

Chapter 1

Classical Thermodynamics: The First Law

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1 Classical Thermodynamics: 1st law

1.1 Introduction

We first review related year 1 courses (such as PHYS 10352 - Properties of Matter) and introduce some basic concepts in thermodynamics.

Microscopic systems: one or few particle systems, e.g., a hydrogen atom with one electron moving about one proton, a water molecule (H_2O), etc.

Macroscopic systems: systems consisting of very large number of particles ($\sim 10^{23}$, Avogadro's number 6×10^{23} /mole), e.g., a piece of metal, a cup of water, a box of gas, etc.

Laws that govern the microscopic world are the Newton's laws (classical), or Schrödinger equation (quantum), etc. In principle, these laws are applicable to the macroscopic systems, but it is often impractical to solve individual equation for each particle of a macroscopic system.

Furthermore, there are new quantities and new laws which govern the relations between these new quantities, in the macroscopic world. The subject of thermal and statistical physics is the study of particular laws which govern the behavior and properties of macroscopic bodies.

For example, if we film the collision of two balls in snooker, we cannot tell which way time is running. This is a demonstration of the time invariance of the laws in microscopic world, such as Newton's laws and Schrödinger equation. Consider another example. If we set a volume of gas molecules expand into a larger volume by removing a partition, by experience we know that after equilibrium the gas will not go back to the restricted region. This implies that there is a direction in time.

Equilibrium state: a state of a macroscopic system which is independent of time. By our experience, we know that an isolated system will always move to the equilibrium state. For example, hot water will cool down and ice will melt until they reach the temperature of its environment. Questions: what is the isolated system in these cases? Answer water (or ice) + environment.

Briefly, *Thermodynamics* is a phenomenological science which determines the relations between observable macroscopic quantities, such as temperature T , pressure P , etc. *Kinetic theory* attempts to understand the relationships in terms of fundamental interactions between individual particles, etc. And *statistical mechanics* provides foundation for the equilibrium properties from

the microscopic point of view. However, it does not say how a system approaches equilibrium and it cannot overcome the anomaly of the direction of time.

The basic assumption in thermodynamics is that only a few macroscopic quantities (thermodynamic parameters) are needed to describe the equilibrium state of a system. The following is a list of "things" you should know from your year 1 courses:

Basic Definitions in Thermodynamics

1. Thermodynamic (TD) systems: any macroscopic system which consists of a very large number of separate particles ($\sim 10^{23}$, Avogadro's number 6×10^{23} /mole), e.g., a piece of metal, a cup of water, etc.
2. TD variables (parameters): measurable macroscopic quantities associated with the system and are defined experimentally, e.g., P, V, T, H_a etc., where H_a is an applied field. These quantities are either *intensive* or *extensive*, i.e., either independent or linearly dependent on the amount of matter. Question: which of these are intensive and which are extensive?
3. A TD state is specified by a set of all values of all TD parameters necessary for a complete description of the system.
4. State functions: any function of thermodynamic variables P, V, T , etc. Like TD variables, a state function is either extensive or intensive. Example of state functions are internal energy, entropy, etc. Question: what is entropy?
5. Thermodynamic equilibrium prevails when TD state of system does not change with time. TD is concerned with equilibrium. All change of state are supposed to occur through successive states of equilibrium.
6. Equation of state relates the TD variables for a state in equilibrium, e.g., $f(P, V, T) = 0$ for a gas. Equation of state can not be determined by thermodynamics. It can only be obtained by either many observations (experiments) or from microscopic analysis, i.e. statistical mechanics.

7. Thermodynamic transformation: a change of state. If the initial state is an equilibrium state, then the transformation can be brought about only by change in the external condition of the system, The transformation is *quasi-static* if the conditions change so slow that at any instance the system is approximately in equilibrium. It is *reversible* if the transformation reverses its history in time when the external conditions retrace their history. A reversible transformation is quasi-static; converse not necessary true.
8. P - V diagram for a gas: the projection of the equation of state onto the P - V plane. A reversible transformation is a continuous path in the P - V plane. Specific paths are called *isotherms* (constant temperature) and *adiabats* (no heat exchanged). Note: If a TD system is not at an equilibrium state, its TD variables are not defined and a path in P - V plane cannot be drawn.
9. Work done on a gas:

$$W = -P\Delta V$$

where the minus sign denotes the decrease in volume due to compression. More examples will be given later. Note: work done by a gas is $-W = P\Delta V$ (work done on a gas - gas energy increases, work done by a gas - gas energy decreases).

10. Heat: what is absorbed by the system if its temperature rises. When no work is done, the heat is given by

$$Q = C \Delta T$$

where C is the heat capacity. For different ways of heating the system through ΔT , Q is different. Thus C depends on method of heating. We usually discuss C_P (constant pressure) and C_V (constant volume) for a gas system. Heat capacity per unit mass (or per particle) is called *specific heat*. We will learn work W and heat Q are not state function.

11. Thermal isolation: no exchange of heat with outside world. May be achieved by surrounding system with an adiabatic wall. Any transformation occurring in thermal isolation is said to take place adiabatically.

12. Equation of state for an ideal (perfect) gas (the behavior of all gases when sufficiently dilute). The variables are P, V, T and from experiment, the equation of state is

$$PV = Nk_B T \quad \text{or} \quad PV = nRT$$

where N is the number of particles, $k_B = 1.38 \times 10^{-23}$ Joule/degree, is the Boltzmann's constant, and $R = 8.31$ Joule mole $^{-1}$ deg $^{-1}$ with $n = N/N_A$ with $N_A = 6.02 \times 10^{23}$ molecules/mole.

1.2 The first law of thermodynamics

As mentioned before, the assumption in TD is that there are only a few numbers of macroscopic variables for a complete description of a state of a system. Definitions of physical state functions of these variables, the constraints of and relations between these state functions are the main subject of thermodynamics.

The main mathematics in TD: functions of many variables and their (partial) derivatives.

1st law: In an arbitrary TD transformation, let Q = net amount of heat absorbed by the system, and W = net amount of work done on the system. The 1st law states

$$\Delta E = Q + W \quad (1)$$

is the same for all transformations leading from a given initial state to a final state (Joule's law), where E is the **total energy** (or internal energy, or just energy) of the TD system. Clearly, E , Q and W are all measured in energy unit (SI: Joule).

Mancunian James Joule (born Salford 1818, died Sale 1889, brewer and physicist) did many experiments in the 1840's to establish the equivalence of heat and work as forms of energy.

Please note: (a) Thermally isolated system: contained within adiabatic (perfectly insulated) walls. we have

$$Q = 0, \quad \Delta E = W.$$

For mechanically isolated system: $W = 0$. Hence $\Delta E = Q$, all heat turns to internal energy. (b) Internal energy E is a function of state, a macroscopic variable, but has its origin of in microscopic constituents. In general, it is simply the sum of the kinetic energies of the molecules of the system and potential energy arising from the interaction force between them.

The first law of thermodynamics is a statement of energy conservation and defines the internal energy E as an extensive state function. In an infinitesimal transformation, the first law reduces to

$$dE = dQ + dW \quad (2)$$

where dE is a total (exact) differential for infinitesimal transformation. However, dQ and dW are not exact (Q and W are not state functions); Q and W in a thermodynamics transformation are process-dependent. All these are properties of functions of more than one variables.

Since E is a state function, it depends on the TD parameters, say P, V , and T . Since the equation of state can be made to determine one of these in terms of other two, we have, for a gas,

$$E \equiv E(P, V) = E(V, T) = E(T, P) .$$

Hence

$$dE = \left(\frac{\partial E}{\partial P} \right)_V dP + \left(\frac{\partial E}{\partial V} \right)_P dV .$$

Two other similar equations can be written.

Consider a gas. In an infinitesimal, reversible transformation, for which work done by the gas $dW = -PdV$, the heat

$$dQ = dE + PdV. \tag{3}$$

By the definition of heat capacity at constant V ,

$$C_V \equiv \left(\frac{dQ}{dT} \right)_V = \left(\frac{\partial E}{\partial T} \right)_V \tag{4}$$

and similarly, the heat capacity at constant pressure, using Eq. (3)

$$C_P \equiv \left(\frac{dQ}{dT} \right)_P = \left(\frac{\partial E}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P . \tag{5}$$

The difference between C_V and C_P clearly shows dQ is not exact, but depends on the details of the path, namely, heat Q is not a state function.

Note: Many authors use $dW (= PdV)$ to mean the work done by the system. We use $dW = -PdV$ to mean work done on the system and lower case $dw = -dW = PdV$ to mean work done by the system.

Example: Consider 2 different ways of taking a fixed mass of an ideal gas from an initial state (V_0, T_0) to a final state $(2V_0, T_0)$: (a) Free expansion in a container with adiabatic walls as shown in the top of Fig. 1 Clearly $Q = 0$ and $W = 0$. We have

$$\Delta E = 0.$$

For ideal gas, $E = E(T)$ (more discussion of this equation later). Hence $T = T_0 = \text{const.}$ (b) Expansion against an external force, with T held fixed at T_0 by contact with a heat bath as shown in the bottom two diagrams of Fig. 1. In this case, work is done by the gas.

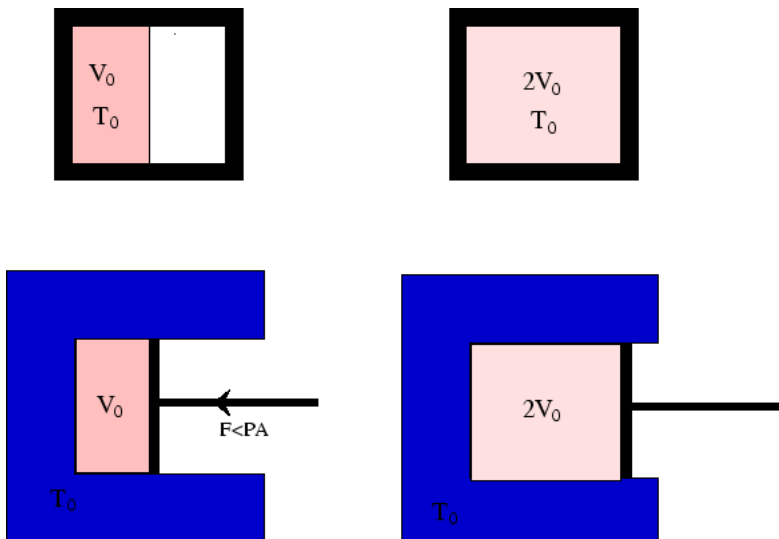


Fig. 1 (a) Free expansion (top two diagrams). (b) Expansion against an external force (bottom two diagrams).

As $\Delta E = 0$, we have

$$Q = -W > 0, \quad W = - \int F dx < 0.$$

Conclusion of these two examples are: Q and W are not state function but sum of them E is.

1.3 Real and Ideal gases: A Review

All gases which cannot be easily liquefied are found experimentally obey the following two laws:

(a) Boyles's law

$$PV = \text{const. at fixed temperature.}$$

(b) Charles's law (Gay-Lussac's law): At constant pressure, the volume of a gas varies linearly with temperature, say θ on some arbitrary scale, e.g., Centigrade,

$$V = V_0 \left(\frac{1 + \theta}{T_0} \right) \quad \text{at fixed } P = P_0.$$

where T_0 is constant (experiments show T_0 nearly same for all gases. If both laws are obeyed exactly

$$PV = P_0 V_0 \left(\frac{1 + \theta}{T_0} \right) = P_0 V_0 \frac{T}{T_0}$$

where $T = \theta + T_0$ is temperature on an absolute scale. As P and T are intensive, and V is extensive

$$\frac{PV}{T} \propto N$$

or, the ideal gas law

$$PV = Nk_B T = nRT \quad (6)$$

where k_B is the Boltzmann constant, $R = k_B N_A$ is universal gas constant, N_A is Avogadro's number, $n = N/N_A$ is number of mole. For the case of real gases, only the limit as $P \rightarrow 0$ does the equation of state assume the above form.

Later in Statistical Physics, we can understand ideal gas microscopically as a gas with point-like, non-interacting molecules. All gases tend to that of an ideal gas at low enough pressure. The noble gas (e.g., helium, argon) are very close to ideal at STP; even our air at STP is quite well approximated as ideal.

For real gas in general, the internal energy $E = E(T, P) = E(T, V)$. For an ideal gas, this simplifies to $E = E(T)$, as a function of T only, as we see below. By definition, the ideal gas satisfies the equation

$$PV = nRT, \quad E = E(T) \quad \text{for ideal gas.} \quad (7)$$

Notice that for ideal gas

$$\left(\frac{\partial E}{\partial P} \right)_T = 0, \quad \left(\frac{\partial E}{\partial V} \right)_T = 0.$$

From Eq. (4), for ideal gas,

$$C_V = \frac{dE}{dT}, \quad dE = C_V dT. \quad (8)$$

In general, heat capacity may change with T . But if $C_V = \text{constant}$, $E = C_V T$, after we define zero of energy as $E = 0$ at $T = 0$.

The result of statistical mechanics (kinetic theory) show that for an ideal gas,

$$E = \frac{\nu_f}{2} N k_B T = \frac{\nu_f}{2} n R T \quad (9)$$

where ν_f is the active degrees of freedom. The above equation states that each molecule has an average internal energy of $\frac{1}{2} k_B T$ per active degree of freedom. (i) Monatomic gases, $\nu_f = 3$; (ii) diatomic gases, $\nu_f = 5$ (3 translational and 2 rotational; vibrational modes are frozen out).

We can also prove

$$C_P - C_V = nR; \quad (10)$$

for ideal gas. And for reversible adiabatic process on an ideal gas

$$P V^\gamma = \text{const.}, \quad \gamma = \frac{C_P}{C_V}. \quad (11)$$

See Ex. 2. For a monatomic ideal gas, $\gamma = 5/3$; for diatomic ideal gas, $\gamma = 7/5$.

Now we consider real gases. Many attempts exist to modify the ideal gas equation of state for real gases. Two common ones are:

(a) The hard-sphere gas: we continue to neglect the interaction except at short range where we treat the molecules as hard spheres

$$V(r) = \begin{cases} \infty, & \text{for } r \leq r_0; \\ 0, & \text{for } r > r_0. \end{cases} \quad (12)$$

Most of the ideal gas results continue to hold except $V \rightarrow V - nb$, where b is the "excluded volume", proportional to the volume occupied by 1 mole of gas (i.e., $b \propto N_A r_0^3$). The equation of state for a hard sphere gas becomes

$$P(V - nb) = nRT, \quad \text{or } P(V - N\beta) = Nk_B T, \quad \beta = \frac{b}{N_A}.$$

(b) The van der Waals gas. Apart from the hard-sphere interaction at short distance, we now allow the weak intermolecular attraction at larger distances, as shown in Fig. 2. The extra attraction for $r > r_0$ clearly reduces the pressure for a given V and T , since a molecule striking the vessel wall experiences an additional inward pull on this account. Call this intrinsic pressure π . So

if the observed pressure is P and that expected if there were no attraction is p , $p - P = \pi$, the hard-sphere equation of state

$$P = \frac{nRT}{V - nb} \rightarrow P + \pi = \frac{nRT}{V - nb}.$$

Van der Waals argued that π is the result of mutual attraction between bulk of gas, i.e., the tendency of molecules forming pairs, and hence should be proportional to $N(N - 1)/2 \propto N^2$, or to N^2/V^2 as it is intensive. Hence $\pi = an^2/V^2$.

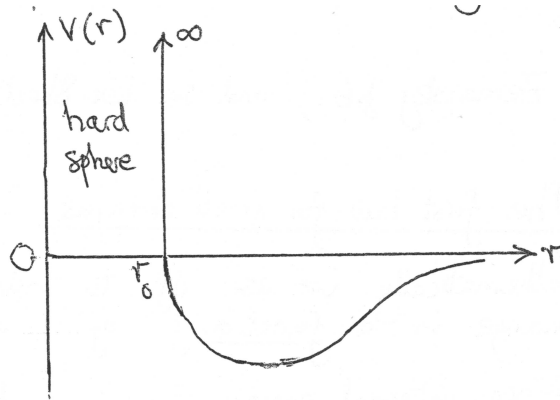


Fig. 2 A schematic diagram for the interaction potential between two molecules.

The equation of state for van der Waals gas is

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$$

or

$$\left(P + \frac{\alpha N^2}{V^2}\right)(V - N\beta) = Nk_B T, \quad (13)$$

where $\beta = b/N_A$ and $\alpha = a/N_A^2$. [Refs. Zemansky 6; and Ex. Sheets 2 and 3]

1.4 The first law for cycles

In thermodynamics, we often deal with cycles, changes in a system which take it through various equilibrium or nonequilibrium states, but ending in exactly the same state as the start. Clearly, by definition, all state variables (such as E) are unchanged in a cycle, i.e.

$$\oint_C dE = 0$$

around *any* closed cycle C , or

$$\oint_C dQ + \oint_C dW = 0;$$

although in general $\oint_C dQ \neq 0$ and $\oint_C dW \neq 0$; and such integrals depend on the closed path C .

Example: for a heat engine (see Chap. 2.1 below), Q_1 is absorbed in the outward path of cycle, Q_2 is emitted in return path of cycle: $\oint dQ = Q_1 - Q_2 = Q$; work done by engine, $w = -W = Q_1 - Q_2$, so that $W + Q = 0$.

[Refs. (1) Mandl Chap. 1.3; (2) Zemansky Chap. 3.5]

1.5 Reversible process

Of particular importance in thermodynamics are reversible changes to a system. For example, imagine a cylinder, with a perfectly smooth piston, which contains gas. If we push with a force infinitesimally larger than that needed to overcome the internal pressure, the volume will decrease infinitesimally. Then, if we decrease the force infinitesimally, again, the volume will increase infinitesimally. This is the hallmark of a *reversible process*: on infinitesimally change in the externally applied conditions suffices to reverse the direction of the change. Clearly, heat flow is only reversible if the temperature difference between the bodies is infinitesimally small.

For a process to be reversible two conditions must be satisfied: (i) it must be quasistatic, and (ii) there must be no friction or other hysteresis effects present. A quasistatic process is defined as succession of equilibrium states of the system. Clearly it is an idealization, since it requires to be carried out infinitely slowly. In practice the changes need to be slow compared to relevant relaxation times involved.

Because reversible processes are (infinitely) slow, the system is always essentially in equilibrium. Thus, all its state variables are well defined and

uniform, and the state of the system at all times can be represented on a diagram of the independent variables (e.g., a $P - V$ diagram). A finite reversible process passes through an infinite set of such states, and so can be drawn as a solid line as shown by paths L_1 or L_2 . By contrast, *irreversible* process pass through non-equilibrium states and cannot be so represented. They are often indicated schematically as a straight dashed line joining the initial and final states $i \rightarrow f$. (Note: in such irreversible cases, the work done during the process is NOT equal to the area under the line, as is the case for reversible processes.

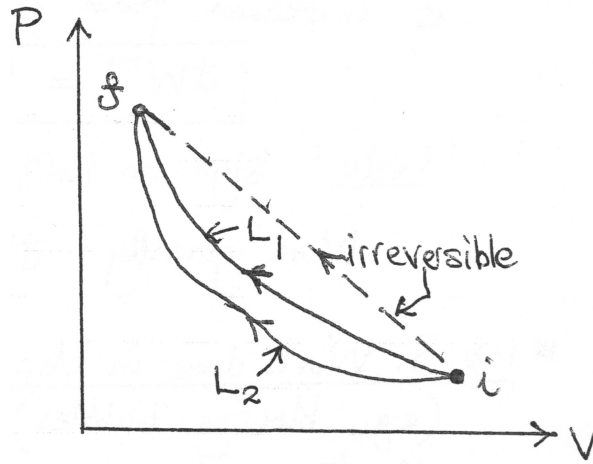


Fig. 3 Reversible processes (such as L_1 and L_2) and irreversible process between initial (indicated by i) and final (f) states.

[Refs.: (1) Mandl Chap. 1.3, (2) Bowley and Sanchez Chap. 1.6, (3) Zemansky Chap. 8]

1.6 Work

We now consider the work done by infinitesimal change in various thermodynamic systems.

(a) Work done in changing the volume of a hydrostatic system (or fluid). As shown in Fig. 4. let the piston move a distance $dx > 0$ to compress the

gas. If the process is frictionless, the work done on the gas is

$$\bar{d}W^{rev} = F dx = (PA) dx = P|dV|.$$

But, note this is positive for compression $dV < 0$, so

$$\bar{d}W^{rev} = -PdV \tag{14}$$

work done on system. If friction is present $F > PA$. $\bar{d}W > -PdV$ with $dV < 0$. In general

$$\bar{d}W \geq -PdV; \quad dV < 0$$

where equality holds for reversible processes.

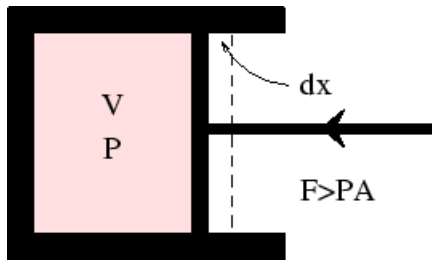


Fig. 4 Work done by changing the volume of hydrostatic system.

(b) Work done in changing the length of a wire. If the tension in the wire is Γ and the length is increased from $l \rightarrow l + dl$; work done on the wire is

$$\bar{d}W^{rev} = \Gamma dl. \tag{15}$$

Note: the sign on RHS now is positive, since $\bar{d}W^{rev} > 0$ if $dl > 0$. More generally, $\bar{d}W \geq \Gamma dl$, with equality for reversible processes.

(c) Work done in changing the area of a surface film (e.g. blowing bubbles). If the surface tension of the film is σ (energy/unit area) and the area is increased from $A \rightarrow A + dA$, work done on the surface is

$$\bar{d}W^{rev} = \sigma dA. \tag{16}$$

Note: similar comment as given in part (b) applies.

(d) Work done on magnetic materials by changing the field. Different textbooks take different viewpoints. We will take Mandl's. The basic problem is to agree on what is SYSTEM and what is SURROUNDINGS. We define work done on magnetic material by an external field

$$dW^{rev} = -\mathbf{m} \cdot d\mathbf{B} \quad (17)$$

where $\mathbf{m} = \int \mathbf{M}dV = \mathbf{M}V$ is the total magnetic dipole moment of the system, \mathbf{B} is the applied magnetic field. Many other text books define $dW' = V\mu_0\mathbf{H} \cdot d\mathbf{M}$. Using the definition $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$, we have

$$dW' = d(V\mu_0\mathbf{H} \cdot \mathbf{M}) - V\mu_0\mathbf{M} \cdot d\mathbf{H}$$

where the first term is a perfect derivative and it is convenient to regard it as part of internal energy. Hence, in the limit $M \ll H$, dW' reduces to our definition dW given by Eq. (17).

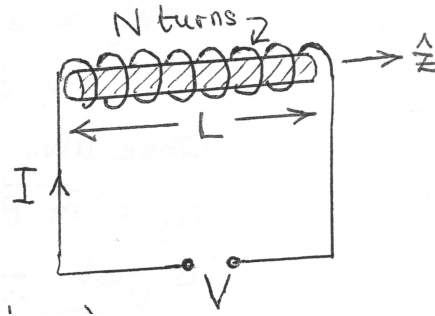


Fig. 5 A magnetizable material in a solenoid.

Note: (i) For a magnetic material the thermodynamic basic variables are (B, m, T) ; and (P, V, T) for a gas, (Γ, l, T) for a stretched wire and (σ, A, T) for a surface film. (ii) If we represent reversible process by lines on a $P - V$ plot for a fluid (or a $\Gamma - l$ plot for a stretched wire etc.) then the magnitude of the work is equal to the area under the line. Examples are shown in Fig. 6.

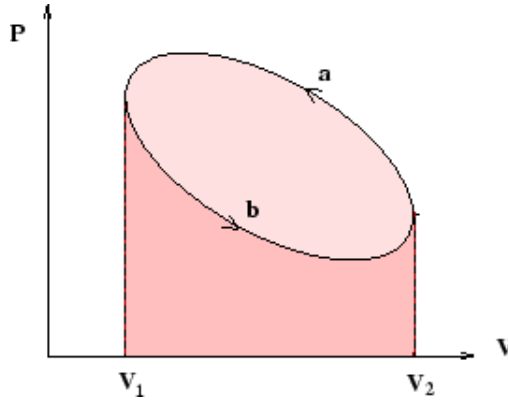


Fig. 6 A magnetizable material in a solenoid.

Work done in compressing from $V_i \rightarrow V_f$ is

$$W = - \int_{V_i}^{V_f} P dV$$

depends on path. e.g., path A : $W_A = \text{area under curve } A$; path B : $W_B = \text{area under curve } B$. The difference $W_A - W_B = - \oint_C P dV = \oint_C dW \neq 0$ where C is the cycle as shown in Fig. 6.

For examples see Example Sheets 2-4.

[Refs. (1) Mandl Chap. 1.3-1.4, (2) Bowley and Sanchez Chap. 1.6, (3) Zemansky Chap. 3]

1.7 The zeroth law of thermodynamics and temperature

After the first law we now turn to the zeroth law! The most basic concept in thermodynamics (or statistical mechanics) is *temperature*. What is it? We have an intuitive feel for it, but it is somewhat elusive. (e.g., a mass which is twice as large or a force which is twice as strong is easily understood. But a temperature twice as hot is intrinsically trickier). All attempts to quantify rest on the zeroth law:

If two bodies are each in thermal equilibrium with the third, then they are also in thermal equilibrium with each other.

This is intuitively obvious, but it now permits the definition of something measurable, called *temperature*, whereby bodies in thermal equilibrium are at the same temperature.

To measure temperature we can use any property of matter that change when heat is absorbed or emitted (e.g., resistance of a platinum wire, the volume (and hence length) of a volume of liquid mercury in a glass tube, the pressure of a given quantity of gas in a fixed volume, etc.) Such devices can be used to verify the zeroth law experimentally. They are called thermoscopes (but since no scale is yet involved, they are not yet thermometers).

A thermometer is just a calibrated thermoscope. Any thermoscope can be used to define a numerical temperature scale over some range by using two fixed points (e.g., the ice freezing point and steam boiling point of water). However, thermoscopes based on the volume of gases finally led to the notion of an *absolute scale* based on a single fixed point. This is the *ideal gas temperature scale*, measured in Kelvin (K) which is defined to be 273.16 K at the triple point of water (the single fixed point of the scale), agreed universally in 1954. (Note: The freezing (ice) point of water is some 0.01 K lower (273.15 K) in temperature than the triple point (273.16 K).) Hence, by definition

$$T = \lim_{P \rightarrow 0} \left[\frac{PV}{(PV)_{triple}} \right] \times 273.16K \quad (18)$$

in the Kelvin scale. This scale is based on the ideal gas law and low pressure ($P \rightarrow 0$) limit is taken because all real gases approach ideal behavior in that limit. The (otherwise strange and arbitrary) value of 273.16 K was simply chosen so that the new Kelvin scale matched the earlier Celsius scale as closely as possible (i.e., so that $1 \text{ K} = 1^\circ\text{C}$). Unlike earlier scales with 2 fixed points the second fixed point is dispersed with because the zero of the kelvin scale is *absolute zero* at which the pressure of an ideal gas vanishes).

Note: Later on we will meet 2 more absolute scales of temperature (one based on Carnot cycles on Chap. 2 and one based on statistical concept in Chap. 3). They will turn out to be identical to each other. However, to avoid tautology in proving they are identical temperature in the ideal gas scale will be written θ in this context, compared to temperatures T on the scale based on the Carnot cycle. We will then prove $\theta = T$. This is the reason why some books, e.g. Zemansky, used θ for temperature in the early stages. We will use T throughout, except where necessary to prove the identity $\theta = T$ later.

With such an absolute scale $k_B T$ (as in the ideal gas law) is just a measure

of thermal energy at the atomic scale; whereas RT is measure at the molar (macroscopic) scale. At room temperature $T \approx 300\text{K}$, $k_B T \approx \frac{1}{40}\text{eV}$.

[Refs.: (1) Mandl Chap. 1.2, (2) Bowley and Sanchez Chap. 1.2, (3) Zemansky Chap. 1.]

Let us move on again, to the 2nd law, Chap. 2. The basic observations that lead to 2nd law are remarkably simple: (a) When two systems are placed in thermal contact they tend to come to equilibrium with each other - the reverse process, in which they revert to their initial states, never occurs in practice; (b) Energy prefers to flow from hotter bodies to cooler bodies (and temperature is just a measure of the hotness). It is everyday experience that heat tends to flow from hot bodies to cold ones when left to their own devices (i.e., with no heat engines or heat pumps or refrigerators).

As we will see in Chap. 2 the 2nd law is built on these mundane experimental observations.