

Thermal Physics

Asaf Pe'er¹

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1. Basic definitions

We know from everyday life, that when *friction* exists in a system, it loses mechanical energy. This loss is accompanied by heating, namely, temperature increase. This allows extension of the concept of energy, to include temperature.

Nearly all substances, being solid, liquid or gases, expand when heated. This allows a relatively easy way to measure the temperature of a substance. An example is the “classical” mercury thermometer. Note that the scaling, though, is arbitrarily chosen. E.g., in the Celsius scale, 0 is defined to be the temperature of a melting ice, while 100 is defined as the temperature of boiling water. Other scales are also in use (e.g., Fahrenheit).

The most natural scale for the temperature is the **Kelvin**, which is directly associated to the kinetic motion of gases. For a gas held in a container of a fixed volume, the temperature T linearly depends on the pressure, P , $T = AP$, where A is a constant that is calibrated at *the triple point*, in which ice, water and water vapor coexist in equilibrium (the temperature of this point is 0.01° Celsius). At $T[K] = 0^\circ$, the gas is not in motion, and thus its pressure is $P = 0$. The scale of the Kelvin units is similar to that of Celsius, implying that $0^\circ[K] = -273.16^\circ[C]$. This is known as **ideal gas temperature scale**.

2. Heat capacity

Consider a (closed) system, namely a system which is thermally insulated. If a mechanical work W is done on the system, it increases the internal energy U of the system. It is found (experimentally) that a linear increase in the internal energy results in a linear increase in the temperature,

$$\frac{dW}{dt} = \frac{dU}{dt} \propto \frac{dT}{dt}. \quad (1)$$

¹Physics Dep., University College Cork

The proportionality constant is called **the heat capacity** of the system,

$$C \equiv \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta U}{\Delta T} \right). \quad (2)$$

One can define the heat capacity per unit mass, known as **specific heat capacity** by

$$c \equiv \frac{C}{M} = \frac{1}{M} \frac{dU}{dT}, \quad (3)$$

where M is the mass of the material involved.

3. Thermal conductivity and convection

As we know, heat can flow from hot areas (or bodies) into colder bodies. The two main ways in which this is done are called **conduction** and **convection**. (the third way in which a body loses energy is via **radiation** which will be discussed in the next section).

Conduction. Consider a solid bar, that on the one side is connected to a cold body of temperature T_1 , and on the other side connected to a hot body of temperature $T_2 (> T_1)$. Inside the bar, heat flows from the hot side to the cold side.

The rate of flow of heat through an area ΔA perpendicular to the flow direction x is $\Delta \mathcal{P} \propto \Delta A (\partial T / \partial x)$. Here, $\Delta \mathcal{P}$ is the power (energy per unit time), and use was made of **partial derivative**, $(\partial T / \partial x)$ to denote the change of temperature in the x direction. We used partial derivative, rather than full derivative, since the temperature may also vary in the y direction as well. The power transferred per unit area can thus be written as

$$\frac{\partial \mathcal{P}}{\partial A} = \lambda \frac{\partial T}{\partial x}, \quad (4)$$

where λ is a constant that depends on the material, and is called **thermal conductivity**. E.g., for Copper, $\lambda = 400 \text{ W m}^{-1} \text{ K}^{-1}$, for water $\lambda = 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ while for air $\lambda = 0.026 \text{ W m}^{-1} \text{ K}^{-1}$. Since $\lambda(\text{water}) > \lambda(\text{air})$, it is a bad idea to get into water in cold weather !.

Equation 4 can also be written in a different form. If the cross-sectional area of the bar is A , since $\mathcal{P} = \partial Q / \partial t$ (Q is the amount of heat), one can write

$$\frac{\partial Q}{\partial t} = \lambda A \frac{\partial T}{\partial x}, \quad (5)$$

Convection. Consider a hot solid object surrounded by colder fluid, say air. The object will heat the fluid next to it, causing the fluid to rise and be replaced by colder fluid.

Thus, currents, which are known as **convection currents** are set up in the fluid. These essentially transport heat energy from the object, thus cooling it.

A solid body surrounded by fluids thus loses its energy via both *conduction and convection*. However, since the thermal conductivity of fluids is often small, often *convection* is the most efficient way. We always feel colder in a wind !.

In nearly all cases, a thin layer of fluid will tend to adhere the surface of the solid body. This layer is called **boundary layer**, through which heat is conducted before being carried away by convection currents.

A good model for heat conduction is that within the boundary layer of thickness b the heat is carried by conduction, while at larger distances nearly 100% of the heat is carried by convection. Thus, the power leaving a unit surface area can be written as

$$\frac{\partial \mathcal{P}}{\partial A} = \frac{\lambda}{b}(T - T_A), \quad (6)$$

where T is the body's temperature and T_A is the temperature of the fluid outside the boundary layer. The rate of heat energy loss of a body of surface area A is thus

$$\mathcal{P} \equiv \frac{\partial Q}{\partial t} = \frac{\lambda}{b}A(T - T_A). \quad (7)$$

The quantity $h \equiv \lambda/b$ is called **heat transfer coefficient**.

Cooling which obeys Equation 7 is called **Newtonian cooling**. For air, the typical boundary layer is ≈ 1 mm. In order to decrease heat loss through a window, e.g., a double glazing glass produces a much thicker layer of still air trapped between the two glasses, significantly reducing the heat losses from a room.

4. Thermal radiation

While an isolated body in vacuum cannot lose energy by convection or conduction, it can still lose energy by **radiation**. Examples are the heat we feel from a fire, or the heat from the sun.

The power transferred per unit surface area of a body of surface temperature T by radiation is given by the **Stefan-Boltzmann law**,

$$\frac{d\mathcal{P}}{dA} = \epsilon\sigma T^4. \quad (8)$$

Here, $0 < \epsilon < 1$ is a dimensionless number which is called the **emissivity**, that depends on the properties of the radiating surface, while $\sigma = 2\pi^5 k^4 / 15c^2 h^3 = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is a fundamental constant of nature, known as **Stefan-Boltzmann constant**.

4.1. Blackbody radiation

In 1859, Gustav **Kirchoff** showed that the **absorption** of thermal radiation by a body is the exact reverse of the **emission** process. Thus, polished surface (e.g., mirror), for which $\epsilon \rightarrow 0$, reflects the radiation rather than absorbing it. On the other extreme, a very efficient emitter ($\epsilon \rightarrow 1$) is also a very efficient absorber. For $\epsilon = 1$, all radiation that falls on the body will be absorbed. The body thus appears black, and is called **blackbody**.

The term, though, is misleading, since an efficient absorber is also an efficient emitter. While a body at a given temperature emits at all wavelength, as was shown by **Wien**, the peak emission frequency linearly proportional to the body's temperature, $\nu_{\max} \propto T$ (this is known as *Wien's displacement law*). Thus, while relatively cold bodies emit (mainly) at the infra-red (and thus remain “black”) as bodies get warmer, they eventually emit at observed wavelength. For example bodies at temperature of $\sim 800 - 1000^\circ$ Kelvin emit at red (e.g., burned wood in a fire). At about 6000° Kelvin the emission is yellow; see the sun.

Of course, a body exchanges heat with its surrounding, the net radiated energy is

$$\frac{dQ}{dt} = \epsilon\sigma A(T^4 - T_s^4), \quad (9)$$

where T_s is the temperature of the surroundings.

5. Thermal expansion

As materials are heated they expand. While in solid the expansion is often small, in gases it can be considerable. It is found experimentally that $\Delta V/V \propto \Delta T$. Since a change in pressure also changes the volume, in order to measure the expansion due to heat one needs to keep the pressure fixed. One can thus define the **cubic expansion coefficient**,

$$\alpha_V \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p=const}. \quad (10)$$

Note that generally, $\alpha_V = \alpha_V(T)$. Similarly, one can define the **linear expansion coefficient**,

$$\alpha_L \equiv \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_{p=const}, \quad (11)$$

where L is the linear dimension (of a solid). For *isotropic* solids, since $\alpha \ll 1$, $\alpha_V = 3\alpha_L$.

6. The first law of thermodynamics

When energy is added to a system, it contributes to increasing both to the *internal* energy, ΔU and to do *mechanical work* as the body expands against an external force or pressure, $\Delta W = p\Delta V$. Thus, denoting by ΔQ the amount of heat added to a thermal system, one can write

$$\Delta Q = \Delta U + \Delta W = \Delta U + p\Delta V. \quad (12)$$

Equation 12 represents energy conservation, where energy can appear both as mechanical energy and thermal energy. It is known as **the first law of thermodynamics**.

The concept of heat capacity introduced in §2 needs to be generalized to include situations in which the system can expand. The quantity defined in §2 was defined for constant volume, and is thus the **heat capacity at constant volume**, which is (re-)defined by

$$C_V \equiv \left(\lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} \right)_{V=const} = \left(\frac{\partial U}{\partial T} \right)_{V=const} \quad (13)$$

Note that **the thermodynamic state of a system depends on the values of three variables: p , T and V** , and thus we must specify which variable changes and which is held constant when a specific process takes place. Hence the use of partial derivation in Equation 13.

Similarly, we can define the **heat capacity at constant pressure**,

$$C_p \equiv \left(\lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} \right)_{p=const}. \quad (14)$$

Using Equation 12 and taking the limit $\Delta T \rightarrow 0$, we find

$$\begin{aligned} \left(\frac{\Delta Q}{\Delta T} \right)_{p=const} &= \left(\frac{\Delta U}{\Delta T} \right)_{p=const} + p \left(\frac{\Delta V}{\Delta T} \right)_{p=const} \\ C_p &= \left(\frac{\partial U}{\partial T} \right)_{p=const} + p \left(\frac{\partial V}{\partial T} \right)_{p=const}. \end{aligned} \quad (15)$$

If the internal energy depends on the temperature only (and NOT on V or p), then

$$\left(\frac{\partial U}{\partial T} \right)_{p=const} = \frac{\partial U}{\partial T} = \left(\frac{\partial U}{\partial T} \right)_{V=const} = C_V, \quad (16)$$

and one gets

$$C_p = C_V + p \left(\frac{\partial V}{\partial T} \right)_{p=const} = C_V + pV\alpha_V \quad (17)$$

(see Equation 10).

For most solids or liquids, at atmospheric pressure $C_p \approx C_V$. However, for gases, the distinction is very important.

6.1. Enthalpy

When treating processes in which the pressure is kept constant, it is often very useful to work with a thermodynamic quantity called **enthalpy**, which is defined by

$$H \equiv U + pV. \quad (18)$$

At constant pressure, the first law of thermodynamics (Equation 12) can be written as $\Delta Q = \Delta U + p\Delta V = \Delta(U + pV) = \Delta H$, from which

$$C_p = \left(\frac{\partial H}{\partial T} \right)_{p=const}. \quad (19)$$

Note that enthalpy has similar units to energy.

6.2. Phase change and latent heat.

When a solid is being heated, its temperature increases monotonically (although not necessarily *linearly*!). Once the solid gets into a certain temperature, known as **the melting temperature**, T_M , if heat is continually added to the system, the solid will not increase its temperature anymore. Rather, it will start melting. Only after the solid completely melted and became liquid, continuous heating will result in further increase in the temperature (see Figure 1).

A melting process, and similarly a boiling process in which a liquid becomes gaseous, are examples of **phase transition**. The amount of energy required to melt a body is known as **latent heat of fusion**, and denoted by L_F . Similarly, there is **latent heat of evaporation**, L_V . It is often easier to work with **specific latent heat**, which is the latent heat per unit mass. For water, e.g., $l_F = L_F/M = 3.3 \times 10^5 \text{ J kg}^{-1}$ and $l_V = 2.3 \times 10^6 \text{ J kg}^{-1}$.

7. Equation of state of an ideal gas

The state of any system is determined by the values of three parameters: p , V and T . We saw that in the limit of low pressure, all gases obey Boyle's law, $pV = \text{const}$ (at a fixed temperature). Furthermore, we saw that for a gas held at a fixed volume, $T \propto p$ (see §1). Combined together, we find that for a fixed mass of an ideal gas,

$$pV = KT, \quad (20)$$

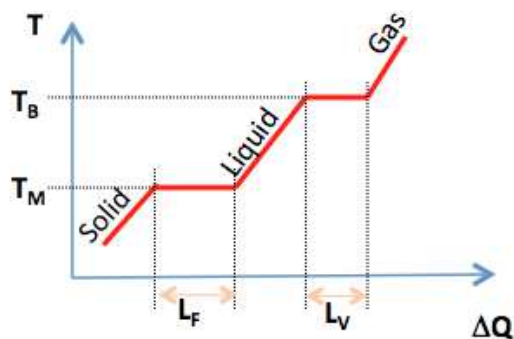


Fig. 1.— As a solid is heated, its temperature increases, until it reaches the melting point. Further increase in the heating results in melting, rather than increase in the temperature. The heat needed is called *latent heat*.

where K is constant. This equation is known as **the equation of state of an ideal gas**, and provides a good description of the behavior of all gases in the limit $p \rightarrow 0$.

Using the equation of state (Equation 20), we can write the cubic expansion coefficient (Equation 10) as

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p=\text{const}} = \frac{1}{V} \left(\frac{\partial}{\partial T} \left(\frac{KT}{p} \right) \right)_{p=\text{const}} = \frac{1}{V} \frac{K}{p} = \frac{1}{T} \quad (21)$$

putting this result in Equation 17, we can re-write the equation of state as

$$pV = (C_p - C_V)T \quad (22)$$

8. Thermodynamic processes

The state of any thermodynamic system is determined by three variables: p , V and T . The equation of state (Equations 20, 22) connects these three variables: for example, if p and T are known, then V is determined, etc. Thus, only two can be treated as independent variables. We can take, e.g., p and V as independent variables. For every value of p and V , T is determined.

8.1. Isothermal processes

We can present the state of a system in a $p - V$ diagram (see Figure 2). For every point in the $p - V$ space there is a corresponding temperature. We can draw curves of fixed temperature on this plot. These are known as **isotherms**. Consider a process that takes place at a constant temperature. The system changes its location on the $p - V$ diagram, from point A to point B , *along an isotherm*. Such a process is called **isothermal process**.

Example. Consider an ideal gas expanding isothermally (at temperature T_0) from volume V_1 to volume V_2 . The mechanical work done by the gas is

$$W_{A \rightarrow B} = \int_A^B p dV = \int_{V_1}^{V_2} \frac{KT_0}{V} dV = KT_0 \int_{V_1}^{V_2} \frac{1}{V} dV = KT_0 \log \left(\frac{V_2}{V_1} \right). \quad (23)$$

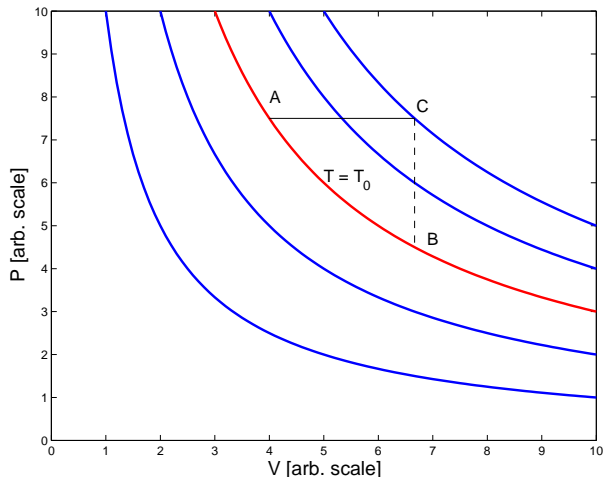


Fig. 2.— pV diagram shows curves of constant temperature.

8.2. Isobaric processes

Isobaric processes are processes that take place at constant pressure (e.g., the line $A-C$ in Figure 2). In such a process, the gas expands from V_1 to V_2 when the pressure is kept constant, and so the end temperature T_2 must be higher than the initial temperature T_1 . Clearly, in order for such a process to occur, heat must be supplied to the system.

The mechanical work done in Isobaric process is

$$W_{A \rightarrow C} = \int_A^C p dV = p_1 \int_{V_1}^{V_2} dV = p_1(V_2 - V_1) \quad (24)$$

8.3. Adiabatic process

A process that occurs without any energy exchange with the surroundings is called **adiabatic process**. Such processes can occur in closed (thermally isolated) systems, or if the processes are so rapid that there is no time for the external system to exchange energy with the environment. In such processes, thus $\Delta Q = 0$. Using Equations 12, 13, we find that in adiabatic process

$$\Delta Q = 0 = \Delta U + p\Delta V = C_V\Delta T + p\Delta V \rightarrow \Delta T = -\frac{p}{C_V}\Delta V. \quad (25)$$

Differentiating the Equation of state of an ideal gas (Equation 22) using Equation 25, one finds

$$\begin{aligned} \Delta(pV) &= (C_p - C_V)\Delta T = -\frac{C_p - C_V}{C_V}p(\Delta V) \\ p(\Delta V) + V(\Delta p) &= -\frac{C_p}{C_V}p(\Delta V) + p(\Delta V) \\ V\Delta p + \frac{C_p}{C_V}p(\Delta V) &= 0 \\ \frac{\Delta p}{p} + \frac{C_p}{C_V}\frac{\Delta V}{V} &= 0 \\ \int \frac{dp}{p} + \frac{C_p}{C_V}\int \frac{dV}{V} &= 0 \\ \log p + \frac{C_p}{C_V}\log V &= \text{Const.} \end{aligned} \quad (26)$$

It is convenient to define

$$\gamma \equiv \frac{C_p}{C_V}, \quad (27)$$

and write Equation 26 in the form

$$pV^\gamma = \text{Const.} \quad (28)$$

which is satisfied for any adiabatic process. Adiabatic curves are shown in Figure 3 by dashed (green) lines. Since $\gamma > 1$, (for non-relativistic, mono-atomic ideal gas, $\gamma = 5/3$ while for relativistic ideal gas $\gamma = 4/3$), in adiabatic expansion a system ends up at a lower temperature; heat was converted to mechanical energy of expansion.

Since in ideal gas $pV/T = \text{Const}$, Equation 28 can also be written as $TV^{\gamma-1} = \text{Const}$.

The mechanical work done in adiabatic expansion of an ideal gas from volume V_1 to V_2 (the dark-green path $A - D$ in Figure 3) is

$$W_{A \rightarrow D} = \int_A^D pdV = \int_{V_1}^{V_2} \frac{\text{const}}{V^\gamma} dV = \text{const} \left(\frac{V_2^{1-\gamma}}{1-\gamma} - \frac{V_1^{1-\gamma}}{1-\gamma} \right) = \frac{1}{1-\gamma} (p_2V_2 - p_1V_1) \quad (29)$$

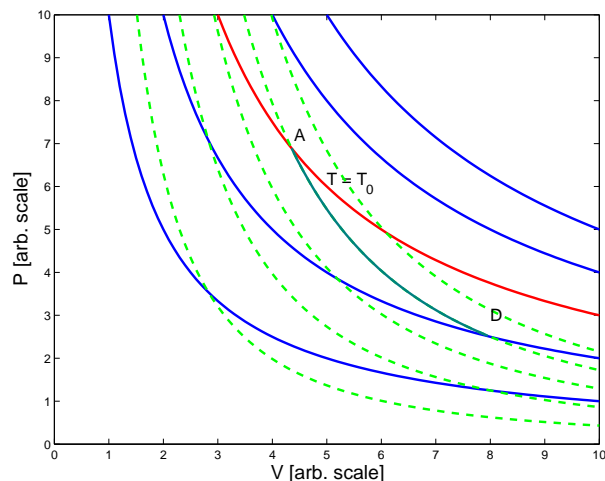


Fig. 3.— Adiabatic curves in a pV diagram are shown by dashed (green) lines. Solid lines represent curves of constant temperature.

8.4. Free expansion (also: adiabatic free expansion)

Consider an isolated container divided into two. In one side, of volume V_1 there is a gas, held there by a partition that can be removed. At a certain time the partition is removed. The gas expands freely into the vacuum until it ultimately sets into new equilibrium filling the entire container.

During the expansion, a state of thermal equilibrium does not exist: for example, the pressure may not be identical at all points. Therefore, there is no path in the $p - V$ diagram which the gas takes. This process is **irreversible**.

As the gas expands into vacuum, there is no external pressure acting upon it, and thus there is no mechanical work done by the gas and $\Delta W = 0$. Since the system is insulated, $\Delta Q = 0$, and thus, using the first law of thermodynamics $\Delta U = 0$. It was checked experimentally (first by Joule) that the gas temperature remains constant. Since the pressure and volume change in this process, this means that **in ideal gas, the internal energy depends only on the temperature**, $U = U(T)$.

Note the following. While in *adiabatic* expansion, the temperature drops as $T_{final} = T_{initial} \times (V_{final}/V_{initial})^{1-\gamma}$ and $\gamma > 1$, in *free expansion*, the temperature is fixed, although there is no heat exchange ($\Delta Q = 0$). The reason is that adiabatic process is **reversible**: the expansion is done by “pushing the walls”, namely converting the internal energy (temperature) to mechanical work. In a free expansion, on the other hand, no work is done, and the

process is **irreversible**.

9. The Carnot cycle

When a thermodynamic system is moved from state A to state B , the mechanical work done in the process is $W_{A-B} = \int_A^B p dV$. If the process is cyclic, namely the system returns to state A at the end then

$$W_{cycle} = \oint p dV = \int_A^B p dV + \int_B^A p dV = \int_A^B p dV - \int_A^B p dV. \quad (30)$$

This is equal to the area enclosed within the cycle in the $p - V$ diagram.

A **Carnot cycle** is an important example of a cyclic process, in which an ideal gas goes through four successive reversible stages as follows:

1. $A \rightarrow B$: isothermal expansion to volume V_B at constant temperature T_2 .
2. $B \rightarrow C$: adiabatic expansion to volume V_C , accompanied by temperature drop.
3. $C \rightarrow D$: isothermal compression to volume V_D at constant temperature, T_1 ;
4. $D \rightarrow A$: adiabatic compression to the original state of the system.

It can be shown that Carnot cycle is the most efficient way of converting thermal energy into work, or, conversely, creating a temperature difference (e.g., in a refrigerator) by doing a given amount of work.

As a result of the processes, a net amount of mechanical work is done (equal to the shaded area in Figure 4). First, an amount ΔQ_2 of heat is absorbed from the surrounding at temperature T_2 during the process $A - B$. An amount of energy ΔQ_1 is deposited to the environment at temperature T_1 during the isothermal compression $C - D$. Since the system ends up at the same state as it started with, there is no net change of internal energy, and thus $\Delta Q_2 - \Delta Q_1 = \Delta W$.

The over all effect is that mechanical work is done by taking energy from the environment at high temperature (T_2) and deposit a smaller amount of energy into the reservoir at a lower temperature T_1 . Such a device is called a **heat engine**. The reverse process, in which mechanical energy is used to take energy out of the low temperature reservoir and deposit in the high temperature reservoir is also possible. The machine is called a **refrigerator**.

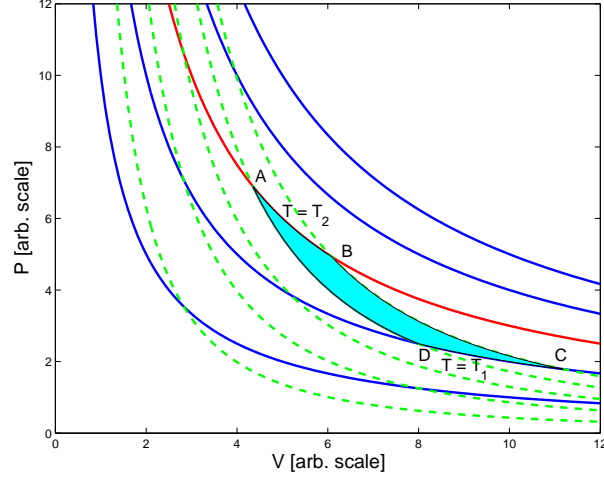


Fig. 4.— A Carnot cycle is composed of isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression. The work done is equal to the shaded (light blue) area in the $p - V$ diagram.

The efficiency of a heat engine is defined as the ratio of the mechanical work to the heat energy withdrawn from the higher temperature reservoir,

$$\eta \equiv \frac{\Delta W}{\Delta Q_2} = \frac{\Delta Q_2 - \Delta Q_1}{\Delta Q_2} = 1 - \frac{\Delta Q_1}{\Delta Q_2}. \quad (31)$$

In a Carnot cycle, we know that (see Equation 23), $|\Delta Q_2| = kT_2 \log(V_B/V_A)$, $|\Delta Q_1| = kT_1 \log(V_C/V_D)$. For the adiabatic processes, using the discussion below Equation 28, $T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1}$ (process $B - C$), and $T_1 V_D^{\gamma-1} = T_2 V_A^{\gamma-1}$ (process $D - A$). Thus,

$$\left(\frac{V_D}{V_A}\right)^{\gamma-1} = \frac{T_2}{T_1} = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D} \quad (32)$$

We therefore find

$$\frac{|\Delta Q_1|}{|\Delta Q_2|} = \frac{kT_1 \log(V_C/V_D)}{kT_2 \log(V_B/V_A)} = \frac{T_1}{T_2}, \quad (33)$$

and thus the efficiency of a Carnot cycle is $1 - T_1/T_2$.

We further see that the amount of energy put in a reservoir during an isothermal process, ΔQ , is linearly proportional to the temperature T of the reservoir. The quantity ΔQ can therefore be used to measure the temperature. The scale - known as Kelvin - is *identical* to the ideal gas scale. $1^\circ \text{ Kelvin} = 1/273.16$ of the temperature of the triple point of water.

10. Entropy and the second law of thermodynamics

Every **reversible** cycle can be thought of being composed of very large number of Carnot cycles. For each of these cycles, Equation 33 holds. Thus, overall, for any reversible cycle we can write

$$\sum_i \frac{\Delta Q_i}{T_i} = 0, \quad (34)$$

with the convention that ΔQ_i is positive if heat is added to the system, and negative if heat is taken away from the system.

We further note that generally, $\int_A^B dQ$ depends on the **path** between A and B . Thus, Q (as well as W) cannot be treated as a thermodynamic variable. However, for **reversible** process, the quantity $\int_A^B d'Q/T$ is **path-independent**. We can therefore **define** a new thermodynamic quantity, called **entropy** of a system by

$$\Delta S \equiv \frac{\Delta Q}{T} \quad (35)$$

(note that we really define the difference in entropy; for full definition of entropy, we need the third law of thermodynamics). The SI unit of entropy is JK^{-1} .

In *adiabatic process*, $\Delta Q = 0$, hence $\Delta S = 0$. Indeed, we can re-define an adiabatic process as a process which takes place at constant entropy. Using the entropy, one can write the first law of thermodynamics (Equation 12) as

$$T\Delta S = \Delta U + p\Delta V \quad (36)$$

Equation 36 is known as **the fundamental thermodynamic relation**.

Examples

1. Change in entropy in an expansion of ideal gas: When an ideal gas expands from point A (volume V_1) to point B (volume V_2), its entropy is changed according to:

$$\begin{aligned} \Delta S = S_B - S_A = \int_A^B \frac{d'Q}{T} &= \int_{V_1}^{V_2} \frac{dU}{T} + \int_{V_1}^{V_2} \frac{pdV}{T} \\ &= C_V \int_{T_1}^{T_2} \frac{dT}{T} + (C_p - C_V) \int_{V_1}^{V_2} \frac{dV}{V} \\ &= C_V \log\left(\frac{T_2}{T_1}\right) + (C_p - C_V) \log\left(\frac{V_2}{V_1}\right), \end{aligned} \quad (37)$$

where in the second line we have used Equations 13 and the Equation of state (Equation 22).

By definition, in *adiabatic expansion*, $\Delta S = 0$.

2. Change of entropy in phase transition:

$$\Delta S = \int \frac{d'Q}{T} = \frac{L}{T_t}, \quad (38)$$

where L is the latent heat, and T_t is the transition temperature.

10.1. The second law of thermodynamics

This is an observational law of fundamental importance. It states that

For an isolated thermodynamic system, $\Delta S \geq 0$.

The equality sign holds only for reversible processes. This law defines the **arrow of time**. As entropy must increase in non-reversible process, this discriminates between 'early' and 'late': For example, heat flows from hot region to cold region, but not vice versa; A broken glass does not 'fix' itself; etc.

Example. Consider the following **irreversible** process: two metal blocks of mass m and heat capacity c having temperatures T_1 and T_2 are held in a box which is thermally insulated from the surrounding. When the two blocks are brought into contact, heat flows from the hot block to the cold block, until both blocks reach the same temperature, $(T_1 + T_2)/2$.

The change in entropy in the process is

$$\begin{aligned} \Delta S &= \int_{T_1}^T \frac{d'Q}{T} + \int_{T_2}^T \frac{d'Q}{T} \\ &= mc \int_{T_1}^T \frac{dT}{T} + mc \int_{T_2}^T \frac{dT}{T} \\ &= mc \log \left(\frac{T}{T_1} \right) + mc \log \left(\frac{T}{T_2} \right) \\ &= mc \log \left(\frac{T^2}{T_1 T_2} \right) \\ &= 2mc \log \left(\frac{(T_1 + T_2)/2}{\sqrt{T_1 T_2}} \right) \end{aligned} \quad (39)$$

Since $(T_1 + T_2)^2 = (T_1 - T_2)^2 + 4T_1 T_2 > 4T_1 T_2$, one finds that $(T_1 + T_2)/(2\sqrt{T_1 T_2}) > 1$, hence the logarithm in Equation 39 is larger than 0, and $\Delta S > 0$. Entropy is thus **gained** in the process.

11. The Helmholtz and Gibbs functions

As we saw in §7, the state of any system is determined by the values of three parameters: p , V and T . These, however, are connected by the Equation of state, and so only 2 variables are independent.

In general, any thermodynamic function can be considered as a function of any two of these variables, e.g. $f = f(p, V)$ or $f = f(p, T)$, etc. If $f = f(p, V)$, a small change in either V or p necessarily leads to a change in f via

$$\Delta f = \frac{\partial f}{\partial p} \Delta p + \frac{\partial f}{\partial V} \Delta V \quad (40)$$

Similar statements can be made if $f = f(p, T)$ or $f = f(V, T)$. One can thus define two useful thermodynamic functions. The first is **Helmholtz function** (or **free energy function**), defined by

$$F \equiv U - TS \quad (41)$$

Thus, $\Delta F = \Delta U - \Delta(TS) = \Delta U - T\Delta S - S\Delta T$. Using the fundamental thermodynamic relation (see Equation 36), this can be written as

$$\begin{aligned} \Delta F &= \Delta U - (\Delta U + p\Delta V) - S\Delta T \\ &= -p\Delta V - S\Delta T. \end{aligned} \quad (42)$$

This function is thus very useful in situations in which the volume and the temperature change.

Another function is the **Gibbs function** (or **free enthalpy**), defined by

$$G \equiv H - TS, \quad (43)$$

where $H = U + pV$ is the enthalpy, defined in §6.1

Similarly, $\Delta G = \Delta U + \Delta(pV) - \Delta(TS) = \Delta U + p\Delta V + V\Delta p - T\Delta S - S\Delta T$, which, when using the fundamental thermodynamic relation (Equation 36) one gets

$$\Delta G = V\Delta p - S\Delta T. \quad (44)$$

This function is thus convenient when dealing with systems in which the pressure and the temperature change, as is typical for many chemical reactions, as well as phase transition.

12. Microscopic interpretation of the temperature

In deriving the microscopic theory of gases, we saw that $pV = \frac{2}{3}N \langle \frac{1}{2}mv^2 \rangle$, where N is the number of molecules of mass m , and $\langle \frac{1}{2}mv^2 \rangle$ is the average kinetic energy per molecule. Comparing with the equation of state for an ideal gas (Equation 20), $pV = KT$, we find

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2} \left(\frac{K}{N} \right) T = \frac{3}{2}kT \quad (45)$$

The constant k is known as **Boltzmann's constant**, and is equal to $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$. This constant links the macroscopic world to the microscopic one: it enables to define the temperature in terms of kinetic energy of the molecules.

The Equation of state (Eq. 20) takes the form

$$pV = NkT \quad (46)$$

This form also enables understanding the temperature scale, as a temperature is linearly related to the (average) kinetic energy per molecule.

A measure of the *average speed* of the molecules is given by the **root mean square (rms)** of the velocity, defined by

$$v_{rms} \equiv \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}. \quad (47)$$

For example, the average velocity of oxygen molecules (O_2 , 8 protons and 8 neutrons in an atom) at room temperature is $\sqrt{\frac{3 \times (1.38 \times 10^{-23}) \times 300}{(32) \times (1.67 \times 10^{-27})}} \approx 480 \text{ m s}^{-1}$.

Internal energy is now understood as the total mechanical energy of the system of N molecules,

$$U \equiv N \left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}NkT \quad (48)$$

Thus, heat energy is interpreted as mechanical energy associated with the random motion of the molecules.

Heat Capacity. Heat capacity at a constant volume of an ideal gas is

$$C_V = \frac{dU}{dT} = \frac{3}{2}Nk. \quad (49)$$

Using Equation 22 ($C_p - C_V = pV/T$) and Equation 46, one finds

$$C_p = \frac{5}{2}Nk. \quad (50)$$

Molar gas constant. One can define the molar gas constant by $R \equiv N_A k$, and write the equation of state (Equation 46) in the form $pV_m = RT$, where $V_m \equiv V/n$ is the molar volume, and n is the number of moles.

12.1. Microscopic interpretation of entropy

Consider a gas filling part of a container, held by a partition. When the partition is removed, the gas expands and fills the entire container; this is an irreversible process and the entropy is increased by the process. The system can be thought of as evolving from a somewhat ordered configuration to a less ordered one.

This leads to the interpretation of entropy as a quantity measuring the **degree of disorder** in a system. A system can spontaneously evolve from an ordered to a less-ordered state, but not vice versa (without external intervention).