Thermodynamics

Course Notes

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Contents

1 Basic Concepts

1.1 Systems and Surroundings

The system is the entity we are interested in, while the surroundings are the external environment that the system can interact with.

Type of Systems	Exchange of...		Constant Parameters	Ensemble
	Mass	Energy		
Isolated system	No	No	N, V, U	Microcanonical ensemble
Closed system	No	Yes	N, V, T	Canonical ensemble
Open system	Yes	Yes	μ, V, T	Grand canonical ensemble

1.2 Variables

- Extensive variables scale with system size (U, V, N, etc.);

  For many extensive quantities we can define a **specific value** through dividing by the amount of material. The most perplexing one may be the specific volume, which is actually the reciprocal of density.

- Intensive variables are independent of the amount of material (p, $\mathbf{B}$, etc.).

  Intensive state variables are uniform throughout the system for a system in thermodynamic equilibrium, but may not be when the system is not in equilibrium.

1.3 Equilibrium

The term **thermodynamic equilibrium** summarizes the following three equilibria:

- Mechanical equilibrium: balance of forces;

- Chemical equilibrium;

- Thermal equilibrium: temperature is well-defined for the system.

1.4 Equation of State

The equation of state constrains the possible values of state variables in a system. For an ideal gas,

$$pV = Nk_BT. \tag{1}$$

2 Common State Variables

2.1 Temperature: Zeroth Law

The intensive variable temperature is only defined for the system when it is in thermal equilibrium ($\neq$ thermodynamic equilibrium).

> **The Zeroth Law of Thermodynamics**
>
> If two systems A and B are both in thermal equilibrium with a third system C, then they must be in thermal equilibrium with each other. The concept of temperature follows.
> The zeroth law does not itself define a temperature scale.

2.2 Internal Energy: First Law

Internal energy is the energy stored inside the system. As an extensive variable, U is always well defined. U does not include the kinetic energy of the system itself. For an ideal monatomic gas with N molecules,

$$U = \frac{3}{2}Nk_BT \tag{2}$$

only depends on T. For non-ideal gases, U depends on both V and T.

2.3 Entropy: Second Law

The extensive variable entropy is always defined. It relates to the degree of disorder at the microscopic scale. Microscopically, the greater the number of possible microstates the system could be in, the greater the entropy. A system where the microscopic state is completely defined and unique has an entropy of zero. Macroscopically, we associate entropy with the tendency of energy and particles to disperse through random motion. We observe this as an asymmetry in nature: total entropy never decreases.

> **Macroscopic Definition of Entropy**
>
> We define the change in entropy of a system in terms of **reversible** heat flow:
>
> $$\Delta Q = T\Delta S \tag{3}$$
>
> for heat ΔQ supplied to a system in thermodynamic equilibrium at temperature T.

Note that this definition implies thermal equilibrium throughout: this must be an **isothermal** process. Later we shall also see that the process should also be **quasistatic**.

3 First Law of Thermodynamics

> **The First Law of Thermodynamics**
>
> The first law of thermodynamics is essentially talking about conservation of energy:
>
> $$\Delta U = Q - W, \tag{4}$$
>
> where Q is the heat into the system and W is the work done by the system.
>
> Written in differential form,
>
> $$\mathrm{d}U = \delta Q - \delta W, \tag{5}$$
>
> where the symbol δ (imperfect differential) is used to indicate that Q and W are path dependent: they are not state variables after all.

Variables	Path Dependence	Differentials
State variables	No	Perfect / exact (d)
Process variables	Yes	Imperfect (δ)

> Work is a consequence of **ordered motion** or change against macroscopic forces.
>
> $$\Delta W = \mathbf{F} \cdot \Delta \mathbf{r} \quad \Rightarrow \quad \delta W = p \, \mathrm{d}V. \tag{6}$$
>
> Heat is thermal energy <u>in transit</u>. It is a consequence of energy transfer by **random motion** at the microscopic level.

4 Compression and Expansion of Ideal Gases

A closed system has two independent variables. The equilibrium states can be represented on either a pV diagram or a TS diagram.

Not all states can be represented on the diagrams. For example, when not in thermal equilibrium, T is then ill defined. However, if we apply changes sufficiently slowly such that T and p remain equalized, then we can represent the system by equilibrium states throughout the process. This leads to the concept of quasistatic processes.

4.1 Quasistatic & Reversible Processes

A quasistatic process is one in which the system is in thermodynamic equilibrium during the entire process. Only for quasistatic processes can we claim that

$$\delta W = p \, \mathrm{d}V \qquad \text{and} \qquad \delta Q = T \, \mathrm{d}S \,,$$

as the intensive variables get ill defined when not in thermodynamic equilibrium.

> A process is quasistatic if at every point in the process the system is in **equilibrium with itself**. A process is reversible if it is quasistatic and at every point in the process the system is in **equilibrium with its surroundings**.

To summarize,

Equation	Comments
$\mathrm{d}U = \delta Q - \delta W$	Always true
$\delta Q = T \, \mathrm{d}S$	Only true for reversible changes
$\delta W = p \, \mathrm{d}V$	Only true for reversible changes
$\mathrm{d}U = T \, \mathrm{d}S - p \, \mathrm{d}V$	Always true

For irreversible changes,

$$\delta W \leq p \, \mathrm{d}V \qquad \text{and} \qquad \delta Q \leq T \, \mathrm{d}S \,,$$

and magically, they miss by exactly the same amount and make a triumph of the **fundamental equation of thermodynamics**:

$$\mathrm{d}U = T \, \mathrm{d}S - p \, \mathrm{d}V \,. \tag{7}$$

4.2   Thermodynamic Processes

Firstly, let us introduce ourselves to the **heat capacity**:

$$C \equiv \frac{\delta Q}{\mathrm{d}T},$$

(8)

where the expression itself implies this is a path dependent quantity.

The following table summarizes four basic thermodynamic processes:

Process	Property
Isothermal	Constant T ($\Delta U = 0$)
Isochoric	Constant V ($W = 0$)
Isobaric	Constant p
Isentropic (Adiabatic & reversible)	Constant S ($Q = 0$)

- For ideal gases we see

$$U = \frac{f}{2} N k_B T,$$

(9)

so the constant volume heat capacity is

$$C_V = \frac{f}{2} N k_B.$$

(10)

- Using the equation of state once, we see the constant pressure heat capacity:

$$C_p = C_V + N k_B.$$

(11)

- Adiabatic index: heat capacity ratio

$$\gamma = \frac{C_p}{C_V} = 1 + \frac{2}{f}$$

(12)

For adiabatic processes, we shall notice that

$$\mathrm{d}U = C_V \, \mathrm{d}T = -p \, \mathrm{d}V = -(C_p - C_V)\frac{T}{V} \, \mathrm{d}V \,,$$

and this gives the <u>adiabatic relations</u>:

$$\begin{cases} TV^{\gamma-1} = \text{const.} \\ pV^{\gamma} = \text{const.} \\ p^{1-\gamma}T^{\gamma} = \text{const.} \end{cases}$$

(13)

5 Independent Variables and Differentials

Partial differentiation sucks, doesn't it? In thermodynamics we apply an ingenious notation where the variables being kept constant are included as a subscript of the partial derivative. Owing to this extensive use of partial derivatives in thermodynamics, physicists had to work out precious conclusions regarding partial differentiation that may come in handy and in exams.

From ideal gas equation,

$$pV = Nk_BT, \tag{14}$$

we see how the "thruple" p, V, and T depends on each other. To be more general, consider the three variables x, y, and z where each one depends on the other two.

$$x(y,z)$$

$$y(x,z)$$

$$z(x,y)$$
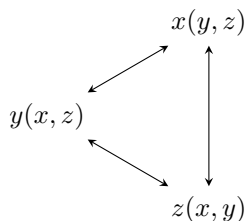
5.1 The Reciprocal Rule

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}, \quad \text{or} \quad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1. \tag{15}$$

5.2 The Cyclic Rule

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{16}$$

Sometimes we may want to combine the cyclic rule with reciprocal rule:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x. \tag{17}$$

5.3 The Compound Rule

The compound rule says

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial A}\right)_B \left(\frac{\partial A}{\partial y}\right)_z + \left(\frac{\partial x}{\partial B}\right)_A \left(\frac{\partial B}{\partial y}\right)_z. \tag{18}$$

To see why that is the case, consider the following diagram.

We should consider two special cases where B is y or z.

- $B = y$:
$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial A}\right)_y \left(\frac{\partial A}{\partial y}\right)_z + \left(\frac{\partial x}{\partial y}\right)_A. \tag{19}$$
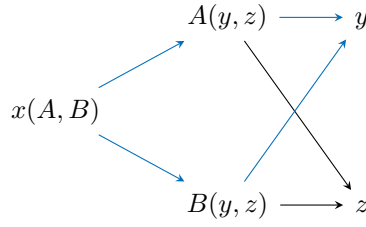
- $B = z$:
$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial A}\right)_z \left(\frac{\partial A}{\partial y}\right)_z. \tag{20}$$

5.4 The Mixed Derivatives Rule: Maxwell Relations

If the mixed derivatives are continuous, then the following must hold:

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}. \tag{21}$$

In thermodynamics, this technique leads to Maxwell Relations, where abstract partial derivatives are converted to more measurable ones. Firstly, let us meet the four thermodynamic potentials. By the fundamental equation of thermodynamics, we see

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \qquad \Rightarrow \qquad U = U(S, V), \tag{22}$$

where S and V are called natural variables of the internal energy.

By appropriate algebraic manipulations we can see thermodynamic potentials with different natural variables:

	Expression	Natural Variables	Differential
Internal Energy	U	S, V	$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$
Enthalpy	$H = U + pV$	S, p	$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p$
Helmholtz Function	$F = U - TS$	T, V	$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$
Gibbs Function	$G = U + pV - TS$	T, p	$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$

> **Maxwell Relations**
>
> Through the mixed derivatives we should find the following equations with ease:
>
> $$\left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$$
> $$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$
> $$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad (23)$$
> $$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$
>
> Every thermodynamic potential generates one relation, and one can see it by looking at the independent variables. One mnemonic device here is to find p, S, T, V ("positive") in order.

For generalized variables, we see the intensive p as a general force and the extensive V as a general displacement. The following tables shows a summary of them:

System	Intensive Variable	Extensive Variable	Work Term
Hydrostatic fluid	pressure, p	volume, V	$-p\,dV$
Particles	chemical potential, μ	number, N	$\mu\,dN$
Surface film	surface tension, γ	area, A	$\gamma\,dA$
Wire	tension, J	extension, L	$J\,dL$
Dielectric solid	electric field, $\mathbf{E}$	electric dipole moment, $\mathbf{p}$	$\mathbf{E}\cdot d\mathbf{p}$
Magnetic solid	magnetic induction, $\mathbf{B}$	magnetic moment, $\mathbf{m}$	$\mathbf{B}\cdot d\mathbf{m}$
Capacitor	potential difference, V	charge, q	$V\,dq$
Electrical cell	electromotive force, $\mathcal{E}$	charge, q	$\mathcal{E}\,dq$

We shall see the general results of a hydrostatic pV system apply in a magnetic system using the substitution $\{-p, V\} \to \{B, m\}$. As an example, we may see

$$U \to \left(\frac{\partial B}{\partial S}\right)_m = \left(\frac{\partial T}{\partial m}\right)_S, \qquad G \to \left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B. \qquad (24)$$

5.5   Examples: Heat Capacities for Real Gases

Let us now proceed to find the heat capacities for a generic gas, which need not be ideal.

5.5.1 Constant-Volume Heat Capacity

We know the first law of thermodynamics:

$$\delta Q = \mathrm{d}U + \delta W. \tag{25}$$

In investigation of heat capacity where T is involved under constant V, we should choose T and V as the independent variables of U.

In reversible changes,

$$\delta Q = \mathrm{d}U + p\,\mathrm{d}V$$
$$= \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + p\,\mathrm{d}V$$
$$= \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T,$$
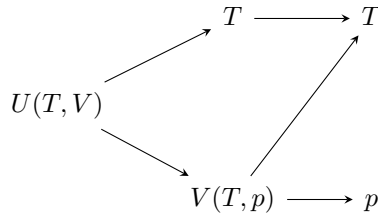
so the constant-volume heat capacity C_V is:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V. \tag{26}$$

5.5.2 Constant-pressure Heat Capacity

In a similar manner, we may begin with T and p as the independent variables. In reversible changes,

$$\delta Q = \mathrm{d}U + p\,\mathrm{d}V$$
$$= \left(\frac{\partial U}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial U}{\partial T}\right)_p \mathrm{d}T + p\,\mathrm{d}V$$
$$= \left(\frac{\partial U}{\partial T}\right)_p \mathrm{d}T + p\left[\left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T\right]$$
$$= \left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right] \mathrm{d}T$$

We would like to compare C_p with C_V, and accordingly we would like to change $\left(\frac{\partial U}{\partial T}\right)_p$.

By compound rule we see

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p.$$

Therefore,

$$C_p = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_p + C_V. \tag{27}$$

6 Heat Engines

6.1 Thermodynamic Processes

- In pV diagrams, we shall see the isentropes steeper than the isotherms. The area under the curve is the work done by the system.

$$\begin{cases} \text{Isotherm:} & pV = Nk_BT = \text{const.} \\ \text{Isentrope:} & pV^\gamma = \text{const.} \end{cases} \tag{28}$$

- In TS diagrams, we shall see the isochores steeper than the isobars. The area under the curve is the heat put into the system by its surroundings.

$$\begin{cases} \text{Isochore:} & \delta Q = T\,\mathrm{d}S = C_V\,\mathrm{d}T \\ \text{Isobar:} & \delta Q = T\,\mathrm{d}S = C_p\,\mathrm{d}T \end{cases} \tag{29}$$
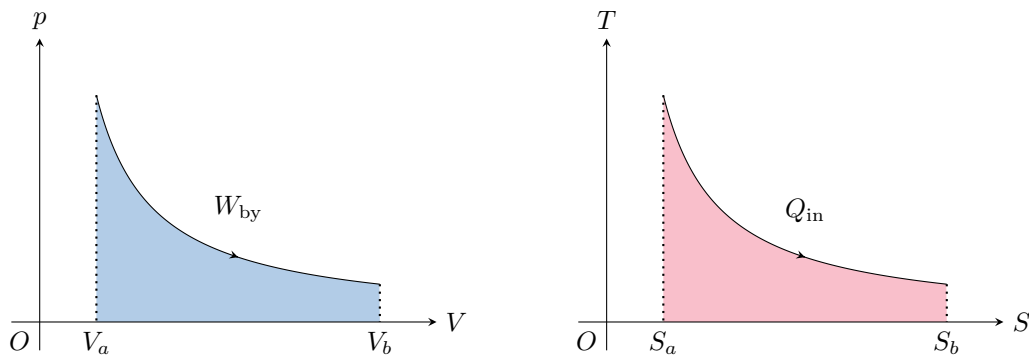
The following diagram summarizes the four thermodynamic processes in pV space and form a thermodynamic cycle. The total work done by the system in one cycle is $W = A - B$.
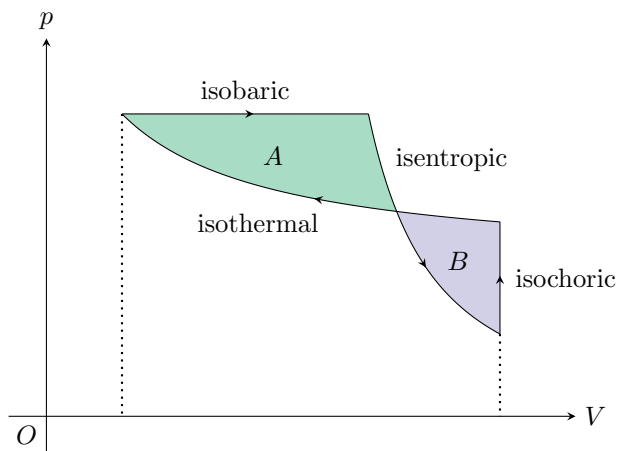
The following diagram summarizes the four thermodynamic processes in TS space. The total heat supplied to the system in one cycle is $Q = C - D$.
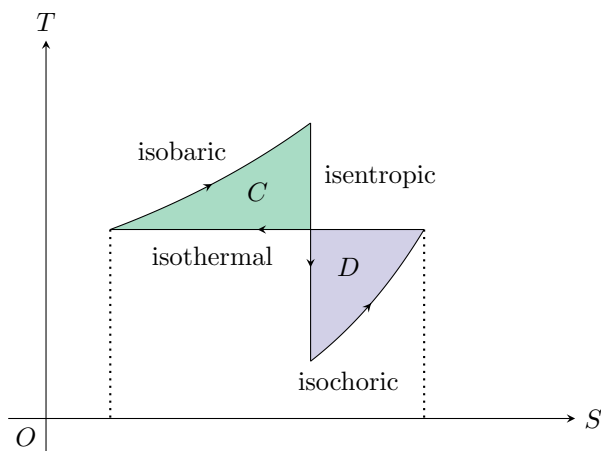
By conservation of energy we shall write:

$$Q_{\text{in}} = \Delta U + W_{\text{by}}. \tag{30}$$

6.2 Heat Engines

Thermodynamic Cycle

A thermodynamic cycle is a series of thermodynamic processes on a system.

A heat engine is a device that converts heat into work. It may be a thermodynamic cycle, but it need not be. (Remember that only states in corresponding equilibria can be represented on the diagram.)

Heat Engine Efficiency

We are interested in the work done by the system, which is actually the difference of the heat entering and leaving the system. The heat we supply to the system is the heat entering the system. Therefore

$$\eta = \frac{W}{Q_{\text{in}}} = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}}. \tag{31}$$

Ideally, for maximum efficiency, $Q_{\text{out}} = 0$, corresponding to the complete conversion of heat to work, but we shall see that this is not achievable.

Typically, a heat engine can work between a hot reservoir and a cold reservoir. It is called a heat reservoir engine.

7 Heat Pumps and Refrigerators

7.1 Reversible Processes

A reversible process is one in which both the system and the surroundings can be restored to their original state.

> To be reversible, the process has to be both quasistatic and non-dissipative (i.e. frictionless).

7.2 Refrigerators

Work W is done on the system such that it draws heat Q_C from the cold reservoir. From the definition we define the coefficient of performance for a refrigerator:

$$\omega_F = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}. \tag{32}$$

7.3 Heat Pumps

Similarly, work W is done on the system such that it draws heat Q_H from the hot reservoir (e.g. to provide heating for a building). Therefore, the coefficient of performance for a heat pump is:

$$\omega_P = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_C}. \tag{33}$$

The following diagram compares the three types of engines working between reservoirs.

Heat Engine

Refrigerator / Heat Pump
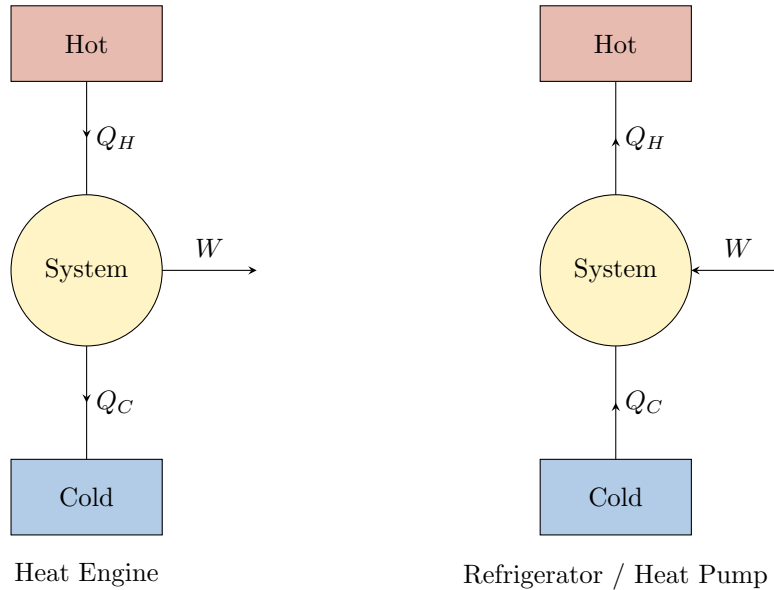
8 The Second Law of Thermodynamics

8.1 Equivalent Statements

- Kelvin's statement:

  No process is possible in which the sole effect is the absorption of heat from a reservoir and its complete conversion into work.

  In other words, there is no perfect heat engine.

- Clausius' statement:

  No process is possible in which the sole effect is the transfer of heat from a cold reservoir to a hotter reservoir.

  In other words, there is no perfect refrigerator.

- Statement of entropy:

  For any system there exists a property, entropy, S. For any process, $\mathrm{d}S \geq \delta Q/T$, equality holding in the limit of a reversible process.

8.2 Carnot Engine

> **Irreversible and Reversible Heat Flow**
>
> If heat flows directly between two systems that are not in thermal equilibrium, that is necessarily an irreversible process.
>
> For direct heat flow to be reversible, it has to occur between bodies that are in thermal equilibrium, i.e. at the same temperature. That is to say, **only isothermal heat transfer can be reversible**.

A Carnot engine essentially joins the reversible processes together to make a reversible thermodynamic cycle. The isotherms and adiabats are the only possible processes allowed if the cycle is to be reversible.
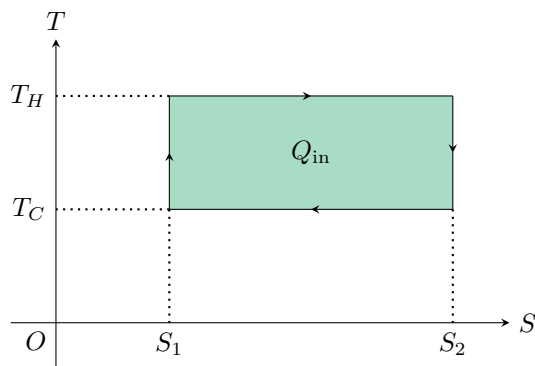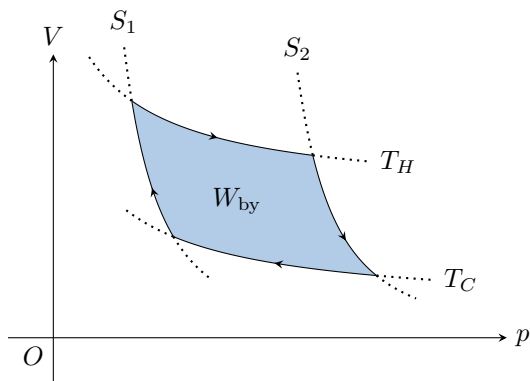
After some calculation we can show the efficiency of the Carnot engine:

$$\eta = 1 - \frac{T_C}{T_H}. \tag{34}$$

> **Carnot's Theorem**
>
> No heat engine operating between two reservoirs can be more efficient than a reversible engine operating between the same two reservoirs.

To prove Carnot's theorem, consider the engine A having a higher efficiency that a Carnot engine.
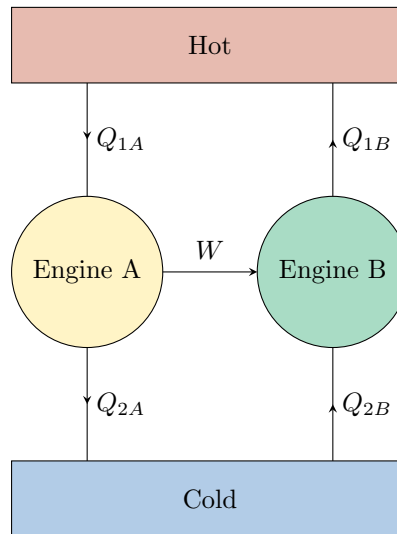
We shall verify that the two statements by Clausius and Kelvin are really equivalent. To see this, we observe how a Kelvin violator works to violate Clausius' statement, and vice versa.
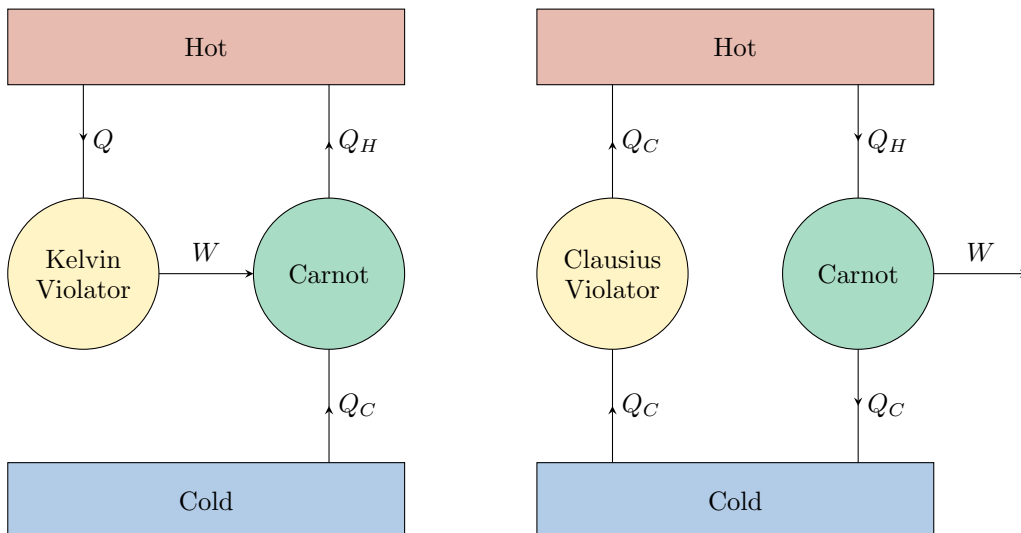
9 The Clausius Inequality and Entropy

9.1 Clausius Inequality

Consider the thermodynamic system below, where a Carnot engine and an engine S form a complex system.
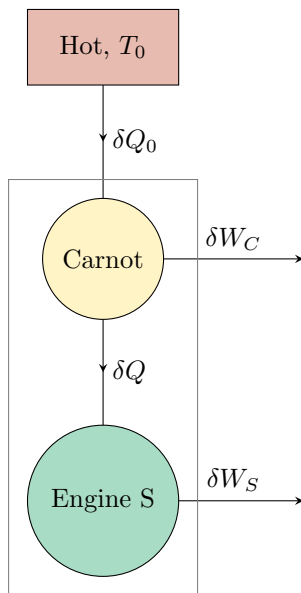
All Carnot engines operating between two reservoirs always have the same efficiency, and this leads us to

$$\frac{Q_{\text{out}}}{Q_{\text{in}}} = \frac{T_C}{T_H}. \tag{35}$$

Let the engine S have a temperature T, so we have

$$\delta Q_0 = \frac{T_0}{T} \delta Q.$$

Therefore, for one complete cycle,

$$Q_0 = \oint \delta Q_0 = T_0 \oint \frac{\delta Q}{T}.$$

By the first law, the total work done is $W = Q_0$. However, Kelvin's statement tells us that $W \leq 0$, and since $T_0 > 0$,

$$\oint \frac{\delta Q}{T} \leq 0.$$

This must be true for any cycle followed by the system. For reversible cycles, it is possible to run the

system through the cycle in the opposite direction, so

$$\oint \frac{-\delta Q}{T} \leq 0.$$

This implies

$$\oint \frac{\delta Q}{T} = 0 \qquad (36)$$

for reversible cycles. Hence, we get the Clausius inequality:

$$\oint \frac{\delta Q}{T} \begin{cases} = 0 & \text{for a reversible cycle, and} \\ < 0 & \text{for an irreversible cycle.} \end{cases} \qquad (37)$$

9.2 Entropy

We've shown that if the heat flow is reversible, then the quantity $\frac{\delta Q}{T}$ is path independent; this provokes the definition of a function of state. Therefore, we define the entropy S with

$$\mathrm{d}S = \frac{\delta Q_{\mathrm{rev}}}{T}, \qquad (38)$$

where δQ_{rev} is a reversible infinitesimal heat flow. As a function of state, the following equations must hold:

$$\oint \mathrm{d}S = 0, \qquad S_B - S_A = \int_A^B \mathrm{d}S. \qquad (39)$$

Consider a cycle consisting an irreversible process from A to B followed by a reversible one going from B back to A. Therefore, we have

$$\oint \frac{\delta Q}{T} < 0 \quad \Rightarrow \quad \int_A^B \left(\frac{\delta Q}{T} \right)_{\mathrm{irrev}} + \int_B^A \left(\frac{\delta Q}{T} \right)_{\mathrm{rev}} < 0.$$

Invoking the definition of S, we see

$$\int_A^B \left(\frac{\delta Q}{T} \right)_{\mathrm{irrev}} < \int_A^B \mathrm{d}S \quad \Rightarrow \quad \frac{\delta Q_{\mathrm{irrev}}}{T} < \mathrm{d}S,$$

since this inequality must be true for any path. Thus, we have

$$\frac{\delta Q}{T} \begin{cases} = \mathrm{d}S & \text{for a reversible process, and} \\ < \mathrm{d}S & \text{for an irreversible process.} \end{cases} \qquad (40)$$

To find entropy change for irreversible processes, just find some other reversible process and use that to calculate the entropy via the heat. Also, it is **impossible to have an irreversible adiabatic process**.

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9.3   Total Entropy never Decreases

This important result is worth a new page to be presented. For a thermally isolated system, we know $\delta Q = 0$ for any processes, so the equation becomes

$$\mathrm{d}S \begin{cases} = 0 & \text{for a reversible process, and} \\ > 0 & \text{for an irreversible process.} \end{cases} \tag{41}$$

The entropy of a non-isolated system may decrease, but accompanied is an equivalent, possibly larger, increase in entropy of its surroundings. For isolated systems like the universe, entropy never decreases, and we write

$$\mathrm{d}S \geq 0. \tag{42}$$

10 Thermodynamic Potentials and the Maxwell Relations

This section is discussed extensively before, so we are here to reiterate some important concepts:

> **The Fundamental Equation of Thermodynamics**
>
> $$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V\,. \tag{43}$$

- Enthalpy:

  We used enthalpy extensively in high school chemistry; this is because chemistry labs have constant p. The reason why we then switched to Gibbs function is the same.

- Helmholtz function:

  We discuss internal energy and then the Helmholtz function deliberately in statistical physics, in the context of the three ensembles. This is because we assume constant volume of the system throughout these models.

> **Ideal Gas Entropy**
>
> By the fundamental equation, rearranging gives
>
> $$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{p}{T}\,\mathrm{d}V\,.$$
>
> Integration leads us to
>
> $$S = S_0 + \frac{f}{2}Nk_B \ln\left(\frac{T}{T_0}\right) + Nk_B \ln\left(\frac{V}{V_0}\right)\,.$$
>
> From the equation we can easily see $S \to -\infty$ as $T \to 0$. By the third law we shall see $S \to 0$ as $T \to 0$; this leads us to the fact that no gases remain ideal at low temperatures.

11 Expansions of Real Gases

11.1 Adiabatic Expansion

If quasistatic, the process of adiabatic expansion is reversible, followed by no change in entropy.

> Just being adiabatic is not enough for reversibility; an adiabatic process is reversible only if it is also progressed slow enough (quasistatic).
>
> To see this, consider an isolated system ($Q = 0$ all the time), whose entropy never decreases.

We want to see how the temperature of gas changes as it expands; this means we're investigating partial derivatives with respect to V. By cyclic and reciprocal rule,

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

Through a Maxwell relation and the definition of heat capacity, we get the relevant thermodynamic coefficient:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V}\left(\frac{\partial p}{\partial T}\right)_V. \tag{44}$$

For any substance, C_V and $\left(\dfrac{\partial p}{\partial T}\right)_V$ are always positive, so the gas will always cool as it expands.

11.2 Free (Joule) Expansion

A free expansion is where the gas is allowed to **expand without doing any work**. In a thermally isolated container, this means no change in internal energy. Therefore, the relevant thermodynamic coefficient is

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U. \tag{45}$$

Similarly,

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T.$$

By the fundamental equation,

$$dU = T\,dS - p\,dV$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

This means
$$\eta = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]. \tag{46}$$

For an ideal gas, U is only a function of T; this means $\eta = 0$. For a Van der Waals gas,

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T \tag{47}$$

gives

$$\eta = -\frac{aN^2}{C_V V^2} \tag{48}$$

For dilute gases, this is small and negative, resulting in cooling.

11.3   Joule-Thompson Expansion

A Joule-Thompson (or Joule-Kelvin) expansion is where the gas is allowed to expand by forcing it through a porous plug or throttle valve, driven by a constant pressure difference.

For a thermally isolated system, the expansion is adiabatic, but not reversible - the gas must pass through non-equilibrium states. The net work done by the gas is:

$$W = p_1 \int_{V_1}^{0} dV + p_2 \int_{0}^{V_2} dV = p_2 V_2 - p_1 V_1.$$

As the process is adiabatic, then

$$\delta U + W = 0 \quad \Rightarrow \quad U_2 + p_2 V_2 = U_1 + p_1 V_1. \tag{49}$$

This means the initial and final enthalpies are equal: the process is isenthalpic. The volumes here are determined by the pressure differences, so the relevant thermodynamic coefficient is

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T. \tag{50}$$

By the fundamental equation,

$$dH = T\,dS + V\,dp\,, \tag{51}$$

giving

$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = C_p.$$

Also,

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = -T\left(\frac{\partial V}{\partial T}\right)_p + V = -V(T\beta - 1),$$

where the thermal expansivity is

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p.$$

(52)

This gives us, finally,

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}(T\beta - 1).$$

(53)

For an ideal gas, $T\beta = 1$, and $\mu = 0$. For real substances, μ can be either positive or negative.

12 Chemical Potential

Now we move on to systems where the number of particles can vary. By adding a new independent variable N, we get

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{V,S} dN$$

$$= T\,dS - p\,dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN.$$

Chemical Potential

Therefore, we define the chemical potential as the conjugate variable to N in the fundamental equation:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \tag{54}$$

The chemical potential is an intensive state variable. It can be interpreted **the energy required to add one particle**.

By recognizing different species in a system, we can write

$$dU = T\,dS - p\,dV + \sum \mu_i\,dN_i. \tag{55}$$

12.1 Phase Equilibria

Consider an isolated system with two distinct phases that are in contact. The total amount of the substance is fixed, but particles can move between the two phases, so the total amount of each phase is variable. We shall consider each phase as a system in its own right. The constraints should be conspicuous from the context:

$$dU_2 = -dU_1, \qquad dV_2 = -dV_1, \qquad dN_2 = -dN_1. \tag{56}$$

By the fundamental equation,

$$dU = T\,dS - p\,dV + \mu\,dN,$$

we get the entropy:

$$dS = dS_1 + dS_2 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1.$$

Equilibrium corresponds to the state in which entropy is maximum such that no further spontaneous

changes may occur. This means

$$T_1 = T_2, \qquad p_1 = p_2, \qquad \mu_1 = \mu_2, \tag{57}$$

each corresponding to thermal equilibrium, mechanical equilibrium, and chemical equilibrium.

12.2 Gibbs Free Energy

From above we already see that T, p, and N act as natural variables. These are also the typical variables we may control in the chemistry lab. In this case, the Gibbs free energy, which uses the corresponding variables as natural variables, should be more appropriate:

$$dG = -S\,dT + V\,dp + \sum \mu_i\,dN_i. \tag{58}$$

In this case we may write the chemical potential as

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T,p,N_{j \neq i}}, \tag{59}$$

so the chemical potential can also be interpreted as the Gibbs free energy per particle. The latter concept is given a symbol $\hat{g}(T, p)$.

Be defining the specific Gibbs function, we arrive at

$$\mu = \hat{g} = \frac{m}{N} g, \tag{60}$$

which means that the specific Gibbs function, Gibbs free energy per particle, and chemical potential are equivalent.

> We can also interpret chemical potential in terms of other thermodynamic potentials, based on our specific needs.
>
> We shall also show that in a chemical reaction, at equilibrium, the sum of chemical potentials of reactants must equal to the sum of chemical potentials of products, in their corresponding proportions.

13 Phase Transitions

- Phases of matter:

  A phase of matter is a distinct volume in which the chemical and the physical properties are uniform. Most real materials exhibit multiple phases for a given state.

- Length scales and uniformity:

  Some substances may exhibit relative uniformity on a macroscopic scale, but may not be uniform at smaller scales.

- Phase boundaries:

  A phase boundary is where two distinct phases of matter touch. It is a sharp (microscopic) discontinuity in the material properties. A gradual transition would not constitute a phase boundary.

- Phase transitions:

  A phase transition is the change of matter from one phase to another without the introduction of removal of material. It is always accompanied by discontinuous changes in some physical properties or in their derivatives.

  For a first order phase transition, the gradients of the intersecting Gibbs surfaces are different at the intersection resulting in a first-order change to the Gibbs function and discontinuities in first and higher order derivatives. Higher order phase transitions involve discontinuities beginning at higher derivatives.

- Latent heats:

  First-order phase transitions always involve transfer of heat. The latent heat of fusion of a solid is the heat required for the solid to change to liquid while the external temperature and pressure remain constant. The latent heat of vaporization is defined in a similar fashion.

  Since the temperature is constant, the heat capacity is effectively infinite.

14 Clausius-Clapeyron Relation

The Clausius-Clapeyron relation describes the behavior of phase transitions on a pT diagram. The phase boundary between two phases is a curve on the pT diagram along which both phases can coexist in equilibrium. At equilibrium, the Gibbs function achieves a minimum. Therefore,

$$\mathrm{d}G_t = \mathrm{d}G_1 + \mathrm{d}G_2 = -(S_1 - S_2)\,\mathrm{d}T + (V_1 - V_2)\,\mathrm{d}p = 0,$$

and this implies

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{\Delta s}{\Delta v}, \tag{61}$$

where the lowercase symbols are specific entropy and specific volume. As the specific entropy is related to the specific latent heat directly, we know

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l}{T\Delta v}. \tag{62}$$

For liquid-vapor boundary, the volume of vapor is much larger than that of the liquid. This gives us

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l}{Tv_g} = \frac{lp}{RT^2}. \tag{63}$$

15 The Third Law of Thermodynamics

15.1 Non-equivalent Statements

- Nernst's statement:

  Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.

- Planck's statement:

  The entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.

  > Planck made this statement in the context of perfect crystals, but who cares?

- Simon's statement:

  The contribution to the entropy of a system by each aspect of the system which is in internal equilibrium tends to zero as $T \to 0$.

- Unattainability of absolute zero:

  It's impossible to cool to $T \to 0$ with a finite number of steps.

15.2 Consequences

- Heat capacities $\to 0$ as $T \to 0$:
$$C = \frac{\partial Q}{\partial T} = T \frac{\partial S}{\partial T} = \frac{\partial S}{\partial \ln T} \to 0. \tag{64}$$

- Cessation of Thermal Expansion: As $\mathrm{d}S \to 0$ as $T \to 0$, this gives

$$\left(\frac{\partial S}{\partial p} \right)_T \to 0 \quad \text{as} \quad T \to 0.$$

  Therefore, by a Maxwell relation,

$$\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left(\frac{\partial S}{\partial p} \right)_T \to 0. \tag{65}$$

- As we've shown before, the entropy of an ideal gas would tend to infinity as $T \to 0$, but $S \to 0$ as $T \to 0$ in reality. This suggests that the ideal gas approximation fails at low temperatures.