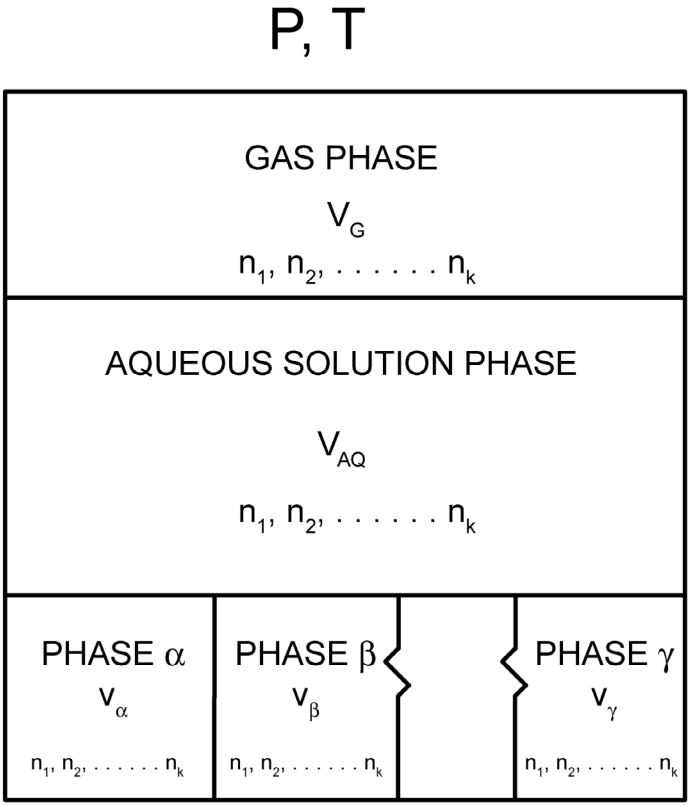

Figure 1-4. Simplified model for the thermodynamic description of natural water systems.

Table 1-4. Expressions for the Thermodynamic Work *dW* Done on a System

Type	Intensive Property	Extensive Variation	Expression
Expansion	Pressure, P	Volume, dV	$-PdV$
Electrical	Potential, E	Charge, de	$-Ede$
Gravitational	Force, mg	Height, dh	mg dh
Chemical	Chemical potential, μ	Moles, dn	μdn
Surface	Interfacial tension, γ	Area, dA	γdA

Source: Stumm and Morgan

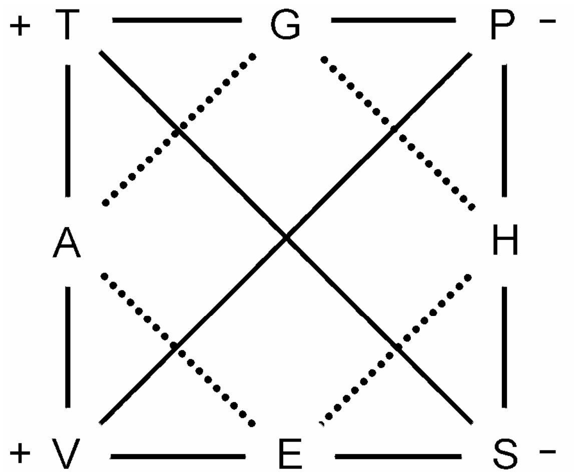

Figure 1-5. Thermodynamic functions based on group theory [from T.F. Yen, J. Chem Edu. 31, 610 (1954)]. Code sentence "The Gibbs Potential Has Shown Endless Valuable Applications".

$$\left(\frac{\partial E}{\partial V}\right)_S = -P$$
$$\left(\frac{\partial G}{\partial P}\right)_T = V$$
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$
$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad [1\text{-}24b]$$
$$\left(\frac{\partial H}{\partial P}\right)_S = V$$
$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$
$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

The Maxwell relationship can be obtained by considering the right triangle with the same base; for example, ΔTVS, ΔPSV

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$-\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \qquad [1\text{-}24c]$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

from the corners of the diagram

$$\left(\frac{\partial V}{\partial S}\right)_E = \frac{T}{P}$$

$$\left(\frac{\partial T}{\partial V}\right)_A = \frac{-P}{S}$$

$$-\left(\frac{\partial P}{\partial T}\right)_G = \frac{-S}{V} \qquad [1\text{-}24d]$$

$$-\left(\frac{\partial S}{\partial P}\right)_H = \frac{V}{T}$$

from the trapezoid *EATS*, *AGPV*, and so on.

$$E - A = TS$$

$$A - G = -PV$$

$$G - H = -ST \qquad [1\text{-}24e]$$

$$H - E = VP$$

and chemical potentials such as

$$\mu = \left(\frac{\partial E}{\partial n}\right)_{S,V} = \left(\frac{\partial A}{\partial n}\right)_{V,T} = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial n}\right)_{P,S} \quad [1\text{-}25]$$

The symmetry is based on group theory.

A definite quantity of heat is required to raise the temperature of a given mass of any material by one Celsius degree. This quantity is called the heat capacity of the system, C. Thus,

$$C = \frac{dq}{dT} \quad [1\text{-}26]$$

If a unit mass is taken as the basis for heat capacity, the equation becomes $dq = m\,C\,dT$, where m represents mass and C is now called **specific heat capacity**. The specific heat capacity of water is approximately 1(cal)/(g)(^{o}C). When the volume is held constant, by combining the preceding equation and $\Delta E = q - w$ — that is, Equation [1-8] and [1-26] — C_v at a constant volume can be obtained:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad [1\text{-}27]$$

Similarly, by some simple manipulation, we can get C_p at constant pressure.

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \quad [1\text{-}28]$$

The general equation to describe the C_p and C_v is

$$C_P - C_V = \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \quad [1\text{-}29]$$

The actual value of the difference for an ideal gas could easily be found to equal R. Table 1-5 lists the molar heat capacities for various gases.

Table 1-5. Molar Heat Capacities of Gases*

Gas	C_P	C_V	$C_P/ C_V = \gamma$
Argon, A	4.97	2.98	1.67
Helium, He	4.97	2.98	1.67
Mercury, Hg	4.97	2.98	1.67
Hydrogen, H_2	6.90	4.91	1.41
Oxygen, O_2	7.05	5.05	1.40
Nitrogen, N_2	6.94	4.95	1.40
Chlorine, Cl_2	3.25	6.14	1.34
Nitric oxide, NO	7.11	5.11	1.39
Carbon monoxide, CO	6.97	4.97	1.40
Hydrogen chloride, HCl	7.05	5.01	1.41
Carbon dioxide, CO_2	8.96	6.92	1.29
Nitrous oxide, N_2O	9.33	7.29	1.28
Sulfur dioxide, SO_2	9.40	7.30	1.29
Ammonia, NH_3	8.63	6.57	1.31
Methane, CH_3	8.60	6.59	1.31
Ethane, C_2H_4	12.71	10.65	1.19
Dimethyl ether, C_2H_4O	15.89	13.73	1.16

*in cal deg^{-4} mole^{-1} at 25°C

1.2.6 Applications to Solid Systems

The following is a discussion leading to the understanding of some properties of metals, ceramic materials, and rubbers. From Figure 1-5, we can easily obtain the **Helmholtz free energy** equation, as shown here

$$A = E - TS$$

or

$$dA = dE - TdS - SdT \qquad [1\text{-}24f]$$

Also from Figure 1-5

$$E = H - VP$$

$$dE = dH - VdP - PdV \qquad [1\text{-}24g]$$

and Figure 1-5

$$dH = VdP + TdS$$

Thus, combining this relation with Equation [1-24f]

$$dE = TdS - PdV$$

Then, substituting into Equation [1-24e], it follows that

$$dA = -PdV - SdT \qquad [1\text{-}24h]$$

For an elastomer, **chain extension** will take place isothermally with a change of ΔL from the length of polymeric chains, and $dW = -PdV$ from Equation [1-24h], as shown here

$$\therefore dA_T = dW = FdL \qquad [1\text{-}24i]$$

where F is the force required to extend or to compress the chain segment. Thus one can rewrite the Helmholtz free energy equation as

$$F = \left(\frac{\partial A}{\partial L}\right)_{T,V} = \left(\frac{\partial E}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V} \qquad [1\text{-}30]$$

because deformation takes place with no volume change. For the preceding equation, the first term becomes important in the case of metals and ceramics

$$F = \left(\frac{\partial E}{\partial L}\right)_{T,V} \qquad [1\text{-}30a]$$

However, internal energy causes heatup and fracture with extension for rubber. The opposite conditions apply to elasticity as entropy decreases with extension and a large change of chain segment conformations

$$F = -T\left(\frac{\partial S}{\partial L}\right)_{T,V} \qquad [1\text{-}30b]$$

which indicates that the second term becomes important for rubber.

Under deformation the chain segment can be analyzed with an end-to-end distance of the polymer chain. The end-to-end distance can be related to a probability function *P(r),* and the entropy of this chain segment is as follows (here distance r is proportional to *L*):

$$S = S_0 + k\, lnP(r)$$

$$P(r) = \frac{\exp\left[-\left(\frac{r}{\rho}\right)^2\right]}{\left(\rho\pi^{\frac{1}{2}}\right)^3}$$

which has a Gaussian distribution, and where ρ is density. Hence,

$$S = S_o - k\left[3\ln(\pi^{\frac{1}{2}}\rho) + \left(\frac{r}{\rho}\right)^2\right]$$

Thus,

$$\left(\frac{\partial S}{\partial r}\right) = \frac{-2kr}{\rho^2}$$

or,

$$F = \frac{2kTr}{\rho^2} = kr \qquad [1\text{-}31]$$

after substituting with

$$F = -T\left(\frac{\partial S}{\partial L}\right)_{T,V} \qquad [1\text{-}30b]$$

which means the force to extend or compress the chain segment is to distance *r* and is directly proportional to temperature. The chain acts like a spring.

1.3 KINETICS

Thermodynamics is able to tell us what can happen, and to what extent, but it is unable to tell us how a change will actually occur. **Chemical kinetics** searches for the factors that influence the rate of reaction and brings a time factor into consideration. The rate of reaction depends on the nature of the reacting substances, the temperature, and the concentration of the reactants. The **rate of a chemical reaction** is the rate at which the concentrations of reacting species vary with time; that is, $-dC/dt$, where C is the concentration of the reactant. The sum of all the exponents to which the concentrations in the rate equation are raised is the **order** of the chemical reaction. Thus, a rate equation is expressed as

$$-\frac{dC}{dt} = kC_1^{n_1}\,C_2^{n_2}\,C_3^{n_3}\ldots. \qquad [1\text{-}32]$$

where

k = rate constant

n = order of the reaction $(n_1 + n_2 + \ldots..)$

1.3.1 First-Order Reactions

A **first-order reaction** is one in which the rate of reaction is proportional to the concentration of the reactant. For example, the following reaction is a first-order reaction:

$$N_2O_5 \rightarrow 2\ NO_2 + 1/2\ O_2$$

Therefore

$$-\frac{dC}{dt} = kC \qquad [1\text{-}33]$$

If the initial concentration, at $t = 0$, is C_o, the concentration (C) at some later time (t) can be found by integrating the preceding equation, which gives

$$-\int_{C_0}^{C} \frac{dC}{C} = k \int_0^t dt$$

and

$$-\ln \frac{C}{C_o} = \ln \frac{C_o}{C} = kt$$

or

$$C = C_o \exp(-kt) \qquad [1\text{-}34]$$

The **half-life** of the reaction can be determined by inserting the requirements that at $t = t_{1/2}$ and the concentration $C = \frac{1}{2} C_o$ into Equation [1-34], that gives

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \qquad [1\text{-}35]$$

1.3.2 Second-Order Reactions

For a **second-order reaction**; for example, A + B $\rightarrow$ products, the rate equation can be expressed as follows

$$-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B$$

or

$$\frac{dX}{dt} = k\,(a-x)(b-x)$$

where

x = amount of the reactants consumed

a = initial concentration of A

b = initial concentration of B

If $a \neq b$, the following equation can be obtained through simple mathematical manipulation:

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)} \quad [1\text{-}36]$$

The order of reaction can be evaluated by a graphical method (see Appendix A).

1.3.3 Consecutive Reactions

Chemical reactions such as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

which proceed from reactants to products through one or more intermediate stages are called **consecutive reactions**. The rate equations are as follows:

$$-\frac{dC_A}{dt} = k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B$$

If at $t = 0$ we have $C_A = C_{A0}$, $C_B = C_C = 0$, then a solution for the concentration of each component at time t is as follows (it is a good exercise to solve the following equations):

$$C_A = C_{A0} e^{-k_1 t} \quad [1\text{-}37]$$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left\{ e^{-k_1 t} - e^{-k_2 t} \right\} \quad [1\text{-}38]$$

$$C_c = C_{A0}\left\{1 + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} - \frac{k_2 e^{-k_1 t}}{k_2 - k_1}\right\} \qquad [1\text{-}39]$$

Consecutive reactions are of great importance in engineering. Bacterial nitrification of ammonia can be described by a consecutive reaction. Ammonia is oxidized by *Nitrosomonas* bacteria to nitrite, which is then oxidized by *Nitrobacter* bacteria to nitrate as indicated here:

$$NH_3 \xrightarrow[\text{Nitrosomonas}]{} NO_2^- \xrightarrow[\text{Nitrobactor}]{} NO_3$$

The changes in nitrogen forms are shown in Figure 1-6, where the concentrations of nitrite and nitrate were set equal to zero when t = 0, and k_1 was assumed to be equal to $2k_2$.

There are some other types of complex reactions, such as **parallel types**, in which two reacting species compete with each other to react with a third reacting species.

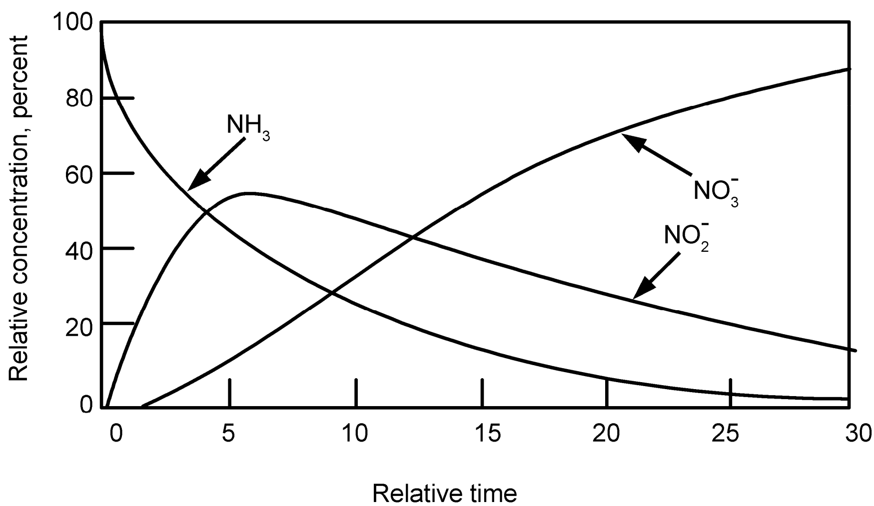

Figure 1-6. Nitrogen changes during nitrification, assuming consecutive first-order reactions.

1.3.4 Temperature Dependence of Reaction Rates

Chemical and biological reaction rates generally increase with increasing temperature. Most of the reactions follow the **Arrhenius-type of temperature dependence**

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \qquad [1\text{-}40]$$

where E_a is a constant termed the activation energy. By integrating the preceding equation, we get

$$\ln k = \frac{-E_a}{RT} + \ln A \qquad [1\text{-}41]$$

or

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

where T is expressed in Kelvin and A is called the frequency factor. A semilog plot of rate constant versus the reciprocal of temperature should be a straight line. Some of the common suggestions such as "the rate of reaction will double if temperature increases by 10^o and half if temperature decreases by 10^o " are based on the Arrhenius form. The frequency or preexponential factor, A is selected to the opportunity of molecular collision frequency.

1.4 UNITS AND CONVENTIONS

Engineers may have to measure or estimate large or small quantities, such as the annual solar energy input to the earth, or the concentration of a pollutant in parts per billion (ppb). Therefore, it is advisable to be familiar with decimal multipliers that are commonly used, as listed in Table 1-6. When the name of a unit is preceded by one of these prefixes, the size of the basic unit is modified by the decimal multiplier. For example, 1 Tg stands for 10^{12} grams and 1 Pg is for 10^{15} grams. In the field of energy, there are special notations for large energy values, where 1 **Quad** = 10^{15} Btu (British thermal unit) and 1 **Quin** = 10^{18} Btu. Accordingly, 1 PBtu = 1 Quad, or 1 EBtu = 1 Quin and 1 Quin = k Quad.

One important conversion factor for air pollution study is that for the conversion of ppm to **μg/g³** or **mg/cm³**, or vice versa. One **ppm** means 1 volume in 1 million volumes. For instance, to convert 1 ppm of SO_2 at 1 atmosphere and 0°C, we would proceed as follows:

$$1 \text{ ppm} = (1/10^6)(1 \text{ mole}/22.4 \text{ liter})(64 \text{ gram/mole})(10^6 \text{ μg/g})(10^3 \text{ liter/m3})$$

$$= 2857 \text{ μg/m}^3$$

or

$$= 2612 \text{ μg/m}^3 \text{ at } 25 \text{ °C}$$

Conversion factors for several air pollutants are given in Table 1-7.

Conversely, 1000 μg/m³ of CO can be calculated as

$$(1000\text{μg/m}^3)(1\text{g}/10^6\text{μg})(1\text{mole}/28\text{g})(22.4\text{L/mole})(1\text{m}^3/10^6\text{cm}^3)(1\text{cm}^3/10^3\text{L})(10^6\text{L/L})$$

$$= 0.8 \text{ ppm}$$

A table of common unit conversions is included in Table 1-8. Throughout the book both English and metric system are used separately. In many cases, special units have been designated for the convenient usages. Many names of elements and constants are based on the International Union of Pure and Applied Chemistry (IUPAC) recommendation. Some useful constants are listed in Table 1-9.

Table 1-6. Decimal Multipliers that Serve as SI Unit Prefixes

Prefix	Origin	Symbol	Multiplying Factor
yotta	Greek or Latin *octo*, "eight"	Y	10^{24}
zetta	Latin *septem*, "seven"	Z	10^{21}
exa	Greek *hex*, "six"	E	10^{18}
peta	Greek *pente*, "five"	P	10^{15}
tera	Greek *teras*, "monster"	T	10^{12}
giga	Greek *gigas*, "giant"	G	10^{9}
mega	Greek *megas*, "large"	M	10^{6}
kilo	Greek *chilioi*, "thousand"	k	10^{3}
hecto	Greek *hekaton*, "hundred"	h	10^{2}
deka	Greek *deka*, "ten"	da	10^{1}
deci	Latin *decimus*, "tenth"	d	10^{-1}
centi	Latin *centum*, "hundred"	c	10^{-2}
milli	Latin *mille*, "thousand"	m	10^{-3}
micro	Latin *micro-* (Greek *mikros*), "small"	μ	10^{-6}
nano	Latin *nanus* (Greek *nanos*), "dwarf"	n	10^{-9}
pico	Spanish *pico*, "a bit," Italian *piccolo*, "small"	p	10^{-12}
femto	Danish-Norwegian *femten*, "fifteen"	f	10^{-15}
atto	Danish-Norwegian *atten*, "eighteen"	a	10^{-18}
zepto	Latin *septem*, "seven"	z	10^{-21}
yocto	Greek or Latin *octo*, "eight"	y	10^{-24}

Table 1-7. Conversion Factors for Air Pollutants

	Temperature (°C)	Pressure (mm)	1 ppm equivalence in μg/m^3
Carbon monoxide (CO)	0	760	1,250
	25	760	1,145
Nitric oxide (NO)	25	760	1,230
Nitrogen dioxide (NO_2)	25	760	1,880
Ozone (O_3)	0	760	2,141
	25	760	1,962
PAN {$CH_3(CO)O_2NO_2$}	0	760	5,938
	25	760	4,945
Sulfur dioxide (SO_2)	0	760	2,860
	25	760	2,620

Source: H.C. Perkins, Air Pollution, McGraw Hill, 1974, p.385.

Table 1-8. Common Unit Conversions

Gas Constant 0.082 liter-atm/mole K 62.36 liter-mm Hg/mole K 8.314 Joule/g-mole K 1.314 atm-ft^3/lb-mole K 1.987 cal/g-mole K 1.987 Btu/lb-mole °R 0.73 atm-ft^3/lb-mole °R 10.73 psi-ft^3/lb-mole °R 1545 ft-lb$_f$/lb-mole °R	Volume 1 ft^3 = 28.316 liter = 7.481 gal 1 in.^{3} = 16.39 cc = 5.787 x 10^{-4} ft^3 1 gal = 3.785 liter = 8.34 lb H_2O 1 m^3 = 35.32 ft^3 = 264.2 gal	Density 1g/cm^3 = 1000 kg/m^3 = 62.428 lb/ft^3 = 8.345 lb/gal = 0.03613 lb/in.^{3}
Length 1 mile = 1609 m = 5280 ft 1 ft = 30.48 cm = 12 in. 1 in. = 2.54 cm 1 m = 3.2808 ft = 39.37 in. 1 nm = 10^{-9}m = 10 A	Viscosity 1 poise = 6.7197×10^{-2} lb$_m$/ft-sec = 2.0886×10^{-3} lb$_f$-sec/ft^2 = 2.4191×10^2 lb$_m$/ft-hr = 1 g/cm-sec	Conversion Factor 1 cal/g-mole = 1.8Btu/lb-mole 1 amu = 1.66063 × 10^{-24}g 1 eV = 1.6022 × 10^{-12}erg 1 radian = 57.3° 1 cm/sec = 1.9685 ft/min 1 rpm = 0.10472 radian/sec

Table 1-8. Continued

Pressure 1 atm = 101325 N/m^2 = 14.696 psi = 760 mmHg = 29.921in.Hg (32 °F) = 33.91 ftH_2O (39.1 °F) = 2116.2 lb_f/ft^2 = 1.0133 bar = 1033.3 g_f/cm^2	Constant h = 6.6262 × 10^{-27}erg-sec k = 1.38062 × 10^{-16}erg/K N_0 = 6.022169 × 10^{23} C = 2.997925 × 10^{10}cm/sec F = 96487 coul/eq e = 1.60219 × 10^{-19}coul g = 980.665 cm/sec^2 =32.174 ft/sec^2	Mass 1 kg = 2.2046 lb 1 lb = 453.59 g 1 ton = 2000 lb = 907.2 kg 1 B ton = 2240 lb = 1016 kg 1 tonne = 2205 lb = 1000 kg 1 slug = 32.2 lb = 14.6 kg
Area 1 m^2 = 10.76 ft^2 = 1550 $in.^2$ 1 ft^2 = 929.0 cm^2	Power 1 HP = 550 ft-lb_f/sec = 745.48 watt 1 Btu/hr = 0.293 watt	Force 1N = 1 kg-m/sec^2 = 10^5 dyne = 0.22481 lb_f = 7.233 lb_m-ft/sec^2
Transfer Coefficient 1 Btu/hr-ft^2 °F = 5.6784 Joule/sec-m^2 K = 4.8825 Kcal/hr-m^2 K = 0.45362 Kcal/hr-ft^2 K = 1.3564x10^{-4}cal/sec-cm^2 K 1 lb/hr-ft^2 = 1.3562 × 10^3kg/sec-m^2 = 4.8823 kg/hr-m^2 = 0.45358 kg/hr-ft^2 1 cal/g °C = 1 Btu/lb_m °F = 1 Pcu/lb_m °C 1 Btu/hr-ft °F = 1.731 W/m K = 1.4882 kcal/hr-m K	Energy & Work 1 cal = 4.184 Joule 1 Btu = 1055.1 Joule = 252.16 cal 1 HP-hr = 2684500 Joule = 641620 cal = 2544.5 Btu 1 KW-hr = 3.6 × 10^6 Joule = 860565 cal = 3412.75 Btu 1 l-atm = 24.218 cal 1 ft-lb_f = 0.3241 cal 1 Pcu = 453.59 cal 1 kg-m = 2.3438 cal	Stress 1 MPa = 145 psi 1 MPa = 0.102 kg/mm^2 1 Pa = 10 dynes/cm^2 1 kg/mm^2 = 1422 psi 1 psi = 6.90 × 10^{-3} MPa 1 kg/mm^2 = 9.806 MPa 1 dyne/cm^2 = 0.10 Pa 1 psi = 7.03 × 10^{-4} kg/mm^2 1 psi $in.^{1/2}$ = 1.099 × 10^{-3} MPa $m^{1/2}$ 1 MPa $m^{1/2}$ = 910 psi $in.^{1/2}$

Table 1-9. Some Useful Constants

Atomic mass	$m_u \approx 1.6605402 \times 10^{-27}$
Avogadro's number	$N \approx 6.0221367 \times 10^{23}$ mol^{-1}
Boltzmann's constant	$k \approx 1.380658 \times 10^{-23}$ J · K^{-1}
Elementary charge	$e \approx 1.60217733 \times 10^{-19}$ C
Faraday's constant	$F \approx 9.6485309 \times 10^{4}$ C · mol^{-1}
Gas (molar) constant	$R = k \cdot N \tilde{}\ 8.314510$ J · mol^{-1} · K^{-1}
	≈ 0.08205783 L · atm · mol^{-1} · K^{-1}
Gravitational acceleration	$g = 9.80665$ m · s^{-2}
Molar volume of an ideal gas at 1 atm and 25 °C	$\overline{V}_{ideal\ gas} \approx 24.465$ L · mol^{-1}
Permittivity of vacuum	$\varepsilon_0 = 8.854187 \times 10^{-12}$ C · V^{-1} · m^{-1}
Planck's constant	$h \approx 6.6260755 \times 10^{-34}$ J · s
Zero of the Celsius scale	0 °C = 273.15 K

Source: IUPAC, 1988.

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PROBLEM SET

1. Generally for gases, the compressibility coefficient, *k*, the expansion coefficient, *a*, and the pressure coefficient, *b*, can be expressed by

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial P} \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$

a) What are their values if those gases are ideal gases and

b) Prove

$$a = kbP$$

c) Show that

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

2. Calculate the maximum work done by the isothermal expansion of one mole of ideal gas at 0°C from 2.24 L to 22.4 L.

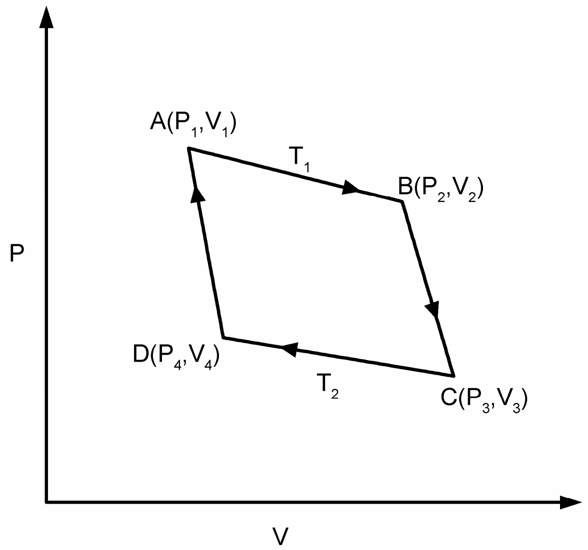
3. For a Carnot cycle as shown in the figure attached.

$$Q_2 = \int_a^b dQ = \int_a^b PdV = \int_a^b \frac{RT_2 dV}{V} = RT_2 \ln\left(\frac{V_b}{V_a}\right)$$

$$Q_1 = -\int_a^b dQ = RT_1 \ln\left(\frac{V_c}{V_d}\right)$$

Prove the efficiency is

$$n = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$



The Carnot Cycle

A to B is an isothermal expansion at temperature T_1, volume change is V_1 to V_2, and heat absorbed is Q_1.

B to C is adiabatic expansion, temperature is T_1 to T_2, volume change is V_2 to V_3, and heat absorbed is 0.

C to D is isothermal compression, temperature is T_2, volume change is V_3 to V_4, and heat absorbed is Q_2.

D to A is adiabatic expansion, temperature is T_2 to T_1, volume change is V_4 to V_1, and heat absorbed is 0.

4. For a consecutive reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

If $A(0) = A_0$ and $B(0) = 0 = C(0)$

and

$$\frac{dA}{dt} = -k_1 A$$

$$\frac{dB}{dt} = k_1 A - k_2 B$$

$$\frac{dc}{dt} = k_2 B$$

calculate A, B, and C.

5. For ideal gas, derive

$$C_P - C_V = R$$

and

$$\gamma = \frac{C_P}{C_V} = 1.67$$