

# PHYS20151 Part 2: Classical Thermodynamics

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## Housekeeping

These notes are not a complete overview of classical thermodynamics, which is an extensive field of physics and has been described in various degrees of detail by a wide number of authors. There are several recommended books that you can use to support your understanding in this course.

These include:

- Young, H. D. & Freedman, R. *University Physics*; [Library link](#)
- Flowers, B. H., & Mendoza, E. *Properties of Matter*; [Library link](#)
- Mandl, F. *Statistical Physics*; [Library link](#)
- Zemansky, M. W. & Dittman, R. H. *Heat and Thermodynamics: an intermediate textbook*; [Library link](#)
- Blundell, S. & Blundell, K. M. *Concepts in Thermal Physics*; [Library link](#)

Another resource which might be of use are some online notes written by Dr. Judith McGovern for an older version of this course. These can be found [here](#). Note, only the thermodynamics parts are relevant.

These notes are the latest version following from two decades of previous resources. The current version is largely the same as those compiled by Dr Lloyd Cawthorne, who drew on notes from Dr. Tommy Smith, Dr. Mike Godfrey, Prof. Tobias Galla, Dr. Judith McGovern and Prof. Peter Mitchel. The notes have been put together from a variety of sources and for that reason should not be distributed without my consent. If anything is unclear, or you spot any mistakes or typos please notify me via email.

# Contents

<b>1</b>	<b>Introduction</b>	<b>5</b>
1.1	Equilibrium and the Zeroth Law of Thermodynamics . . . . .	7
<b>2</b>	<b>The First Law</b>	<b>8</b>
2.0.1	Free expansion of an isolated ideal gas. . . . .	8
2.0.2	Isothermal expansion of an ideal gas. . . . .	9
2.1	The infinitesimal First Law . . . . .	9
2.1.1	Cyclic processes . . . . .	10
2.1.2	Quasistatic processes . . . . .	10
2.1.3	Reversible processes . . . . .	11
2.2	Expressions for reversible work . . . . .	11
2.2.1	Fluid compressed by piston . . . . .	12
2.2.2	Stretching of a string or wire . . . . .	12
2.2.3	Increase in surface area . . . . .	12
2.3	Work done and the indicator diagram . . . . .	12
2.4	Heat Capacity . . . . .	14
2.4.1	Heat capacity at constant volume, $C_V$ . . . . .	14
2.4.2	Heat capacity at constant pressure, $C_P$ . . . . .	15
2.5	Adiabatic processes . . . . .	16
<b>3</b>	<b>The Second Law</b>	<b>18</b>
3.1	Heat engines . . . . .	18
3.2	Heat pumps and refrigerators . . . . .	20
3.3	The Kelvin-Planck and Clausius statements . . . . .	21
3.3.1	Kelvin-Planck statement . . . . .	21
3.3.2	Clausius statement . . . . .	21
3.4	Reversible heat cycles and heat pump cycles . . . . .	22
3.4.1	Carnot's theorem . . . . .	22
3.4.2	The Carnot efficiency, $\eta_C$ . . . . .	23
3.4.3	The Carnot relations . . . . .	25
3.5	Entropy . . . . .	25
3.5.1	Clausius' inequality . . . . .	25
3.5.2	The mathematical definition of entropy . . . . .	27
3.5.3	The law of increase in entropy . . . . .	28
3.5.4	Entropy and heat capacity . . . . .	30
3.5.5	Examples of changes in entropy . . . . .	30
3.5.6	The fundamental thermodynamic relation . . . . .	31
3.6	Summary . . . . .	32
3.6.1	Statistical interpretation of entropy (optional) . . . . .	33
<b>4</b>	<b>Thermodynamic Potentials</b>	<b>34</b>
4.1	The Helmholtz free energy . . . . .	34
4.2	The Gibbs free energy . . . . .	35
4.3	Enthalpy . . . . .	35
4.4	Available work and approach to equilibrium . . . . .	35

4.4.1	Available work . . . . .	36
4.4.2	Approach to equilibrium . . . . .	37
4.5	Interpretation of the potentials . . . . .	38
4.5.1	Internal energy $E(S, V)$ . . . . .	38
4.5.2	Entropy $S(E, V)$ . . . . .	39
4.5.3	Helmholtz free energy $F(T, V) = E - TS$ . . . . .	39
4.5.4	Gibbs free energy $G(T, P) = F + PV = E - TS + PV$ . . . . .	40
4.5.5	Enthalpy $H(S, P) = E + PV$ . . . . .	40
4.5.6	Summary . . . . .	41
4.6	Maxwell's relations . . . . .	41
4.6.1	Applications . . . . .	42
<b>5</b>	<b>Phase Transitions</b>	<b>43</b>
5.1	Phases and states of matter . . . . .	43
5.2	Phase equilibrium . . . . .	43
5.3	Phase diagram of a typical substance . . . . .	45
5.4	Clausius-Clapeyron relation . . . . .	46
5.5	Modelling the liquid-gas transition . . . . .	48
5.5.1	Van der Waals' equation . . . . .	49
5.5.2	Predictions from Van der Waals' equation . . . . .	50
5.6	Classification of phase transitions . . . . .	51
<b>A</b>	<b>Notes on partial derivatives</b>	<b>53</b>
<b>B</b>	<b>Legendre Transformations</b>	<b>54</b>

$A$	Area
$c$	Specific heat capacity
$C$	Heat capacity
$C_P$	Heat capacity at constant pressure
$C_V$	Heat capacity at constant volume
$d$	Infinitesimal change in a path-dependent variable
$e$	Euler's number
$E$	Energy
$F$	Helmholtz Free Energy
$\vec{F}$	Force
$G$	Gibbs Free Energy
$G^m$	Gibbs Free energy per mole
$H$	Enthalpy
$H^m$	Enthalpy per mole
$n$	Number of moles
$N$	Number of molecules, atoms or particles
$N_A$	Avogadro's number, $6.022 \times 10^{23}$
$\vec{p}$	Momentum vector
$P$	Pressure
$Q$	Heat supplied to the system
$Q_C$	In a cycle, heat ejected to cold reservoir
$Q_H$	In a cycle, heat absorbed from hot reservoir
$Q_{\text{irrev.}}$	Irreversible heat supplied to the system
$Q_{\text{rev.}}$	Reversible heat supplied to the system
$\vec{r}$	Position vector
$S$	Entropy
$S^m$	Entropy per mole
$T$	Temperature
$T_C$	Temperature of cold reservoir
$T_H$	Temperature of hot reservoir
$W$	Work done on the system
$W_{\text{irrev.}}$	Irreversible work done on the system
$W_{\text{rev.}}$	Reversible work done on the system
$\gamma$	Heat capacity ratio, $C_P/C_V$ Sometimes used for surface tension
$\Gamma$	Tension per unit length
$\mu$	Chemical potential
$\eta$	Efficiency
$\eta_C$	Carnot efficiency
$\eta_E$	Efficiency of an engine
$\eta_P$	Efficiency of a heat pump
$\eta_R$	Efficiency of a refrigerator
$\rho$	Density per unit volume
$\sigma$	Density per unit area
$\oint$	Integral over a cycle

Table 1: Glossary of mathematical notation used in this text.

# 1 Introduction

Our goal is to understand the properties and behaviour of large numbers of atoms. A *large number* could imply different things in different contexts. Here, we mean of the order  $10^{20}$  atoms; that is around

$$100,000,000,000,000,000,000 \quad \text{atoms.}$$

Systems with this many particles have properties that we can measure such as *temperature* and *pressure*. These are *macroscopic* quantities in that they only really make sense if we have a large number of atoms (we consider the temperature of a gas, not the temperature of an atom). If we were to try and consider *microscopic* quantities that define a system, such as the energy and momentum of each gas particle, we would quickly find that there are infinite configurations. However we can determine the average of these quantities and would see they are intimately related to temperature. This area of study is thus commonly referred to as *Thermal Physics*.

There are a three main approaches to study thermal physics. They are:

- Classical Thermodynamics: deals with macroscopic quantities, ignoring any underlying physics or atomic structure.
- Kinetic Theory of Gasses: considers the probability distributions of microscopic quantities to describe macroscopic behaviour.
- Statistical Mechanics: applies statistical methods to the individual microscopic states of a system to determine macroscopic properties.

You will study the first two in this course and statistical mechanics in second year. We will start our discussion on thermodynamics by outlining some common conventions and definitions.

A commonly used large number is Avogadro's number:

$$N_A = 6.022 \times 10^{23}. \tag{1.0.1}$$

This number defines a *mole*<sup>1</sup> of a substance. This number is useful as it allows us to make quick conversions between the mass of a substance and the number of particles involved, given the mass number. For instance,

- 1 mole of carbon-12 contains  $6.022 \times 10^{23}$  carbon atoms and has a mass of 12g,
- 1 mole of H<sub>2</sub>O contains  $6.022 \times 10^{23}$  water molecules and has a mass of 18g.

In thermodynamics we will frequently perform thought experiments. For instance, consider an isolated box of volume  $V$  containing  $n$  moles of gas at temperature  $T$  and pressure  $P$ . Now, a partition is instantaneously placed such that it divides the box in two. Considering only one half of the box, it now has a volume  $V/2$  and contains  $n/2$  moles of gas. However the temperature and pressure remain  $T$  and  $P$ . This is depicted in figure 1.1. The above thought experiment illustrates the difference between *intensive* and *extensive* variables. Formally, we define these classifications of quantities as:

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<sup>1</sup>Not the small subterranean mammal. For a surprisingly gruesome digression on what would happen if you collected  $6.022 \times 10^{23}$  small furry mammals in one place, click [here](#).

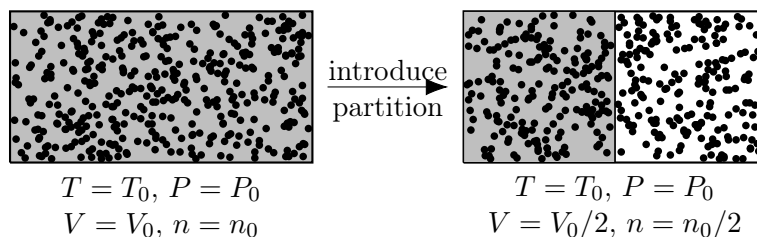


Figure 1.1: An illustration of a thought experiment where a partition instantaneously divides a gas in two. In the shaded regions of the two cases, the temperature and pressure remain the same, whilst the volume and the number of moles change.

- **Intensive variables** are non-additive; their value is not proportional to the amount of substance,
- **Extensive variables** are additive; their value is linearly proportional to the amount of substance.

If a quantity is non-linearly proportional to the amount of substance, then it is neither extensive nor intensive.

When discussing gasses, we will often work in an idealised case where the gas particles are point-like and non-interacting. This defines an *ideal gas*. Despite being fictitious, there is overwhelming empirical evidence to justify these assumptions when working in classical thermodynamics. Mathematically, we can describe an ideal gas at equilibrium with the experimentally found *ideal gas equation* which relates the state variables: pressure,  $P$ , volume,  $V$ , number of moles,  $n$ , and temperature,  $T$ . It is defined as:

$$\boxed{PV = nRT}, \quad (1.0.2)$$

where  $R = 8.315 \text{ J mol}^{-1} \text{ K}^{-1}$  is the molar gas constant. Alternatively, if we work with number of particles instead of moles ( $N = nN_A$ ), then

$$\boxed{PV = Nk_B T}, \quad (1.0.3)$$

where  $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$  is the Boltzmann constant. Hence  $R = N_A k_B$ .

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#### Further reading:

- Sections 1.1, 1.2 & 1.3 in [Blundell & Blundell](#).
- Sections 1.1, 1.2, 1.3 & 1.4 in [Zemansky & Dittman](#).
- Section 1.1 in [Mandl](#).
- Section 1.1 in [Flowers & Mendoza](#).

## 1.1 Equilibrium and the Zeroth Law of Thermodynamics

An isolated system tends to equilibrium with time. We describe the macroscopic steady state with state variables such as  $P$ ,  $V$  and  $T$  which are constant at equilibrium. These thermodynamic quantities are related to one another by an *equation of state*. For example, the equation of state for an ideal gas is the ideal gas law (eqs. [1.0.2](#) & [1.0.3](#)).

The zeroth law of thermodynamics applies to multiple systems in equilibrium. For three systems, it is defined as:

If  $A$  is in thermal equilibrium with  $B$  and if  $B$  is in thermal equilibrium with  $C$ , then  $A$  is in thermal equilibrium with  $C$ .

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### Further reading:

- Section 17.1 in [Young & Freedman](#).
- Sections 1.5 & 2.1 in [Zemansky & Dittman](#).
- Section 1.2 in [Mandl](#).
- Section 4.3 in [Flowers & Mendoza](#).

## 2 The First Law

The first law of thermodynamics is a statement regarding conservation of energy in thermodynamic processes;

$$\underbrace{\Delta E}_{\text{Change in internal energy.}} = \underbrace{W}_{\text{Work done \u{on} system.}} + \underbrace{Q}_{\text{Heat supplied \u{to} system.}} \quad (2.0.1)$$

*Work* here refers to applying a force over a distance. This could be to change a macroscopic variable like  $V$ , or mean work done against friction, etc.

*Heat* refers to changes to the microscopic variables of the system. It does **not** mean temperature, though they are intimately connected. It is the work done on individual molecules in the system which we do not have direct control over.

Throughout this text we will use the convention (unless stated otherwise) that work is done *on* the system and heat is supplied *to* the system. Therefore, provided both quantities are positive, they increase the internal energy of the system. There exists an alternative convention where work is done *by* the system and heat is ejected *from* the system. In this case, the internal energy of the system decreases provided these quantities are positive. In our convention, if the work done *on* the system is negative, it implies the system has done some work against its surroundings. Similarly for negative heat supplied *to* the system.

For a given process, the change in internal energy,  $\Delta E$ , depends only on the initial and final equilibrium states and not on the path between them. Therefore  $E$  is a *function of state*; a function of other thermodynamic variables ( $P$ ,  $V$ ,  $T$ , etc.). In contrast,  $W$  and  $Q$  are path-dependent and hence are not functions of state. We can demonstrate this with two thought experiments:

### 2.0.1 Free expansion of an isolated ideal gas.

In an isolated free expansion, a partition is instantaneously removed allowing the gas to occupy a larger volume. As the process is instantaneous, there is no heat transferred,  $Q = 0$ , and no work is done  $W = 0$ . Therefore  $\Delta E = 0$ . For an ideal gas, energy is a function of temperature only<sup>2</sup>,  $E \equiv E(T)$ , so the temperature is unchanged after removing the partition. This process is illustrated in figure 2.1.

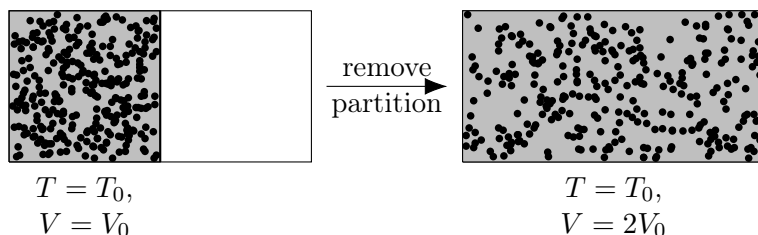


Figure 2.1: An illustration of the free expansion of an isolated gas from  $V_0$  to  $2V_0$ .

<sup>2</sup>We state this without proof for now, though you will prove this later in the course. You will derive the exact form for this when studying the kinetic theory of gasses.



## 2.0.2 Isothermal expansion of an ideal gas.

In an isothermal expansion, the gas is placed in thermal contact with a large heat reservoir. The reservoir acts as an infinite source of heat that could be supplied to the gas. The gas is contained in a piston with one freely movable cap. In this case, the expansion is not instantaneous, however we will only consider the equilibrium states before and after the expansion where the ideal gas law will apply. This process is illustrated in figure 2.2.

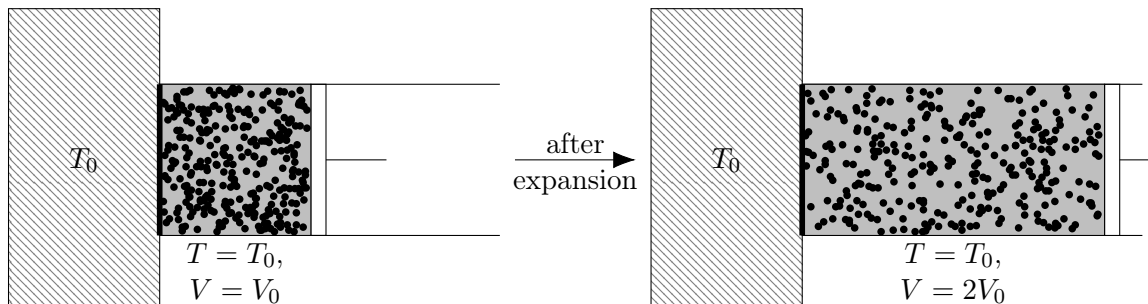


Figure 2.2: A diagram of the isothermal expansion of an ideal gas from  $V = V_0$  to  $V = 2V_0$ . the reservoir is depicted as a hatched rectangle with constant temperature  $T_0$ . The thick line is the thermal contact between the thermal reservoir and the ideal gas.

In this expansion, some heat  $Q > 0$  is supplied to the gas from the reservoir. The piston cap exerts an external force against the pressure of the gas. As the expansion is against this force<sup>3</sup>, work is done by the gas which is negative;  $W < 0$ . The initial and final states of the gas are identical to the free expansion, therefore we have  $\Delta E = 0$  again. However, now  $Q + W = 0$ , with  $Q = (-W) > 0$ .

From these two examples it is clear that  $Q$  and  $W$  depend on the process and not on the initial and final states only. Therefore, these quantities are not functions of state, unlike energy.

**Exercise:** determine which quantity will change in these thought experiments and find a relationship between the initial and final amounts.

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### Further reading:

- Section 1.3 in [Mandl](#).
- Sections 11.1 & 11.2 in [Blundell & Blundell](#).
- Sections 19.1 & 19.4 in [Young & Freedman](#).
- Sections 2.2, 4.1, 4.4 & 4.5 in [Zemansky & Dittman](#).

## 2.1 The infinitesimal First Law

For infinitesimally small changes, the first law reads:

$$\boxed{dE = dQ + dW}, \quad (2.1.1)$$

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<sup>3</sup> $W = \int_{r_i}^{r_f} \vec{F} \cdot d\vec{r}$

where we use the notation  $d$  to denote an infinitesimal change in a path-dependent variable (those that are not functions of state).

As  $E$  is a function of state variables, we can write its exact differential,  $dE$ , in terms of state variables  $P$ ,  $V$  or  $T$ . Only two need to be used as third is related by the equation of state (e.g. the ideal gas law). Writing  $E \equiv E(T, V)$  or  $E \equiv E(T, P)$ , we have

$$dE = \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial E}{\partial V} \right)_T dV \quad \text{or} \quad dE = \left( \frac{\partial E}{\partial T} \right)_P dT + \left( \frac{\partial E}{\partial P} \right)_T dP, \quad (2.1.2)$$

where the subscript outside of the partial derivative denotes the variable being held constant. The form of  $dE$  used depends on which variables we choose to be independent.

**Exercise:** writing  $E \equiv E(V, P)$ , find the third form of  $dE$ .

### 2.1.1 Cyclic processes

A cyclic process is one which starts and ends in the same equilibrium state, and hence  $E_{\text{initial}} = E_{\text{final}}$ . Therefore there is no change in energy over the cycle;

$$\oint dE = E_{\text{final}} - E_{\text{initial}} = 0, \quad (2.1.3)$$

where we have used “ $\oint$ ” to represent the integral over a cycle<sup>4</sup>. From the 1<sup>st</sup> law, this implies

$$\oint dW + \oint dQ = 0, \quad (2.1.4)$$

however the heat supplied and work done need not also be 0, as we saw in the examples at the start of this section. Therefore, for cyclic processes,

$$\oint dQ = - \oint dW. \quad (2.1.5)$$

### 2.1.2 Quasistatic processes

A *quasistatic* process is one that proceeds very slowly such that the system is always in thermal equilibrium. In other words, it passes through a sequence of different equilibrium states. An example of such a process would be the slow compression of a fluid by a piston, see figure 2.3.

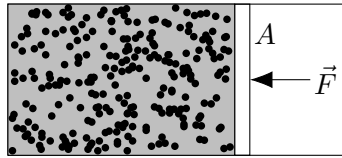


Figure 2.3: A diagram of the compression of a gas by a piston.

If the compression is quasistatic, then the force applied,  $\vec{F}$ , over the area of the piston cap,  $A$ , is equivalent to the pressure of the fluid itself;

$$\frac{|\vec{F}|}{A} \simeq P. \quad (2.1.6)$$

<sup>4</sup>More precisely this represents a line integral around a closed path.

### 2.1.3 Reversible processes

The laws of physics are reversible, however many processes are not. *Reversible* processes are quasistatic processes where friction can be ignored. In the reversed process, the signs of  $dE$ ,  $dW$  and  $dQ$  are reversed.

We can have reversible and irreversible processes with identical initial and final states. An example would be the free and the isothermal expansions seen earlier (subsubsections 2.0.1 & 2.0.2). The free expansion is irreversible because it is not quasistatic (the partition is removed instantaneously). The isothermal expansion can be reversible if there is no friction when moving the piston cap in the chamber. As these two processes share the same initial and final equilibrium states, we can write

$$dQ_{\text{irrev.}} + dW_{\text{irrev.}} = dQ_{\text{rev.}} + dW_{\text{rev.}} \quad (2.1.7)$$

In the free expansion the work done is 0 whilst it is negative in the isothermal expansion, therefore,

$$\boxed{dW_{\text{irrev.}} > dW_{\text{rev.}}} \quad (2.1.8)$$

Similarly, there is no heat exchange in the free expansion whilst heat is supplied from the reservoir in the isothermal expansion, therefore

$$\boxed{dQ_{\text{irrev.}} < dQ_{\text{rev.}}} \quad (2.1.9)$$

The above inequalities hold if we replaced the free expansion with an irreversible process with non-zero changes in heat and work. For instance, if we considered a quasistatic isothermal expansion with friction, then  $dW_{\text{irrev.}}$  includes positive work done against the friction.

In summary, for a process to be reversible:

1. it must be quasistatic,
2. there must be no external friction,
3. it must not cause any permanent change to the system; e.g. stretching a wire beyond its elastic limit such that it becomes permanently stretched.

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#### Further reading:

- Sections 3.2 & 4.6 in [Zemansky & Dittman](#).
- Section 1.3 in [Mandl](#).
- Sections 19.4 & 19.5 in [Young & Freedman](#).
- Sections 11.2 & 12.1 in [Blundell & Blundell](#).

## 2.2 Expressions for reversible work

You will practice using the below expressions in your tutorial sheets.

### 2.2.1 Fluid compressed by piston

In the reversible compression of a gas, we can rearrange the form of the work done to be in terms of state variables  $P$  and  $V$ ;

$$dW = \vec{F} \cdot d\vec{x} = \underbrace{\frac{|\vec{F}|}{A}}_P \underbrace{A dx}_{-dV} = -PdV. \quad (2.2.1)$$

This is illustrated in figure 2.4

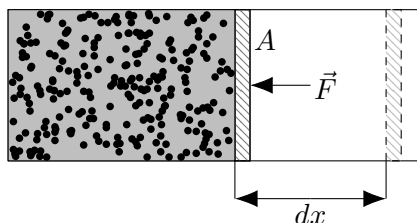


Figure 2.4: A diagram illustrating the calculation of work done in the reversible compression of a gas.

### 2.2.2 Stretching of a string or wire

If a string or wire is under some tension  $\Gamma$  and the infinitesimal change in length is  $dL$ , then the work done is

$$dW = \Gamma dL. \quad (2.2.2)$$

### 2.2.3 Increase in surface area

If a fluid has a surface tension  $\gamma$  and the infinitesimal change in area is  $dA$ , then the work done is

$$dW = \gamma dA. \quad (2.2.3)$$

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#### Further reading:

- Sections 3.3, 3.6, 3.7 & 3.8 in [Zemansky & Dittman](#).
- Section 19.2 in [Yound & Freedman](#).
- Section 11.2 in [Blundell & Blundell](#).
- Section 1.3 in [Mandl](#).

## 2.3 Work done and the indicator diagram

We represent processes by plotting pressure against volume, this is called an *indicator diagram*. The compression of a fluid from state  $i$  to state  $f$  is drawn in figure 2.5.

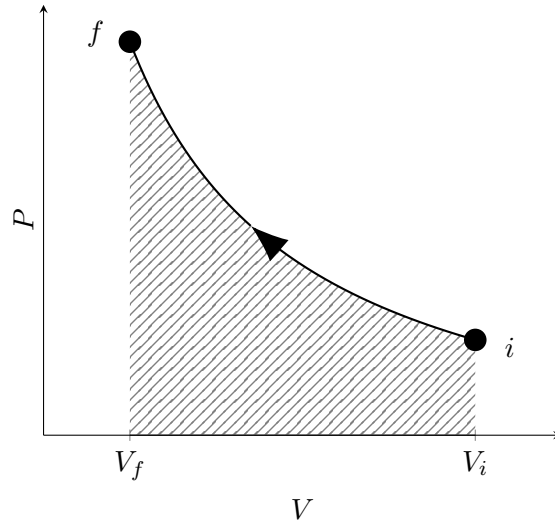


Figure 2.5: Indicator diagram for the compression of a gas from  $V_i$  to  $V_f$ . The shaded region is the work done in this process.

The work done on the fluid is the area under the curve,

$$W = \int_i^f dW = - \int_{V_i}^{V_f} P dV = \int_{V_f}^{V_i} P dV. \quad (2.3.1)$$

For an ideal gas at constant temperature, the work done is

$$\begin{aligned} W &= - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV \\ &= nRT \ln \left( \frac{V_i}{V_f} \right). \end{aligned} \quad (2.3.2)$$

For a cyclic process, the net work done is the area enclosed in the  $P$ - $V$  diagram. If the path is done anti-clockwise, then this is work done on the system. This case is shown in figure 2.6. If the path is clockwise, then it represents work done by the system.

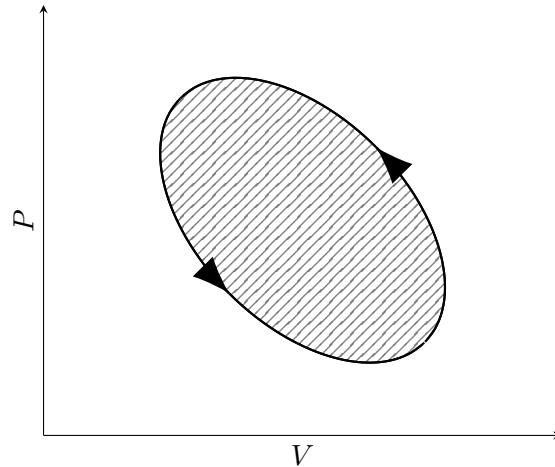


Figure 2.6: Indicator diagram for the work done on a gas in a cyclic process.

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**Further reading:**

- Sections 3.4 & 3.5 in [Zemansky & Dittman](#).
- Section 19.3 in [Young & Freedman](#).
- Section 12.2 in [Blundell & Blundell](#)

## 2.4 Heat Capacity

The *heat capacity*,  $C$ , of an object defines how much heat needs to be supplied to raise its temperature by a small amount  $dT$ , i.e.,

$$dQ = CdT. \quad (2.4.1)$$

$C$  therefore has units of  $\text{J K}^{-1}$ . Another commonly used quantity is the *specific heat capacity*,  $c$ , which defines the heat capacity per unit mass ( $C = mc$ ) and has units of  $\text{J K}^{-1} \text{kg}^{-1}$ . For the bulk of our discussion of classical thermodynamics, we will treat the heat capacity as a constant. However this is not strictly true. Heat capacity depends on state variables, though this dependency might only be manifest at extremes.

We distinguish two separate ways to supply heat to a fluid: at constant volume and at constant pressure.

### 2.4.1 Heat capacity at constant volume, $C_V$

Heating at constant volume is drawn in figure 2.7.

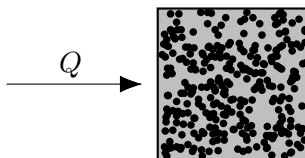


Figure 2.7: An illustration of heat  $Q$  being supplied to a gas at constant volume.

Rearranging the 1<sup>st</sup> law, we find

$$dQ = C_V dT = dE - dW = dE + PdV, \quad (2.4.2)$$

where the subscript  $V$  indicates volume is being held constant. Regarding  $E \equiv E(V, T)$ ,

$$dE = \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial E}{\partial V} \right)_T dV. \quad (2.4.3)$$

Equating the above two expressions we find

$$dQ = C_V dT = \left( \frac{\partial E}{\partial T} \right)_T dT. \quad (2.4.4)$$

Therefore, by equating the coefficients of  $dT$  we have

$$\boxed{C_V = \left( \frac{\partial E}{\partial T} \right)_V}, \quad (2.4.5)$$

which is valid for any fluid.

### 2.4.2 Heat capacity at constant pressure, $C_P$

Heating at constant pressure implies the chamber must expand, this is drawn in figure 2.8.

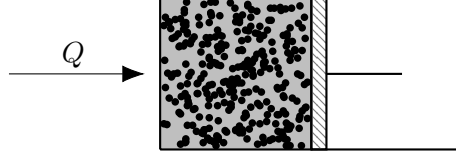


Figure 2.8: An illustration of heat  $Q$  being supplied to a gas at constant pressure. The piston cap on the right is free to move to maintain a constant pressure.

In this case, as work is also done to move the cap, we expect the heat capacity at constant pressure,  $C_P$ , to be greater than the heat capacity at constant volume. From the 1<sup>st</sup> law we have

$$dQ = C_P dT = dE + PdV. \quad (2.4.6)$$

Regarding  $E \equiv E(T, P)$ , we find

$$dE = \left( \frac{\partial E}{\partial T} \right)_P dT + \left( \frac{\partial E}{\partial P} \right)_T dP. \quad (2.4.7)$$

Substituting our value for  $dE$  into our expression for  $dQ$  and writing  $dV = \left( \frac{\partial V}{\partial T} \right)_P dT$ , we find

$$dQ = \left( \frac{\partial E}{\partial T} \right)_P dT + P \left( \frac{\partial V}{\partial T} \right)_P dT. \quad (2.4.8)$$

Equating coefficients of  $dT$ , we obtain

$$C_P = \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P, \quad (2.4.9)$$

which is valid for any fluid.

#### Special case: ideal gas

For an ideal gas  $E \equiv E(T)$ , therefore

$$\left( \frac{\partial E}{\partial T} \right)_P = \left( \frac{\partial E}{\partial T} \right)_V = C_V(T). \quad (2.4.10)$$

From  $PV = nRT$ , we find

$$P \left( \frac{\partial V}{\partial T} \right)_P = nR. \quad (2.4.11)$$

This leaves us with

$$C_P(T) = C_V(T) + nR, \quad (2.4.12)$$

which is in agreement with our previous statement that  $C_P > C_V$ .

---

#### Further reading:

- Section 11.3 in [Blundell & Blundell](#).
- Sections 18.4 & 19.7 in [Young & Freedman](#).
- Sections 4.7, 4.9 & 4.10 in [Zemansky & Dittman](#).

## 2.5 Adiabatic processes

An *adiabatic* process is one where there is no heat transfer;  $Q = 0$ . This is equivalent to saying the system is thermally insulated or isolated.

From the 1<sup>st</sup> law we have

$$dQ = dE - dW = 0. \quad (2.5.1)$$

For an ideal gas, as  $E \equiv E(T)$ , so  $dE = C_V dT$ . From the equation of state we also have

$$T = \frac{PV}{nR}. \quad (2.5.2)$$

The differential of  $T$  is therefore

$$dT = \frac{1}{nR} (PdV + VdP). \quad (2.5.3)$$

Hence we can write the differential of  $E$  as

$$dE = \frac{C_V}{nR} (PdV + VdP). \quad (2.5.4)$$

Substituting the above into of right-hand side of eq. 2.5.1 and assuming a reversible process ( $dW = -PdV$ ), we obtain

$$\begin{aligned} C_V dT + PdV &= \frac{C_V}{nR} (PdV + VdP) + PdV = 0, \\ C_V V dP + \underbrace{(C_V + nR)}_{C_P} PdV &= 0, \\ \Rightarrow \frac{1}{P} dP + \frac{C_P}{C_V} \frac{1}{V} dV &= 0. \end{aligned} \quad (2.5.5)$$

If  $C_P$  and  $C_V$  are approximately constant over the range of temperatures of interest, then  $\gamma = \frac{C_P}{C_V}$  is also constant. Integrating from  $(P_1, V_1)$  to  $(P_2, V_2)$ ,

$$\begin{aligned} \int_{P_1}^{P_2} \frac{1}{P} dP + \gamma \int_{V_1}^{V_2} \frac{1}{V} dV &= 0, \\ \ln \left( \frac{P_2}{P_1} \right) + \gamma \ln \left( \frac{V_2}{V_1} \right) &= 0, \\ \Rightarrow \ln \left( \frac{P_2 V_2^\gamma}{P_1 V_1^\gamma} \right) &= 0. \end{aligned} \quad (2.5.6)$$

Removing the logarithm we yield

$$\boxed{P_2 V_2^\gamma = P_1 V_1^\gamma}. \quad (2.5.7)$$

Equation 2.5.7 holds for any reversible adiabatic process on an ideal gas with constant heat capacities.

We can eliminate  $P_1$  and  $P_2$  from eq. 2.5.7 by using

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1} = nR. \quad (2.5.8)$$



This leaves us with an equivalent form in terms of temperatures and volumes:

$$\boxed{T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}.} \quad (2.5.9)$$

**Exercise:** eliminate  $V_1$  and  $V_2$  to find

$$\boxed{P_1^{\frac{1}{\gamma}-1} T_1 = P_2^{\frac{1}{\gamma}-1} T_2.} \quad (2.5.10)$$

**Exercise:**

Make a poster for your wall summarising the key ideas and equations from this chapter.

---

**Further reading:**

- Section 12.3 in [Blundell & Blundell](#).
- Sections 4.2, 5.3 & 5.5 in [Zemansky & Dittman](#).

### 3 The Second Law

The second law of thermodynamics dictates the direction of heat flow as a system approaches equilibrium. A number of observations suggest such a preference:

- Systems at different temperatures reach equilibrium at an intermediate temperature. The reverse never happens.
- Heat naturally flows from hot bodies to cold bodies. For the reverse to occur, we require a refrigerator and a power supply.
- It is simple to use frictional work to warm a body, though it is far more difficult to produce work from heat; it requires an engine.

These statements also suggest a lack of symmetry between heat and work even though they appear identically in the first law,  $\Delta E = W + Q$ .

We will start by discussing engines and cycles before introducing entropy.

#### 3.1 Heat engines

*Heat engines* are devices that produce work from heat. They operate in a cycle such that

$$\Delta E = \oint dE = 0. \quad (3.1.1)$$

We will centre our discussion on the example of a Sterling engine containing an ideal gas. This engine can be considered as a piston operating between two heat reservoirs: a hot reservoir at a temperature  $T_H$  and a cold reservoir at a temperature  $T_C < T_H$ . The cycle operates in four steps<sup>5</sup>:

- (1) Isothermal expansion.

Work done by gas:  $W_1 = nRT_H \ln \left( \frac{V_B}{V_A} \right)$

Heat absorbed:  $Q_1 = W_1$

- (2) Contact cooling

No work done.

Heat ejected:  $Q_2 = E(T_H) - E(T_C)$

- (3) Isothermal compression.

Work done on gas:  $W_3 = nRT_C \ln \left( \frac{V_B}{V_A} \right)$

Heat ejected:  $Q_3 = W_3$

- (4) Contact heating

No work done.

Heat absorbed:  $Q_4 = E(T_H) - E(T_C)$

---

<sup>5</sup>To see how such an engine can be constructed, have a look at the possible configurations described in [https://en.wikipedia.org/wiki/Stirling\\_engine](https://en.wikipedia.org/wiki/Stirling_engine). This detail is not examinable.

You should be able to find all of the above relations, these are just a consequence of  $dW = -PdV$  and the 1<sup>st</sup> law. This cycle is drawn in figure 3.1.

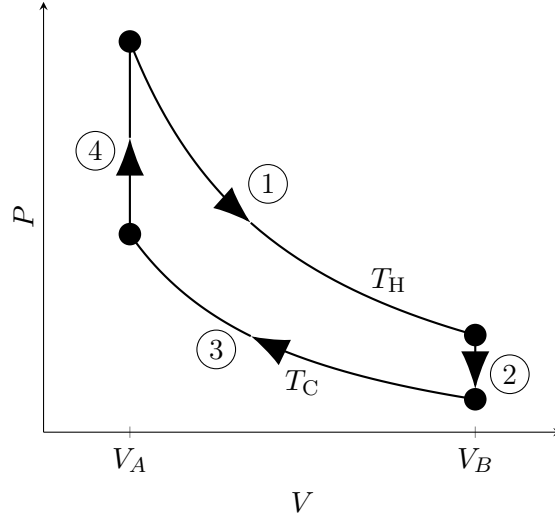


Figure 3.1:  $P$ - $V$  diagram displaying the Sterling cycle between volumes  $V_A$  and  $V_B$ , and temperatures  $T_H$  and  $T_C$ . The numbered steps are described in the text.

The net work done by the gas is

$$\begin{aligned} W &= W_1 - W_3 \\ &= nR(T_H - T_C) \ln \left( \frac{V_B}{V_A} \right). \end{aligned} \quad (3.1.2)$$

The heat absorbed from the hot reservoir at  $T_H$  is

$$Q_H = Q_1 + Q_4, \quad (3.1.3)$$

and the heat ejected to cold reservoir at  $T_C$  is

$$Q_C = Q_2 + Q_3. \quad (3.1.4)$$

From the 1<sup>st</sup> law we have, for the cycle,

$$\Delta E = 0 = (-W) + (Q_H - Q_C). \quad (3.1.5)$$

Therefore,

$$W = Q_H - Q_C. \quad (3.1.6)$$

We often depict engines with a schematic diagram clarifying the reservoirs, heat flow and work done. Such a diagram for the Sterling cycle is drawn in figure 3.2.

We define the *efficiency* of the engine,  $\eta_E$ , as the desired output over the required input, which is equivalent to the ratio of the amount of work done over the heat absorbed; i.e.,

$$\eta_E = \frac{\text{desired output}}{\text{required input}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} < 1. \quad (3.1.7)$$

Empirical observations show that  $\eta_E < 1$  or, equivalently,  $Q_C > 0$  always.

**Exercise:** Comment on the nature of an engine where  $Q_C = 0$ .

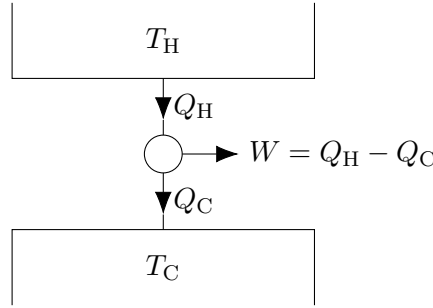


Figure 3.2: An abstract schematic diagram of a general heat cycle that extracts an amount of work  $W$  from a system by supplying it with a net amount of heat  $Q_H - Q_C$ . Since it is a cycle,  $W = Q_H - Q_C$ .

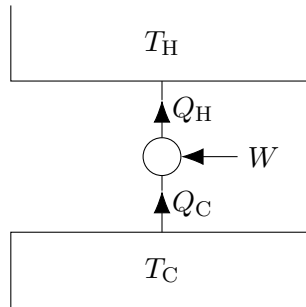


Figure 3.3: An abstract schematic diagram of a heat pump cycle that extracts an amount of heat  $Q_H$  or of a refrigeration cycle that extracts an amount of heat  $Q_C$  from a system by supplying it with a net amount of work  $W$ . Since it is a cycle,  $W = Q_H - Q_C$ .

---

### Further reading:

- Sections 6.1 & 6.4 in [Zemansky & Dittman](#).
- Sections 20.1 & 20.2 in [Young & Freedman](#).

## 3.2 Heat pumps and refrigerators

Heat pumps and refrigerators are the opposite of engines: work is done on the system to extract heat. A depiction of this process is illustrated in figure 3.3.

### Refrigerator

For refrigerator we extract some heat  $Q_C$  from a system to lower its temperature to  $T_C$ . The ratio of desired output over required input is still referred to as an efficiency, however in this case it has a value greater than one<sup>6</sup>;

$$\eta_R = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}, \text{ usually } \eta_R > 1. \quad (3.2.1)$$

---

<sup>6</sup>This is misleading as we think of efficiencies ranging between 0 and 1. If you prefer consider this to be a *coefficient of performance*.

## Heat pump

In a heat pump work is done to extract heat from a cooler thermal reservoir at  $T_C$  to heat a system to  $T_H$ . In this case the desired output is  $Q_H$ , which alters the form of the efficiency:

$$\eta_P = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_C} > 1 \text{ always.} \quad (3.2.2)$$

If an engine is reversible, such that when run in reverse the magnitudes of  $W$ ,  $Q_C$  and  $Q_H$  are unchanged, then we find

$$\eta_P = \frac{1}{\eta_E}. \quad (3.2.3)$$

---

### Further reading:

- Section 20.4 in [Young & Freedman](#).

## 3.3 The Kelvin-Planck and Clausius statements

The second law of thermodynamics can be expressed in different ways. We will consider two important statements that define the second law individually and then argue they are equivalent.

### 3.3.1 Kelvin-Planck statement

*It is impossible to construct an engine which, operating in a cycle, produces no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work. - Kelvin-Planck*

An engine,  $\bar{K}$ , that would violate this statement is shown in figure 3.4. If such an engine were to exist it would have an efficiency of 1 as all heat is converted to work; this would be a perpetual motion machine<sup>7</sup>.

### 3.3.2 Clausius statement

*It is impossible to construct a refrigerator which, operating in a cycle, produces no effect other than the transfer of heat from a cooler body to a hotter one. - Clausius*

An engine,  $\bar{C}$ , that would violate this statement is shown in figure 3.4.

Of course it is possible to think of processes which convert heat into work (expansion of a hot gas in a piston) or which transfer heat from cooler to hotter bodies (real fridges), however in these cases other quantities are also changed (the gas ends up cooler; you have an electricity bill to pay). The key aspect of these definitions is that they are operating in a cycle.

These statements are equivalent. We can show the Clausius statement is equivalent to the Kelvin-Planck statement by placing a heat engine alongside our Clausius statement-violating refrigerator. This heat engine extracts some heat,  $Q'_H$ , to perform some work,  $W$ , and ejects some heat  $Q_C$  to the cold reservoir. The net extracted from the cold reservoir is  $Q_C - Q_C = 0$

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<sup>7</sup>More precisely a perpetual motion machine of the second kind.

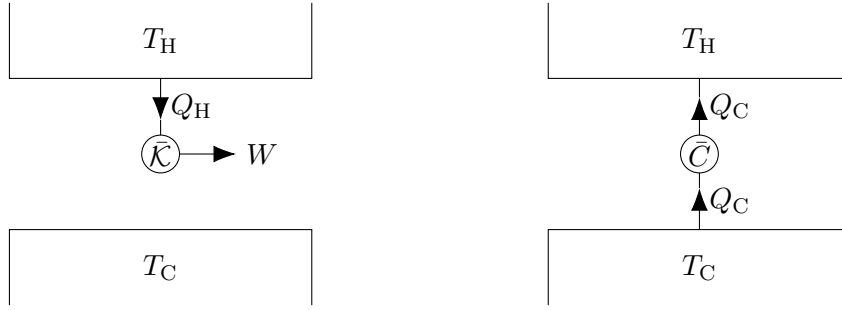


Figure 3.4: Schematic diagrams of an engine  $\bar{K}$  that violates the Kelvin-Planck statement and an engine  $\bar{C}$  that violates Clausius' statement.

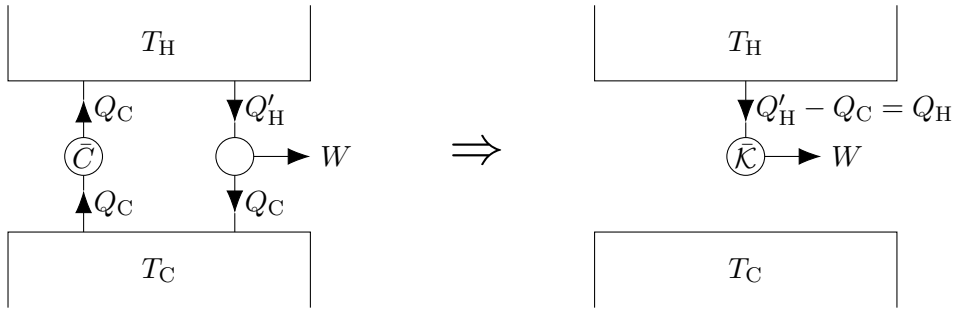


Figure 3.5: Schematic diagrams showing that violation of the Clausius statement leads to violation of the Kelvin-Planck statement.

and the net heat extracted from the hot reservoir is  $Q'_H - Q_C = Q_H$ . Thus the combined system extracts some heat  $Q_H$  and performs some work  $W$ ; the Kelvin-Planck violating engine. This equivalence is depicted in figure 3.5.

**Exercise:** using a similar approach, show that the violation of the Kelvin-Planck statement implies the violation of Clausius' statement.

---

#### Further reading:

- Sections 13.1 & 13.4 in [Blundell & Blundell](#).
- Sections 6.6, 6.7 & 6.8 in [Zemansky & Dittman](#).
- Section 20.5 in [Young & Freedman](#).

### 3.4 Reversible heat cycles and heat pump cycles

What is the greatest efficiency of an engine,  $\eta_E$ , operating between two heat baths  $T_H$  and  $T_C$ ?

#### 3.4.1 Carnot's theorem

1. A reversible engine is the most efficient.
2. All reversible engines, operating between two heat baths, have the same efficiency,

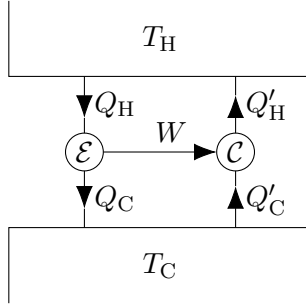


Figure 3.6: A schematic diagram of an irreversible engine  $\mathcal{E}$  driving a reversible Carnot engine  $\mathcal{C}$  in reverse as a heat pump where both cycles are connected to the same thermal reservoirs. This diagram proves that  $\eta_{\mathcal{E}} \leq \eta_{\mathcal{C}}$  as detailed in the prose.

$\eta_{\mathcal{C}}$ , depending only on  $T_H$  and  $T_C$ .

Consider an engine  $\mathcal{E}$ , with efficiency  $\eta_{\mathcal{E}}$  operating between two heat baths, driving a reversible engine  $\mathcal{C}$  operating in reverse, see fig 3.6. From Clausius' statement, it must follow that

$$Q'_H - Q_H \leq 0, \quad (3.4.1)$$

otherwise we are left with a system that only transfers heat from a cold body to a hot one. Therefore,

$$Q'_H \leq Q_H \Rightarrow \frac{1}{Q_H} \leq \frac{1}{Q'_H}. \quad (3.4.2)$$

Which implies an inequality between the efficiencies:

$$\eta_{\mathcal{E}} = \frac{W}{Q_H} \leq \frac{W}{Q'_H} = \eta_{\mathcal{C}}. \quad (3.4.3)$$

In summary, no engine is more efficient than a reversible one. This means that for *any* reversible engine operating between two heat baths, they will have the same efficiency,  $\eta_{\mathcal{C}}$ , regardless of their working substance.

### 3.4.2 The Carnot efficiency, $\eta_{\mathcal{C}}$

We want an expression for  $\eta_{\mathcal{C}}$ . We could use any reversible cycle to determine it. For simplicity, we use the Carnot cycle, applied to an ideal gas with constant  $\gamma = \frac{C_P}{C_V}$ . This cycle is drawn in figure 3.7 and is composed of four steps:

- (1) Isothermal expansion at  $T_H$ ,  $\Delta E = 0$ .
- (2) Adiabatic expansion,  $Q = 0$ .
- (3) Isothermal compression at  $T_C$ ,  $\Delta E = 0$ .
- (4) Adiabatic compression,  $Q = 0$ .

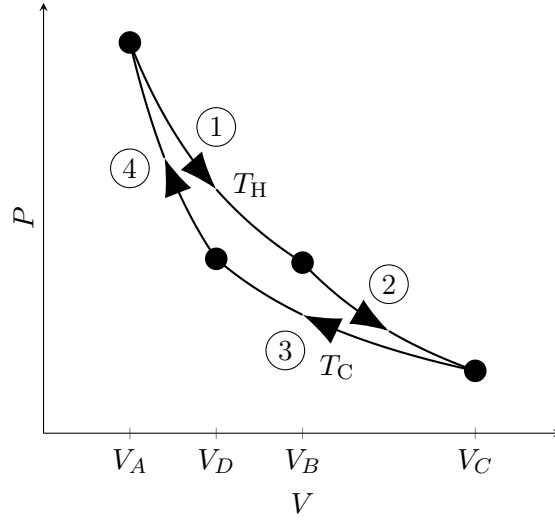


Figure 3.7:  $P$ - $V$  diagram displaying the Carnot cycle between volumes  $V_A$ ,  $V_B$ ,  $V_C$  and  $V_D$ , and temperatures  $T_H$  and  $T_C$ . The numbered steps are described in the text.

The only heat exchanges occur in steps 1 and 3. In step one, some heat  $Q_H$  is absorbed. As this is on an isotherm, we find

$$Q_H = \int_{V_A}^{V_B} \frac{nRT_H}{V} dV = nRT_H \ln \frac{V_B}{V_A}. \quad (3.4.4)$$

Similarly, in step 3 some heat  $Q_C$  is lost<sup>8</sup>;

$$Q_C = nRT_C \ln \frac{V_C}{V_D}. \quad (3.4.5)$$

The efficiency is hence

$$\eta_C = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C \ln(V_C/V_D)}{T_H \ln(V_B/V_A)}. \quad (3.4.6)$$

On the adiabats we know  $TV^{\gamma-1} = \text{const.}$  (eq: 2.5.9), which allows us to relate steps 2 and 4;

$$\begin{aligned} T_H V_B^{\gamma-1} &= T_C V_C^{\gamma-1}, \\ T_H V_A^{\gamma-1} &= T_C V_D^{\gamma-1}. \end{aligned} \quad (3.4.7)$$

Therefore,

$$\begin{aligned} \frac{V_B}{V_A} &= \frac{V_C}{V_D}, \\ \Rightarrow \ln \frac{V_B}{V_A} &= \ln \frac{V_C}{V_D}. \end{aligned} \quad (3.4.8)$$

This leaves us with a final form for the Carnot efficiency as

$$\boxed{\eta_C = 1 - \frac{T_C}{T_H}}. \quad (3.4.9)$$

This is valid for any reversible engine operating between two heat reservoirs with any working substance.

---

<sup>8</sup>Heat ejected *from* the system.



### 3.4.3 The Carnot relations

From the definition of the efficiency and the Carnot efficiency,

$$\eta_C = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}, \quad (3.4.10)$$

we arrive at the Carnot relations:

$$\boxed{\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \quad \text{or} \quad \frac{Q_C}{T_C} = \frac{Q_H}{T_H}.} \quad (3.4.11)$$

These apply to reversible cycles. For  $T_H \neq T_C$ , the heat transfers must be accompanied by work done to be reversible. Heat transferred from a hot reservoir to a cold reservoir without doing any work is always irreversible, as seen previously. Heat transfer in the other direction (cold to hot) is impossible, as stated by Clausius.

From the point of view of the working substance, heats  $Q_H$  and  $Q_C$  are absorbed and lost at temperatures  $T_H$  and  $T_C$  respectively. These satisfy

$$\frac{Q_H}{T_H} + \frac{-Q_C}{T_C} = 0. \quad (3.4.12)$$

Next, we will generalise this as it leads to the concept of *entropy*.

#### Further reading:

- Sections 13.2, 13.3 & 13.6 in [Blundell & Blundell](#).
- Section 20.6 in [Young & Freedman](#).
- Sections 7.1, 7.2, 7.3, & 7.4 in [Zemansky & Dittman](#).

## 3.5 Entropy

Entropy is an abstract concept which as we'll see is related to the passage of time. We will study it in the context of thermodynamics and ideal gasses. Later, in statistical physics, you will see how it quantifies the order (or disorder) of the system. It is studied in surprisingly many fields, for instance, making sense of black-holes.

### 3.5.1 Clausius' inequality

The Clausius inequality states that if a system is taken over a cycle, absorbing infinitesimal amounts of heat,  $dQ$ , from various reservoirs at varying temperatures,  $T$ , throughout, then

$$\boxed{\oint \frac{1}{T} dQ \leq 0.} \quad (3.5.1)$$

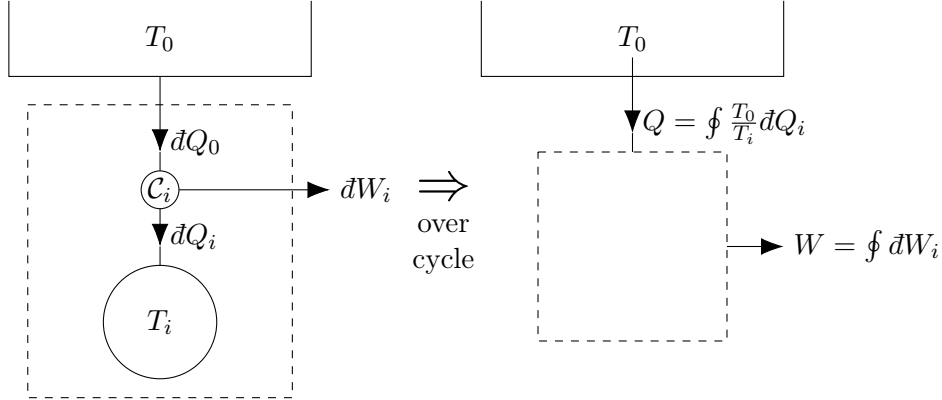


Figure 3.8: A diagram of infinitesimal processes (left) that over a cycle lead to a process that appears to violate the Kelvin-Planck statement (right). Forcing  $Q \leq 0$  results in the Clausius inequality.  $T_0$  is a large thermal reservoir of constant temperature,  $C_i$  is one of infinitely many Carnot heat engines operating between  $T_0$  and a small reservoir at  $T_i$ .  $T_i$  varies in each iteration that form the cycle.

**Proof:**

To prove this we will consider a system that appears to violate the Kelvin-Planck statement about the second law. Requiring that it must satisfy the second law over the cycle places conditions on the change in heat which yield the Clausius inequality.

The overall cycle is a result of infinite infinitesimally small steps where a Carnot engine operating between  $T_0$  and  $T_i$  absorbs some heat  $dQ_0$  and ejects some heat  $dQ_i$  producing some work  $dW_i$ . The reservoir at  $T_0$  is large and so its temperature remains constant. Whilst the reservoir at  $T_i$  is small and its temperature varies over the cycle. This setup is depicted in figure 3.8. As there is a Carnot engine in each infinitesimal step, we can make use of the Carnot relations, eq. 3.4.11, to relate  $dQ_0$  and  $dQ_i$ :

$$dQ_0 = \frac{T_0}{T_i} dQ_i. \quad (3.5.2)$$

Considering only the boxed region in fig. 3.8 around a cycle, we have

$$\begin{aligned} \oint dE &= 0, \\ \Rightarrow \oint dQ_0 &= \oint dW_i; \end{aligned} \quad (3.5.3)$$

remember this is currently represented as work done by the system. However, this appears to violate the Kelvin-Planck statement; we have a system that is converting all heat into work! To resolve this, the total work output must be less than or equal to zero;

$$\oint dW_i \leq 0. \quad (3.5.4)$$

Therefore,

$$\oint dQ_0 = T_0 \oint \frac{dQ_i}{T_i} \leq 0, \quad (3.5.5)$$

which, dropping the labels  $i$ , yields the Clausius inequality:

$$\oint \frac{1}{T} dQ \leq 0. \quad (3.5.6)$$

Which is valid for any cycle.

It might be that for some portion of the cycle the system does output work; this would not violate the Kelvin-Planck statement. The key aspect to this is that over a complete cycle net work is done on the system which supplies heat to the large reservoir.

### Special case: reversible cycle

If the entire cycle in figure 3.8 is reversible, in reverse we replace  $dQ$  with  $-dQ$ :

$$-\oint \frac{dQ}{T} \leq 0 \Rightarrow \oint \frac{dQ}{T} \geq 0. \quad (3.5.7)$$

This is only consistent with Clausius' inequality if, and only if,

$$\boxed{\oint \frac{1}{T} dQ = 0.} \quad (3.5.8)$$

For a different proofs of the Clausius inequality, see section 13.7 in [Blundell & Blundell](#) or section 5.1 in [Finn's Thermal Physics](#).

### 3.5.2 The mathematical definition of entropy

Suppose we have two equilibrium states,  $A$  and  $B$ , that are part of a reversible cycle composed of two processes 1 and 2; see fig. 3.9.

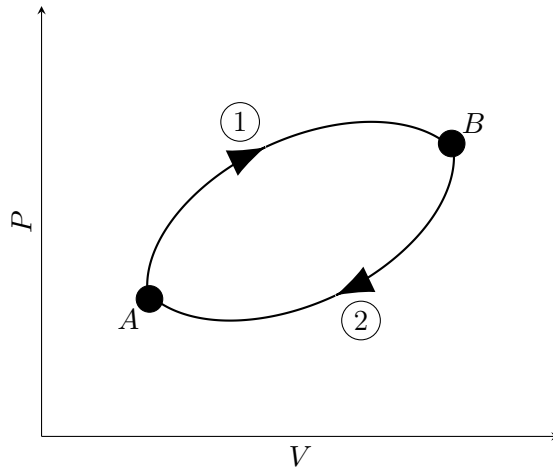


Figure 3.9: Indicator diagram over a reversible cycle passing through equilibrium states  $A$  and  $B$ .

As this process is reversible, we know that the integral of  $dQ/T$  over the cycle is zero.

Splitting this into the two paths, we have

$$\begin{aligned}
\oint \frac{1}{T} dQ &= \underbrace{\int_A^B \frac{1}{T} dQ}_{(1)} + \underbrace{\int_B^A \frac{1}{T} dQ}_{(2)}, \\
&= \underbrace{\int_A^B \frac{1}{T} dQ}_{(1)} - \underbrace{\int_A^B \frac{1}{T} dQ}_{(2)} = 0.
\end{aligned} \tag{3.5.9}$$

Thus  $\int_A^B \frac{dQ}{T}$  is independent of path taken: it is dependent on only the initial and final states and therefore a function of state.

Now we go from  $A$  to  $B$  via some reference state  $O$ ,

$$\begin{aligned}
\int_A^B \frac{dQ}{T} &= \int_A^O \frac{dQ}{T} + \int_O^B \frac{dQ}{T}, \\
&= \int_O^B \frac{dQ}{T} - \int_O^A \frac{dQ}{T}, \\
&= S(B) - S(A).
\end{aligned} \tag{3.5.10}$$

Defining the entropy:

$$\boxed{S(A) = \int_O^A \frac{dQ_{\text{rev.}}}{T}}, \tag{3.5.11}$$

which is a function of equilibrium state  $A$ . As should be clear from our discussion, entropy is defined in terms of a reversible processes. That does not mean there is no change in entropy for irreversible processes, just to compute the change we need to find an equivalent reversible process with the same initial and final equilibrium states.

Note that mathematically entropy appears very similar to gravitation and electrostatics, where  $\oint \vec{F} \cdot d\vec{l} = 0$ . If we do not complete the cycle, we can compute a potential;  $U(\vec{r}) = -\int_{\vec{r}_0}^{\vec{r}} \vec{F} \cdot d\vec{l}$ . Like a potential, we can only compute changes in entropy between two equilibrium states.

### 3.5.3 The law of increase in entropy

Suppose a system goes from a state  $A$  to a state  $B$  via an irreversible path and that  $A$  can be reached from  $B$  following a reversible path; see figure 3.10.

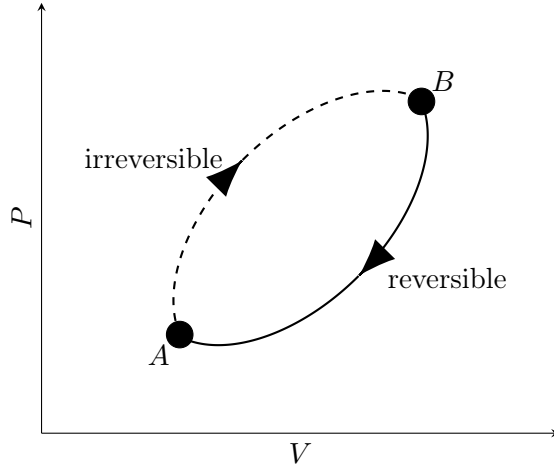


Figure 3.10: Indicator diagram over a cycle composed of an irreversible process from A to B and a reversible process from B to A.

Applying the Clausius inequality (eq. 3.5.1) around the cycle we have

$$\int_A^B \frac{dQ_{\text{irrev.}}}{T} + \int_B^A \frac{dQ_{\text{rev.}}}{T} \leq 0. \quad (3.5.12)$$

As changes in entropy are defined in terms of reversible changes in heat, we can state

$$\begin{aligned} \int_A^B \frac{dQ_{\text{rev.}}}{T} &\geq \int_A^B \frac{dQ_{\text{irrev.}}}{T} \\ S(B) - S(A) &\geq \int_A^B \frac{dQ_{\text{irrev.}}}{T}. \end{aligned} \quad (3.5.13)$$

The inequality must be this way round because  $dQ_{\text{rev.}} > dQ_{\text{irrev.}}$  as we found in eq. 2.1.8 in section 2.1.3. The entropy change for each process is the same; entropy is a function of state and therefore only dependent on the initial and final states. Remember,  $\int_A^B \frac{dQ_{\text{irrev.}}}{T}$  is not entropy.

### Special case: system is thermally isolated

Therefore  $dQ_{\text{irrev.}} = 0$  so,

$$S(B) - S(A) \geq 0. \quad (3.5.14)$$

The entropy of an isolated system can only increase or stay the same.

This is another statement of the second law of thermodynamics. As the only true isolated system is the Universe as a whole, we are stating that the entropy of the Universe never decreases.

If an isolated system is not at equilibrium, its entropy must increase further. At equilibrium functions of state do not change, hence  $dS = 0$ . So, it will reach equilibrium once entropy is maximum. In summary,

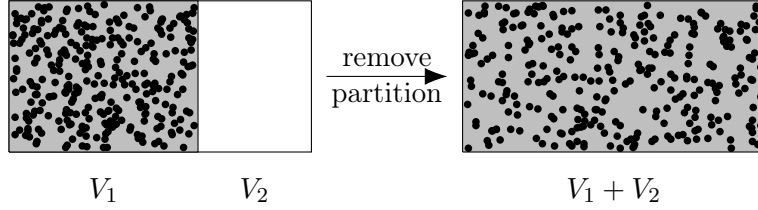


Figure 3.11: A diagram of the Joule expansion of an ideal gas from  $V_1$  to  $V_1 + V_2$ .

an isolated system at equilibrium must be in the state of maximum entropy.

### 3.5.4 Entropy and heat capacity

Entropy is defined as

$$S(A) = \int_0^A \frac{1}{T} dQ_{\text{rev.}} \quad (3.5.15)$$

For an infinitesimal change, we have

$$dS = \frac{dQ_{\text{rev.}}}{T}. \quad (3.5.16)$$

If this change is at constant  $X$  (e.g.  $X = P$  or  $V$ )

$$\begin{aligned} dQ_{\text{rev.}} &= C_X dT, \\ \Rightarrow C_X dT &= T dS. \end{aligned} \quad (3.5.17)$$

Therefore,

$$C_X = T \left( \frac{\partial S}{\partial T} \right)_X. \quad (3.5.18)$$

We can integrate the expression above to obtain

$$S(T, X) - S(T_0, X) = \int_{T_0}^T \frac{C_X(T', X)}{T'} dT' \quad (3.5.19)$$

### 3.5.5 Examples of changes in entropy

#### Irreversible expansion of an ideal gas.

This process is depicted in figure 3.11. If thermally isolated, then  $Q = 0$  and no external work done,  $W = 0$ . Therefore,

$$\Delta E = Q + W = 0. \quad (3.5.20)$$

This implies  $T$  is unchanged (as  $E \equiv E(T)$ ). Entropy is a function of state and changes in entropy are defined in terms of reversible process. So, to calculate the entropy, we choose a reversible process with the same initial and final states: an isothermal expansion from  $V_1$  to  $V_1 + V_2$ . In this case we find

$$\begin{aligned} dE &= 0, \\ \Rightarrow dQ_{\text{rev.}} &= -dW = PdV = \frac{nRT}{V} dV. \end{aligned} \quad (3.5.21)$$

Thus the change in entropy is

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} = \int_{V_1}^{V_1+V_2} \frac{nR}{V} dV = nR \ln \left( \frac{V_1 + V_2}{V_1} \right) > 0. \quad (3.5.22)$$

### Irreversible thermal equilibration of two metal blocks.

Consider two blocks of metal with total heat capacities  $C$  each and initial temperatures  $T_1$  and  $T_2$ , such that  $T_1 < T_2$ . They are placed in thermal contact so heat flows until they reach a final temperature:  $T_f = \frac{1}{2}(T_1 + T_2)$  (*you should be able to show this using conservation of energy*). What is the entropy change of the system?

As entropy is a function of state, we are free to use a reversible path between the two states. This could be made possible using a reversible engine, or if the system found equilibrium with infinite intermediate heat reservoirs in the range  $T_1$  to  $T_2$ . At each step,  $dQ_{\text{rev.}} = CdT$ . Therefore,

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{dQ_{\text{rev.}}}{T} = \int_{T_1}^{T_f} \frac{C}{T} dT = C \ln \left( \frac{T_f}{T_1} \right) > 0, \quad (3.5.23)$$

provided  $T_1 < T_f$ . Similarly,

$$\Delta S_2 = \int_{T_2}^{T_f} \frac{dQ_{\text{rev.}}}{T} = C \ln \left( \frac{T_f}{T_2} \right) < 0. \quad (3.5.24)$$

The total entropy change is then

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = C \ln \left( \frac{T_f}{T_1} \right) + C \ln \left( \frac{T_f}{T_2} \right) \\ &= C \ln \left( \frac{T_f^2}{T_1 T_2} \right). \end{aligned} \quad (3.5.25)$$

**Exercise:** Find the scenarios for when  $\Delta S = 0$  in the above two examples. Then convince yourself entropy can only increase in all other cases.

**Exercise:** Update the calculation for two metal blocks of different heat capacities.

### 3.5.6 The fundamental thermodynamic relation

If two neighbouring equilibrium states of a system are connected by reversible processes, the infinitesimal change of energy can be represented by

$$dE = dQ_{\text{rev.}} + dW_{\text{rev.}}, \quad (3.5.26)$$

$$\boxed{dE = TdS + dW_{\text{rev.}}} \quad (3.5.27)$$

Equation 3.5.27 is known as the Fundamental Thermodynamic Relation (FTR). If the system consists of a fluid, we can update this to:

$$\boxed{dE = TdS - PdV.} \quad (3.5.28)$$

Therefore, we can think of  $E \equiv E(S, V)$  and write

$$dE = \left( \frac{\partial E}{\partial S} \right)_V dS + \left( \frac{\partial E}{\partial V} \right)_S dV \quad (3.5.29)$$

Equating coefficients of  $dS$  and  $dV$  from our two expressions for  $dE$ , we find

$$\Rightarrow T = \left( \frac{\partial E}{\partial S} \right)_V \quad \text{and} \quad P = - \left( \frac{\partial E}{\partial V} \right)_S. \quad (3.5.30)$$

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**Further reading:**

- Sections 13.7, 14.1, 14.2 & 14.3 in [Blundel & Blundell](#).
- Sections 4.2, 4.3, 5.1 & 5.2 in [Mandl](#).
- Section 20.7 in [Young & Freedman](#).
- Sections 8.1, 8.2, 8.4, 8.6, 8.7, 8.8, 8.9, 8.10, 8.11 & 8.12 in [Zemansky & Dittman](#).

### 3.6 Summary

The second law of thermodynamics appears to mean different things in different contexts which are unified by introducing the abstract concept of entropy. This can be confusing.

To summarise, we made some empirical observations about the nature of heat and work which suggest a preferred direction of time. For instance, heat naturally flows from hot bodies to cold bodies. We then studied cyclic processes, in particular engines and how much heat needs to be supplied to produce work. We also considered the reverse process, where work is done to extract heat from a cold body and transfer it to a hot body. From this, we explored the Kelvin-Planck and Clausius statements on the second law regarding engines and heat-pumps and showed they were equivalent. Inspecting reversible cycles, we found that  $\oint \frac{dQ_{\text{rev}}}{T} = 0$ . Expanding this to include irreversible cycles we find  $\oint \frac{dQ}{T} \leq 0$ . From this we then named this heat transfer over temperature to be entropy such that

$$\Delta S = \int_A^B \frac{dQ_{\text{rev}}}{T} \geq 0. \quad (3.6.1)$$

This means that:

- $\Delta S_{\text{Universe}} > 0$  for spontaneous changes.
- $\Delta S_{\text{Universe}} = 0$  for reversible changes, during which

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}. \quad (3.6.2)$$

- Spontaneous changes are always irreversible.
- Reversible, adiabatic changes have  $dS = 0$ .
- An isolated system is at equilibrium at maximum entropy.



With infinitesimal changes in entropy defined as

$$dS = \frac{\bar{d}Q_{\text{rev}}}{T}, \quad (3.6.3)$$

we can then relate this to heat capacities,  $C_X = \left(\frac{\partial Q}{\partial T}\right)_X$ , and the first law of thermodynamics. The latter yielding the fundamental thermodynamic relation, which for a fluid reads

$$dE = TdS - PdV. \quad (3.6.4)$$

### Exercise:

Make a poster for your wall summarising the key ideas and equations from this chapter.

### 3.6.1 Statistical interpretation of entropy (optional)

One route to make sense of entropy is study it using statistical mechanics. Here, we present this as a non-examinable extra to remove some of the abstraction associated with this concept. You will study this in a lot more detail in Statistical Mechanics, PHYS20352, next year.

So far, we have just studied macrostates, that is the overall behaviour of the system according to some measurable quantities (pressure, temperature, etc.). However, we know that this is the result of the individual states of the constituents of the system. For a gas, the position,  $\vec{r}_i$ , and a momentum,  $\vec{p}_i$  of the  $N$  gas particles that compose this gas. So the macrostate of the gas is a result of  $N$  *microstates*. Here, we need to consider the number of available states accessible to the gas. In other words, if the gas has some energy,  $E$ , how many ways that could be distributed across the  $N$  gas molecules. If the gas were to absorb some heat, then this would increase the number of scenarios. If the number of accessible states is given by  $\Omega$ , we can state the Boltzmann definition of entropy:

$$S = k_B \ln \Omega, \quad (3.6.5)$$

where  $k_B$  is the Boltzmann constant. With this we can then relate the increase in entropy of a system to the increase in *disorder*, i.e, the number of possible configurations. As entropy never decreases in an isolated system, the disorder must also never decrease.

## 4 Thermodynamic Potentials

Previously we found the fundamental thermodynamic relation for a fluid, eq. 3.5.28, that allowed us to consider  $E \equiv E(S, V)$ . We also found that

$$T = \left( \frac{\partial E}{\partial S} \right)_V \quad \text{and} \quad P = - \left( \frac{\partial E}{\partial V} \right)_S. \quad (4.0.1)$$

Now, we seek other *energies*, or *potentials*, that depend on other variables which are more directly related to experiment.

We will start by defining the potentials mathematically, then interpret what they correspond to physically. To compliment the mathematical derivations, there are some supplementary notes on derivatives in appendix A which might be of use.

### 4.1 The Helmholtz free energy

From the fundamental thermodynamic relation for a fluid,

$$\begin{aligned} dE &= TdS - PdV, \\ &= TdS + \underbrace{SdT - SdT}_{=0} - PdV, \\ &= d(TS) - SdT - PdV, \\ \Rightarrow d(E - TS) &= -SdT - PdV. \end{aligned} \quad (4.1.1)$$

We define the Helmholtz free energy,  $F(T, V)$ , as<sup>9</sup>

$$\boxed{F(T, V) = E - TS}. \quad (4.1.2)$$

As  $F \equiv F(T, V)$ ,

$$dF = \left( \frac{\partial F}{\partial T} \right)_V dT + \left( \frac{\partial F}{\partial V} \right)_T dV. \quad (4.1.3)$$

Equating coefficients of  $dT$  and  $dV$  we find

$$S = - \left( \frac{\partial F}{\partial T} \right)_V \quad \text{and} \quad P = - \left( \frac{\partial F}{\partial V} \right)_T. \quad (4.1.4)$$

Rearranging eq. 4.1.2 we can write energy as  $E(T, V)$ :

$$E(T, V) = F + TS = F(T, V) - T \left( \frac{\partial F}{\partial T} \right)_V. \quad (4.1.5)$$

Another way we could arrive at the Helmholtz free energy is by applying a *Legendre transformation* on  $E(S, V)$ . We describe this in appendix B, however this is beyond the scope of this course (non-examinable).

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#### **Further reading:**

- Section 16.3 in [Blundell & Blundell](#).

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<sup>9</sup>Physicists use the symbol  $F$ , but many texts (and chemists) use  $A(T, V)$  for Helmholtz free energy.

## 4.2 The Gibbs free energy

To find the Gibbs free energy, we start with the Helmholtz free energy and apply a similar trick<sup>10</sup>,

$$\begin{aligned} d(E - TS) &= -SdT - PdV, \\ &= -SdT + VdP \underbrace{-VdP - PdV}_{=-d(PV)}, \\ \Rightarrow d(E - TS + PV) &= -SdT + VdP. \end{aligned} \tag{4.2.1}$$

We define the Gibbs free energy as:

$$\boxed{G(T, P) = E - TS + PV.} \tag{4.2.2}$$

### Exercise:

Find expressions for  $S$  and  $V$  in terms of derivatives of  $G(T, P)$ .

#### Further reading:

- Section 16.4 in [Blundell & Blundell](#).

## 4.3 Enthalpy

Enthalpy is defined as

$$\boxed{H = E + PV.} \tag{4.3.1}$$

Inspecting its differential, and using the FTR, we find

$$\begin{aligned} dH &= dE + PdV + VdP, \\ &= TdS + VdP. \end{aligned} \tag{4.3.2}$$

Therefore  $H \equiv H(S, P)$ .

### Exercise:

Find expressions for the derivatives of  $H(S, P)$  as we have done for the previous thermodynamic potentials.

#### Further reading:

- Section 16.2 in [Blundell & Blundell](#).

## 4.4 Available work and approach to equilibrium

So far we have introduced various quantities that allow energy to be expressed in terms of different variables. What do they mean? Why is this useful? We will now interpret these quantities physically. To do this, we must first introduce the concept of *available work*.

<sup>10</sup>We could instead apply a second Legendre transformation on  $F(T, V)$  eliminating  $V$ . See appendix [B](#).

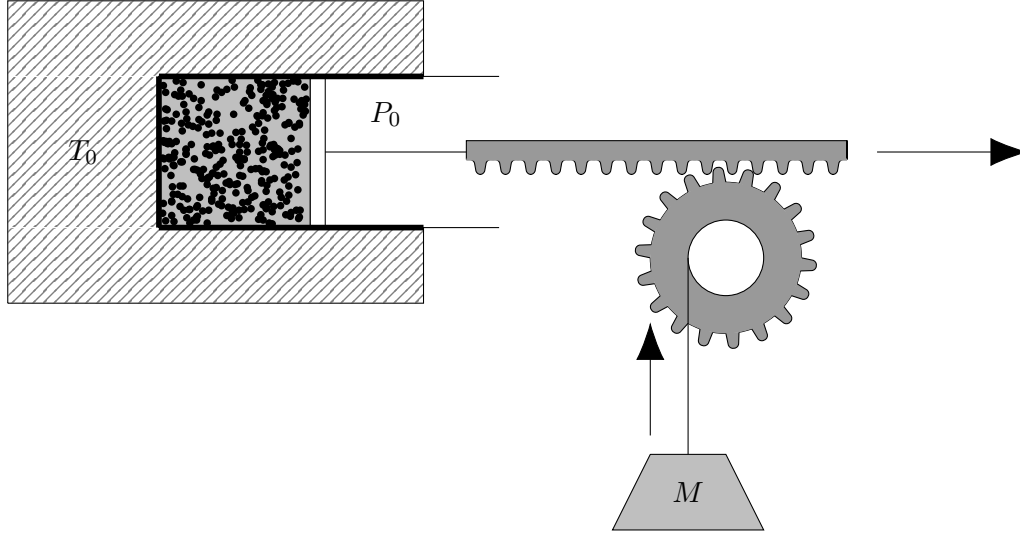


Figure 4.1: A schematic displaying the available work that can be extracted from a system.

#### 4.4.1 Available work

What is the maximum amount of useful work we can extract from a system initially out of equilibrium with its surroundings? Such a system is pictured in figure 4.1 with the surroundings at a temperature  $T_0$  and pressure  $P_0$ . To produce work that will raise the mass  $M$ , the system must expand and therefore:

1. Overcome the external pressure. So some work  $P_0\Delta V$  must be done which cannot be used to raise the mass.
2. Give heat to the surroundings such that the entropy increase in the surroundings compensates for any decrease in entropy in the system,  $\Delta S$ . I.e., by the second law, the system must release some heat  $Q_{\text{out}}$  such that  $\Delta S + Q_{\text{out}}/T_0 \geq 0$ , or  $Q_{\text{out}} \geq -T_0\Delta S$ .

As a consequence not all of the change in internal energy is converted into useful work; work that can *do* something. As the system approaches equilibrium its internal energy will decrease, so we can write the useful work available as,

$$W_{\text{useful}} = (-\Delta E) - Q_{\text{out}} - P_0\Delta V, \quad (4.4.1)$$

using the first law. Specifying that  $Q_{\text{out}} \geq -T_0\Delta S$ , we find

$$\boxed{W_{\text{useful}} \leq -\Delta E + T_0\Delta S - P_0\Delta V}. \quad (4.4.2)$$

From this we define the availability,  $A$ , as

$$A = E - T_0S + P_0V, \quad (4.4.3)$$

such that

$$\boxed{W_{\text{useful}} \leq -\Delta A}, \quad (4.4.4)$$

where equality holds for reversible processes.

As by definition  $T_0$  and  $P_0$  refer to the surroundings, we can relate the available work to thermodynamic potentials:

- For a process that starts at and ends at  $T_0$  and  $P_0$  then

$$\boxed{W_{\text{useful}} \leq -\Delta G.} \quad (4.4.5)$$

- For a process on a system at constant volume<sup>11</sup> that starts and ends at  $T_0$  then

$$\boxed{W_{\text{useful}} \leq -\Delta F.} \quad (4.4.6)$$

### Example

What is the maximum amount of useful work that can be obtained by isochorically cooling 1 mole of an ideal gas from a temperature  $T$  to the temperature  $T_0$  of the surroundings?

As the cooling is isochoric, we have  $\Delta V = 0$ , so

$$W_{\text{max}} = -\Delta E + T_0 \Delta S, \quad (4.4.7)$$

where  $\Delta S < 0$  as it is being cooled. For an ideal gas,

$$\Delta E = C_V \Delta T = C_V (T_0 - T) < 0. \quad (4.4.8)$$

To find the change in entropy, we use a reversible process with the same initial and final states<sup>12</sup>. Hence we use  $dS = dQ/T = C_V dT/T$ , therefore

$$\Delta S = C_V \int_T^{T_0} \frac{dT}{T} = -C_V \ln \frac{T}{T_0} < 0. \quad (4.4.9)$$

The maximum amount of work is therefore

$$W_{\text{max}} = C_V (T - T_0) - C_V T_0 \ln \frac{T}{T_0}. \quad (4.4.10)$$

The rest of the energy is discarded to the surroundings to ensure no overall decrease in entropy.

### Exercise:

Show that  $W_{\text{max}}$  is always positive for any  $T > T_0$ .

#### 4.4.2 Approach to equilibrium

So far we have considered isolated systems and found that they are at equilibrium at maximum entropy, see 3.5.3. If the system can increase its entropy further, it will. A hot and cold block brought into thermal equilibrium, will exchange heat until they are at the same temperature, and not stop half way.

What about non-isolated systems? Of course the entropy of the Universe will increase, but it would be convenient if we could only refer to the system. The availability allows us to do this and this is simple to prove. Suppose we have a system in thermal contact with its surroundings at  $T_0$  and at the pressure  $P_0$  of the surroundings. Taking the system and surroundings together, equilibrium will be reached when entropy is maximised. Imagine

<sup>11</sup>Note: it might be that there are internal volume variables do vary, though their sum must be constant.

<sup>12</sup>This follows the same thought process as the second example in section 3.5.5.

a spontaneous change occurs such that some heat  $Q$  is absorbed by the system such that its volume changes by  $\Delta V$ , so some work  $W = -P_0\Delta V$  is done on the system. From the first law, we have

$$Q = \Delta E + P_0\Delta V. \quad (4.4.11)$$

The total change in entropy for the Universe has two parts:  $\Delta S$  for the system and  $-Q/T_0$  for the surroundings. Therefore,

$$\Delta S_{\text{Universe}} = \Delta S - \frac{Q}{T_0} = \frac{1}{T_0}(T_0\Delta S - \Delta E - P_0\Delta V), \quad (4.4.12)$$

which must be greater than or equal to zero. Thus,

$$\Delta(E - T_0S + P_0V) \leq 0, \quad (4.4.13)$$

$$\Delta A \leq 0; \quad (4.4.14)$$

during any spontaneous change of a system in contact with surroundings at fixed temperature and pressure, the availability does not increase.

#### Exercise:

Check that all the signs in section 4.4 are correct and make sense.

#### Further reading:

- Section 4.6 in [Mandl](#).
- Section 16.5 in [Blundell & Blundell](#).

## 4.5 Interpretation of the potentials

The fundamental thermodynamic relation tells us that energy is constant for processes at constant volume and entropy. Such experimental circumstances are rare to say the least. Furthermore, we cannot directly measure entropy. Therefore, it is useful to introduce other thermodynamic potentials that behave differently to predict the behaviour of a variety of systems.

### 4.5.1 Internal energy $E(S, V)$

If a system is thermally isolated ( $Q = 0$ ), then the change in availability becomes

$$\Delta A = \Delta E + P_0\Delta V = 0. \quad (4.5.1)$$

This is just a statement of the first law in adiabatic processes;

$$\Delta E = -P_0\Delta V. \quad (4.5.2)$$

We simply have that the change in internal energy is equivalent to the work done on the system. Therefore, the internal energy is minimised within the constraints of the system.

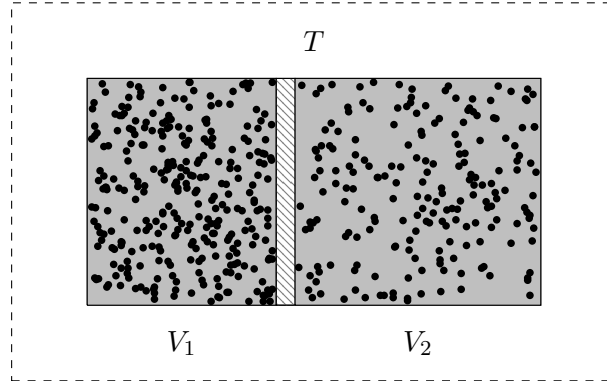


Figure 4.2: A diagram of two fluids separated by a piston in thermal equilibrium with the surroundings as described in the text.

#### 4.5.2 Entropy $S(E, V)$

If the system is thermally isolated at a fixed volume, no heat can enter it and it can do no work. Therefore, both  $E$  and  $V$  are constant. In this case, the change in availability becomes

$$\Delta A = -T_0 \Delta S. \quad (4.5.3)$$

Leaving us with,

$$(\Delta S)_{E,V} \geq 0, \quad (4.5.4)$$

as expected from 3.5.3. All spontaneous changes of this type reach equilibrium when entropy is maximised.

#### 4.5.3 Helmholtz free energy $F(T, V) = E - TS$

If the system undergoes a process that starts and ends at the same temperature and which is at a constant volume, the change in availability becomes

$$\Delta A = \Delta (E - T_0 S) = \Delta F. \quad (4.5.5)$$

Therefore a spontaneous change will reduce the Helmholtz free energy;

$$\boxed{(\Delta F)_{T,V} \leq 0.} \quad (4.5.6)$$

Hence equilibrium will be reached when  $F(T, V)$  is minimised. Though the total volume is constant, there could be *internal variables* that are free to change whilst approaching equilibrium.

#### Example

Consider two fluids separated by a piston in a cylinder of fixed volume,  $V = V_1 + V_2$ , which are also individually in thermal equilibrium with the surroundings at temperature  $T$ . This is drawn in figure 4.2. The total helmholtz free energy is given by

$$F_{\text{tot.}} = F_1(T, V_1) + F_2(T, V_2). \quad (4.5.7)$$

Minimising  $F_{\text{tot}}$  with respect to  $V_1$ ,

$$\begin{aligned}
&\Rightarrow \left( \frac{\partial F_1}{\partial V_1} \right)_T + \frac{\partial(V - V_1)}{\partial V_1} \left( \frac{\partial F_2}{\partial V_2} \right)_T = 0 \\
&\Rightarrow \left( \frac{\partial F_1}{\partial V_1} \right)_T - \left( \frac{\partial F_2}{\partial V_2} \right)_T = 0 \\
&\Rightarrow (-P_1) - (-P_2) = 0 \\
&\therefore P_1 = P_2.
\end{aligned} \tag{4.5.8}$$

So at equilibrium, with respect to varying  $V_1$ , the pressures are equal, as expected.

#### 4.5.4 Gibbs free energy $G(T, P) = F + PV = E - TS + PV$

If the system undergoes a process that starts and ends at the same temperature and pressure, the change in availability becomes

$$\Delta A = \Delta(E - T_0 S + P_0 V) = \Delta G. \tag{4.5.9}$$

Therefore a spontaneous change will reduce the Gibbs free energy;

$$\boxed{(\Delta G)_{T,P} \leq 0.} \tag{4.5.10}$$

In this case, at equilibrium, the Gibbs free energy will be minimised;

$$\boxed{(\Delta G)_{T,P} = 0.} \tag{4.5.11}$$

#### 4.5.5 Enthalpy $H(S, P) = E + PV$

For a system at a constant pressure,  $P_0$ , the work done by the system is  $P_0 \Delta V$ . From the first law,

$$\Delta E = Q - P_0 \Delta V. \tag{4.5.12}$$

The change in enthalpy in this process is,

$$\Delta H = \Delta E + P_0 \Delta V, \tag{4.5.13}$$

therefore

$$\boxed{(\Delta H)_P = Q;} \tag{4.5.14}$$

at constant pressure, the change in enthalpy is equal to the heat.

Note this is always an equality. If the only way to do work is by changing the volume, then the change in enthalpy is the heat released by the system. This is why it is often used in chemistry to study reactions or phase changes.

**Exercise:** earlier we showed that  $C_V = \left( \frac{\partial E}{\partial T} \right)_V$ . Now show that  $C_P = \left( \frac{\partial H}{\partial T} \right)_P$ .



#### 4.5.6 Summary

System	$\Delta E = 0, \Delta V = 0$	$\Delta T = 0, \Delta V = 0$	$\Delta T = 0, \Delta P = 0$
Direction of spontaneous change	$\Delta S \geq 0$	$\Delta F \leq 0$	$\Delta G \leq 0$
Equilibrium achieved when	$\Delta S = 0$	$\Delta F = 0$	$\Delta G = 0$

---

#### Further reading:

- Section 16.5 in [Blundell & Blundell](#).
- Sections 4.4 & 4.5 in [Mandl](#).
- Section 10.1, 10.2 & 10.3 in [Zemansky & Dittman](#).

#### 4.6 Maxwell's relations

Maxwell's relations are a completely unintuitive set of relations between derivatives of thermodynamic quantities. There is no nice physical explanation as to why these are so, however the mathematics to prove them is quite straightforward. They provide us with a valuable link between different quantities, namely relating changes in entropy to variables that are easier to measure experimentally. Appendix A on partial derivatives might be of use here.

From the FTR we can write,

$$dE = TdS - PdV = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV. \quad (4.6.1)$$

Equating coefficients of  $dS$  and  $dV$ ,

$$T = \left(\frac{\partial E}{\partial S}\right)_V \quad \text{and} \quad P = -\left(\frac{\partial E}{\partial V}\right)_S. \quad (4.6.2)$$

As

$$\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S}\right) = \frac{\partial}{\partial S} \left(\frac{\partial E}{\partial V}\right), \quad (4.6.3)$$

then

$$\boxed{\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S}. \quad (4.6.4)$$

Similarly, from

$$dF = -SdT - PdV \quad (4.6.5)$$

we find

$$-\frac{\partial^2 F}{\partial T \partial V} = \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}. \quad (4.6.6)$$

## Exercises

- Using enthalpy,  $H(S, P)$ , find

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \quad (4.6.7)$$

- Using Gibbs free energy,  $G(T, P)$ , find

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \quad (4.6.8)$$

### 4.6.1 Applications

With the Maxwell relations we can show that for an ideal gas  $E \equiv E(T)$ . Starting with the FTR,

$$dE = TdS - PdV, \quad (4.6.9)$$

and writing  $S \equiv S(T, V)$ , we have

$$dE = T \left[ \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \right] - PdV. \quad (4.6.10)$$

However, we can also write  $E \equiv E(T, V)$ , where

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV. \quad (4.6.11)$$

Equating coefficients, we find

$$\begin{aligned} \left(\frac{\partial E}{\partial T}\right)_V &= T \left(\frac{\partial S}{\partial T}\right)_V, \\ \left(\frac{\partial E}{\partial V}\right)_T &= T \left(\frac{\partial S}{\partial V}\right)_T - P. \end{aligned} \quad (4.6.12)$$

Using the second equation, the Maxwell relation stated in eq. 4.6.6 and the ideal gas law, it follows

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = T \frac{nR}{V} - P = P - P = 0. \quad (4.6.13)$$

So  $E$ , for an ideal gas, is only a function of temperature<sup>13</sup>.

### Exercise:

Make a poster for your wall summarising the key ideas and equations from this chapter.

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#### Further reading:

- Section 16.6 in [Blundell & Blundell](#).
- Section 10.5 in [Zemansky & Dittman](#).
- Section 4.5 in [Mandl](#).

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<sup>13</sup>When you study the kinetic theory of gasses you will derive the form of  $E(T)$ .

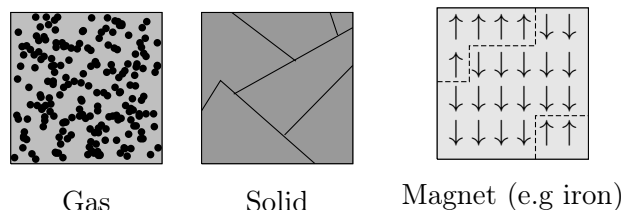


Figure 5.1: Various examples of states of matter. For the case of the magnet, domains of uniform magnetisation are separated by dashed lines.

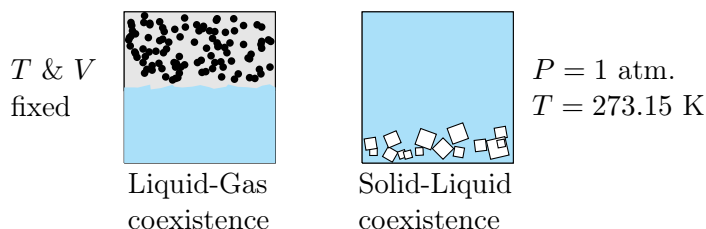


Figure 5.2: Examples of phase coexistence.

## 5 Phase Transitions

We now wish to apply these ideas in thermodynamics to transitions between different states of matter. To do this, we must first clarify what is meant by an *open system*. Until now, we have dealt with closed systems, where the number of particles,  $N$ , has been fixed. We must now accommodate varying  $N$  in our expressions. For example the internal energy for a fluid now becomes

$$E = TS - PV + \mu N, \quad (5.0.1)$$

with FTR,

$$dE = TdS - PdV + \mu dN, \quad (5.0.2)$$

where  $\mu$  is the *chemical potential*. That is an intensive variable which corresponds to the energy required to add a particle to the system.

### 5.1 Phases and states of matter

*States* of matter are distinctive forms in which matter might exist. For instance, gas, liquid, solid, plasma, superfluid, liquid crystal, etc. Some examples are drawn in figure 5.1.

*Phases* of matter are regions of uniform chemical composition and physical state. For instance, the phases of  $\text{H}_2\text{O}$  are typically ice, water and vapour.

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#### Further reading:

- Section 18.6 in [Young & Freedman](#).

### 5.2 Phase equilibrium

For a phase transition to occur, it must be possible for two phases to coexist; see figure 5.2 for some examples.

We can find the conditions for phase equilibrium by considering the total, isolated system to be composed of two open systems:

$$S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2), \quad (5.2.1)$$

where  $E = E_1 + E_2$  and similarly for  $V$  and  $N$ . As the overall system is isolated, it reaches equilibrium when entropy is maximised;  $dS = 0$ , i.e.:

$$dS = \left( \frac{\partial S}{\partial E} \right)_{V,N} dE + \left( \frac{\partial S}{\partial V} \right)_{E,N} dV + \left( \frac{\partial S}{\partial N} \right)_{E,V} dN = 0. \quad (5.2.2)$$

Writing this in terms of the two open systems, and recognising that the system is isolated<sup>14</sup>, we have

$$\begin{aligned} 0 = dS = & \left[ \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} - \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} \right] dE_1 \\ & + \left[ \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} - \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2} \right] dV_1 \\ & + \left[ \left( \frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} - \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} \right] dN_1. \end{aligned} \quad (5.2.3)$$

For the above to equal zero, it must be the differentials are equal for each variable;

$$\begin{aligned} \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} &= \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2}, \\ \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} &= \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2}, \\ \left( \frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} &= \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2}. \end{aligned} \quad (5.2.4)$$

Equating coefficients from eqs. 5.0.2 and 5.2.2, we have three conditions for phase equilibrium:

- $T_1 = T_2$ , no heat flow between the systems.
- $P_1 = P_2$ , the systems are at mechanical equilibrium.
- $\mu_1 = \mu_2$ , there is no preference to be in one state over the other.

It is helpful to view the last condition in the context of the Gibbs free energy. For fixed temperature and pressure,

$$\begin{aligned} G(T, P) &= E - TS + PV, \\ &= N\mu(T, P). \end{aligned} \quad (5.2.5)$$

So the chemical potential is the Gibbs free energy per particle. For a system with  $N_1$  particles in phase 1 and  $N_2$  particles in phase 2, the total Gibbs free energy will be

$$G_{\text{total}} = N_1\mu_1(T, P) + N_2\mu_2(T, P), \quad (5.2.6)$$

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<sup>14</sup> $dE = dV = dN = 0$

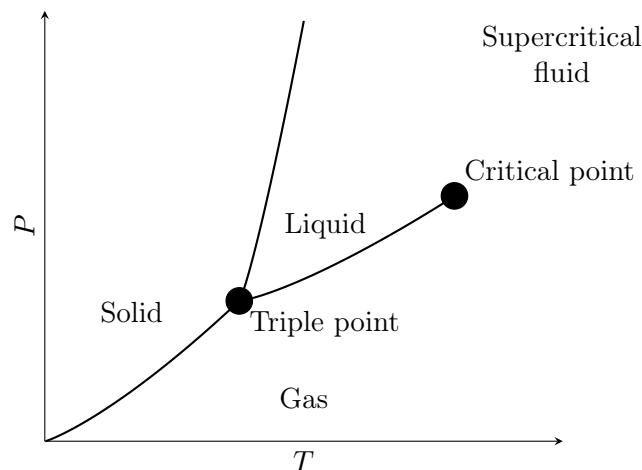


Figure 5.3: Phase diagram for a typical substance illustrating the domains of different phases separated by lines of coexistence. The three coexistence lines meet at the triple point and the liquid-vapour coexistence ends at the critical point. This can be extended to three dimensions by varying  $V$  out of the page.

where  $N_1 + N_2 = N$ , and both  $T$  and  $P$  are fixed. The total Gibbs energy is minimised at equilibrium, so

$$\begin{aligned} \text{if } \mu_1 < \mu_2 &\Rightarrow N_1 = N, N_2 = 0; \\ \text{if } \mu_1 > \mu_2 &\Rightarrow N_1 = 0, N_2 = N. \end{aligned} \tag{5.2.7}$$

---

#### Further reading:

- Sections 8.1 & 8.2 in [Mandl](#).
- Section 28.2 in [Blundel & Blundell](#).
- Section 11.6 in [Zemansky & Dittman](#).

### 5.3 Phase diagram of a typical substance

For a typical substance at fixed pressure, we could increase the temperature and observe a succession of different phases: solid  $\rightarrow$  liquid  $\rightarrow$  gas. We could plot this for a variety of pressures and temperatures on a *phase diagram*. See figure 5.3 for illustration for a typical substance. The lines plotted in a phase diagram are lines of coexistence, where two phases are present at equilibrium. These all meet at the *triple point* where all three phases are present at equilibrium. For water, the triple point occurs at  $T = 273.16$  K and  $P = 611.66$  Pa. If we were to heat ice below this pressure, it would sublime directly to vapour; the liquid phase would not be observed. The liquid-gas coexistence line ends at the *critical point*. Beyond this, we cannot distinguish between the two phases<sup>15</sup>. Therefore, at a fixed pressure between the triple and critical points, if we were to heat ice we would see all three phases. At a pressure above the critical point, we would not observe a liquid-gas transition.

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<sup>15</sup>This is as odd as it sounds. See section 7.1.2 in [Flowers & Mendoza](#) for a detailed exposition.

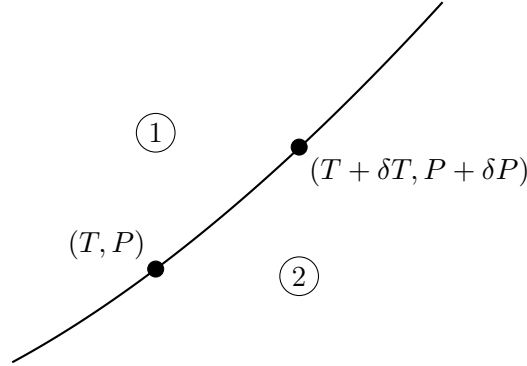


Figure 5.4: Two neighbouring points on a coexistence curve between two states of matter.

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**Further reading:**

- Section 8.3 in [Mandl](#).
- Section 18.6 in [Young & Freedman](#).
- Section 7.1 in [Flowers & Mendoza](#).
- Sections 9.1, 9.2 & 9.3 in [Zemansky & Dittman](#).

## 5.4 Clausius-Clapeyron relation

Consider two neighbouring points on a coexistence curve  $(T, P)$  and  $(T + \delta T, P + \delta P)$ , as illustrated in figure 5.4. For the phases to coexist, their chemical potentials must be equal. As  $\mu(T, P) = G(T, P)/N$ , we could also work with the Gibbs free energy per mole:  $G^m(T, P) = G(T, P)/n$ , or specific Gibbs free energy<sup>16</sup>. Therefore, at phase equilibrium at  $(T, P)$ , we have

$$G_1^m(T, P) = G_2^m(T, P). \quad (5.4.1)$$

Similarly, at  $(T + \delta T, P + \delta P)$

$$G_1^m(T + \delta T, P + \delta P) = G_2^m(T + \delta T, P + \delta P). \quad (5.4.2)$$

Expanding the above expression,

$$G_1^m(T, P) + \delta T \left( \frac{\partial G_1^m}{\partial T} \right)_P + \delta P \left( \frac{\partial G_1^m}{\partial P} \right)_T = G_2^m(T, P) + \delta T \left( \frac{\partial G_2^m}{\partial T} \right)_P + \delta P \left( \frac{\partial G_2^m}{\partial P} \right)_T. \quad (5.4.3)$$

As  $G \equiv G(T, P)$  and  $dG = -SdT + VdP$ , we have

$$\left( \frac{\partial G}{\partial T} \right)_P = -S \quad \text{and} \quad \left( \frac{\partial G}{\partial P} \right)_T = V. \quad (5.4.4)$$

---

<sup>16</sup>Gibbs free energy per unit mass.

Simplifying eq. 5.4.3 and substituting the derivatives, we find

$$\frac{\delta P}{\delta T} = \boxed{\frac{S_2^m - S_1^m}{V_2^m - V_1^m} = \frac{dP}{dT}}, \quad (5.4.5)$$

where  $S^m$  and  $V^m$  refer to entropy and volume per mole respectively. Eq. 5.4.5 is the Clausius-Clapeyron relation which relates different points of phase coexistence. For instance, how the boiling point of water changes with pressure (as demonstrated at different altitudes).

As stated a number of times, entropy is abstract and tricky to relate to experiment. We can rewrite  $\Delta S^m$  as pressure is constant at each point. Starting with the molar Gibbs free energy,

$$\begin{aligned} G_1^m &= G_2^m, \\ E_1^m - TS_1^m + PV_1^m &= E_2^m - TS_2^m + PV_2^m, \\ T(S_2^m - S_1^m) &= \underbrace{E_2^m + PV_2^m}_{H_2^m} - \underbrace{(E_1^m + PV_1^m)}_{H_1^m}, \\ \Rightarrow S_2^m - S_1^m &= \frac{\Delta H^m}{T}. \end{aligned} \quad (5.4.6)$$

So we can write the Clausius-Clapeyron relation in an alternative form dependent on the change in enthalpy per mole:

$$\boxed{\frac{dP}{dT} = \frac{\Delta S^m}{\Delta V^m} = \frac{\Delta H^m}{T\Delta V^m}}. \quad (5.4.7)$$

You might have come across  $\Delta H^m$  before where it was referred to as the *latent heat of transition*.

### Example

Estimate the melting temperature of ice at 400 atm, given that it melts at 0°C at 1 atm, and that:  $\rho_{\text{water}} = 1000 \text{ kg m}^{-3}$ ,  $\rho_{\text{ice}} = 917 \text{ kg m}^{-3}$  and specific latent heat,  $\Delta H = H_{\text{water}} - H_{\text{ice}} = 333.5 \text{ kJ kg}^{-1}$ .

As we are given the specific latent heat, we must work with the specific volumes which are given by

$$V_{\text{water}} = \frac{1}{\rho_{\text{water}}} = 1.000 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \quad \& \quad V_{\text{ice}} = \frac{1}{\rho_{\text{ice}}} = 1.091 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}. \quad (5.4.8)$$

From the Clausius-Clapeyron relation, eq. 5.4.7, we find

$$\begin{aligned} \frac{\delta P}{\delta T} &\cong \frac{dP}{dT} = \frac{\Delta H}{T(V_{\text{water}} - V_{\text{ice}})}, \\ \Rightarrow \delta T &= \frac{T(V_{\text{water}} - V_{\text{ice}})}{\Delta H} \delta P \\ &= \frac{273 \text{ K} (1.000 - 1.091) \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}}{333.5 \text{ kJ kg}^{-1}} (400 - 1) \times 101325 \text{ Pa}, \\ &\simeq -3.0 \text{ K}. \end{aligned} \quad (5.4.9)$$

So the melting point of ice is depressed to  $-3.0 \text{ }^\circ\text{C}$ .

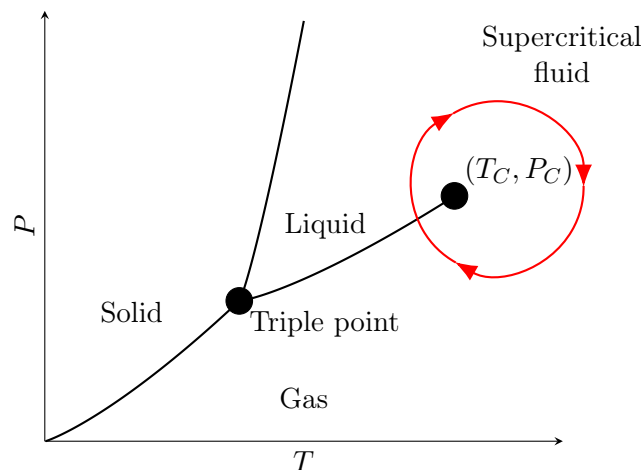


Figure 5.5: Phase diagram for a typical substance displaying a path between liquid and gas phases around the critical point,  $(T_C, P_C)$ , in red.

### Exercise

Check that the units in the calculation do reduce to Kelvin.

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#### Further reading:

- Section 28.3 in [Blundell & Blundell](#).
- Sections 8.4 & 8.5 in [Mandl](#).
- Sections 11.3 & 11.4 in [Zemansky & Dittman](#).

## 5.5 Modelling the liquid-gas transition

As the liquid-gas coexistence line ends at the critical point, we could vary a fluid's pressure and temperature such that it completes a cycle around this point, see figure 5.5. This suggests that from the liquid phase we could reach the gas phase without there being a phase transition (e.g. boiling). Therefore, both liquid and gas could be described by the same equation of state.

We can understand this further by inspecting pressure against volume, see figure 5.6. At the critical point we have both

$$\left(\frac{\partial P}{\partial V}\right)_{T_C} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = 0. \quad (5.5.1)$$

Below the critical point there exists a region of coexistence between the two phases. Suppose a gas is undergoing isothermal compression at a pressure below  $P_C$ . Once the volume enters the coexistence region, then pressure remains constant whilst the two phases coexist. As volume is decreased further, more gas condenses to liquid. Once the entirety of the fluid is in liquid form, the fluid exits the coexistence region and pressure varies sharply with changes in volume.

In figure 5.6 we can also highlight the presence of *metastable states*. These are the continuations of the isotherms within the region of coexistence. These are unstable varieties of liquid or gas that have not yet boiled or condensed. They can survive long enough for their



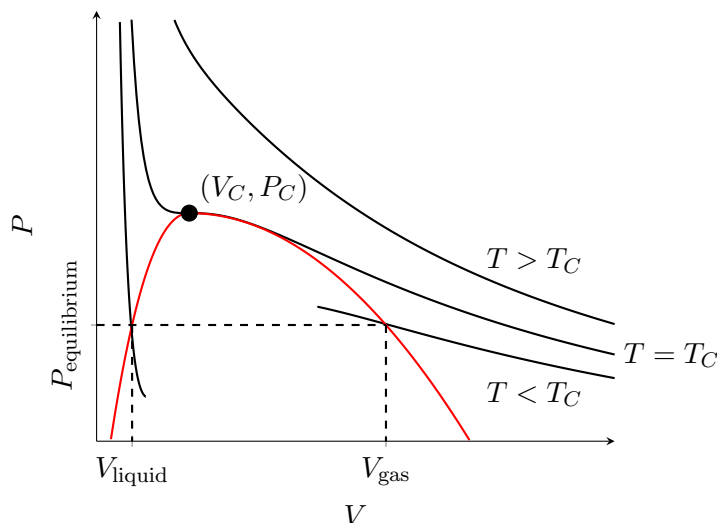


Figure 5.6: Isotherms in a  $PV$  diagram close to the critical point,  $(V_C, P_C, T_C)$ . The area under the red curve shows the region of coexistence between the liquid and gas phases. The continuation of the isotherm within this region are metastable states.

properties to be measured, though will eventually transition to a more stable state of lower Gibbs energy. For water to boil it requires bubbles of vapour to form first. This can happen quickly if they have somewhere to form known as *cavitation points*. These could be a scratch in the container or speck of dust. Without these the water is heated above its boiling point which is known as a *superheated fluid*. Any slight disturbance to this state will cause it to boil all at once<sup>17</sup>.

We could not describe solid-liquid coexistence in the same way as the curve does not end. Typically solids are crystal structures with symmetries that are not present in liquids. Symmetry is either present or absent, we cannot gradually transition from one state to another.

### 5.5.1 Van der Waals' equation

To model the liquid phase we must take into account interactions between molecules. To that end, the ideal gas equation is no longer suffice. We wish to account for short-range strong repulsion and long-range weak attraction between molecules, see figure 5.7 for a possible interaction potential

This effects are present in the Van der Waals equation:

$$P = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}, \quad (5.5.2)$$

where  $nb$  is the smallest volume the fluid can occupy and  $-a \frac{n^2}{V^2}$  represents the effects of the weak attraction between molecules. Both  $a$  and  $b$  are constants extracted from data for a particular substance.

<sup>17</sup>This is why you should never microwave water.

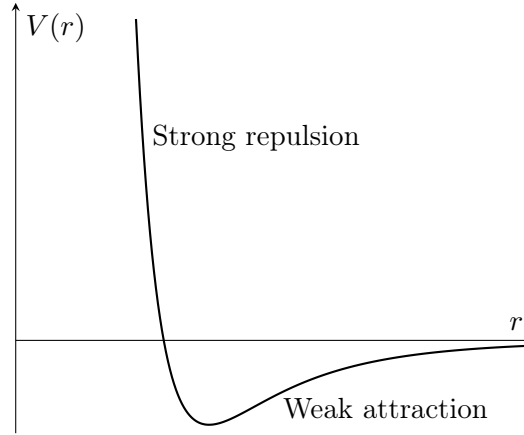


Figure 5.7: Interaction potential between two molecules against the separation between them.

### Exercise

By considering the Van der Waals equation and the FTR with  $dN = 0$ , show that  $E \equiv E(T, V)$ . Comment on the dependency with respect to volume.

### 5.5.2 Predictions from Van der Waals' equation

The Van der Waals equation is cubic for  $V$ :

$$PV^2(V - nb) - nRTV^2 + an^2(V - nb) = 0, \quad (5.5.3)$$

therefore there are either one real root or three. We find this is dependent on the temperature:

- For  $T > T_C = \frac{8a}{27bR}$ , there is only one solution for  $V$  where  $P$  decreases with  $V$ .
- For  $T = T_C$ , the isotherm has a point of inflexion where

$$\left(\frac{\partial P}{\partial V}\right)_{T_C} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = 0 \quad (5.5.4)$$

at  $V_C = 3nb$ .

- For  $T < T_C$  there are three solutions, however one is unphysical where  $\left(\frac{\partial P}{\partial V}\right)_{T_C} > 0$ .

These outcomes are displayed in figure 5.8. In conclusion, the Van der Waals equation succeeds in describing the existence of the critical point and the coexistence of the liquid and vapour below the critical point.

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#### Further reading:

- Section 8.6 in [Mandl](#).
- Sections 7.2, 7.3 & 7.6 in [Flowers & Mendoza](#).

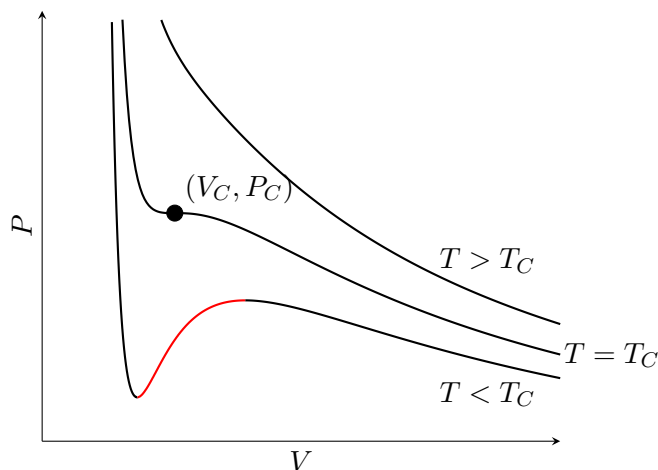


Figure 5.8: Isotherms predicted by the Van der Waals equation in a  $PV$  diagram close to the critical point,  $(V_C, P_C, T_C)$ . The red line in the coexistence region is nonphysical as described in the text.

## 5.6 Classification of phase transitions

The liquid-gas phase transition has a latent heat; i.e. we found that

$$T(S_{\text{gas}}^m - S_{\text{liquid}}^m) = \Delta H^m > 0. \quad (5.6.1)$$

We also know that

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad (5.6.2)$$

therefore  $\left(\frac{\partial G}{\partial T}\right)_P$  is discontinuous at the transition. This is an example of a *first-order* or *discontinuous* transition. A plot illustrating this can be found in figure 5.9.

However not all phase transitions have  $\Delta H \neq 0$ . Examples of these transitions include normal metal-superconductor transitions, normal fluid-superfluid transition in  $^4\text{He}$ , and magnetic non-magnetic transition in iron. All of these have  $\Delta H = 0$ , thus it is often more informative to study the heat capacity over the transition where

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_P \neq 0. \quad (5.6.3)$$

These are known as *second-order* or *continuous transitions*.

### Exercise:

Make a poster for your wall summarising the key ideas and equations from this chapter.

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#### Further reading:

- Section 28.7 in [Blundell & Blundell](#).
- Section 14.4 in [Zemansky & Dittman](#).

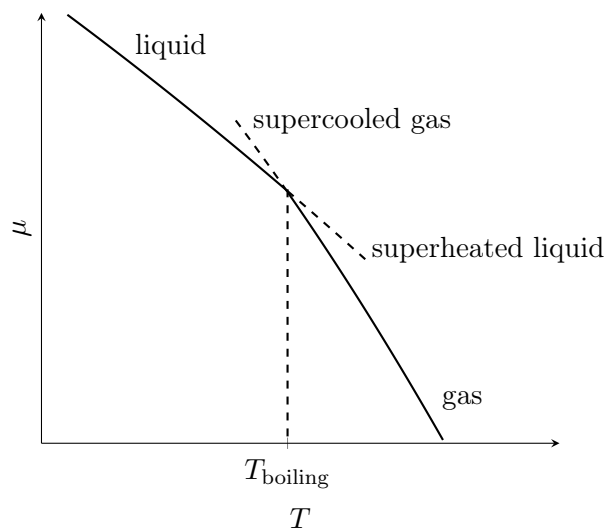


Figure 5.9: Chemical potential against temperature over a liquid-gas phase transition. The dashed extensions to each phase correspond to metastable states.

## A Notes on partial derivatives

Throughout the course we manipulate partial derivatives. Some of the steps appear *wrong* and some of the results are counter-intuitive. Here, we discuss relations between partial derivatives.

Consider some function  $f(x, y, z) = 0$ , such that we can always solve this to express one variable in terms of the other two; e.g.,  $z \equiv z(x, y)$ . This could represent the ideal gas law,  $PV - Nk_B T = 0$ , where we could solve for pressure,  $P = \frac{Nk_B T}{V}$ . Regarding  $z \equiv z(x, y)$ , it has a total derivative given by

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy. \quad (\text{A.0.1})$$

Applying the same approach to  $y(x, z)$  and substituting  $dy$  into eq. A.0.1, we find

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x \left[ \left( \frac{\partial y}{\partial x} \right)_z dx + \left( \frac{\partial y}{\partial z} \right)_x dz \right]. \quad (\text{A.0.2})$$

$dx$  and  $dz$  are independent changes, so their coefficients in eq. A.0.2 must equal. Equating coefficients of  $dz$  we have

$$1 = \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial z} \right)_x. \quad (\text{A.0.3})$$

Which fixes the common relationship between a derivative and its reciprocal, i.e.:

$$\left( \frac{\partial z}{\partial y} \right)_x = \left[ \left( \frac{\partial y}{\partial z} \right)_x \right]^{-1}. \quad (\text{A.0.4})$$

Inspecting coefficients of  $dx$  in eq. A.0.2, we find

$$0 = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_z. \quad (\text{A.0.5})$$

Rearranging,

$$\begin{aligned} \Rightarrow \left( \frac{\partial z}{\partial x} \right)_y &= - \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_z, \\ \Rightarrow \left( \frac{\partial z}{\partial x} \right)_y \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x &= -1, \end{aligned} \quad (\text{A.0.6})$$

where we have used the relationship eq. A.0.3. This relationship is far less obvious than eq. A.0.3.

If we have two functions of  $x$  and  $y$ ,  $u(x, y)$  and  $v(x, y)$ , then

$$\left( \frac{\partial u}{\partial v} \right)_x = \left( \frac{\partial u}{\partial y} \right)_x \left( \frac{\partial y}{\partial v} \right)_x \quad \text{and} \quad \left( \frac{\partial u}{\partial v} \right)_y = \left( \frac{\partial u}{\partial x} \right)_y \left( \frac{\partial x}{\partial v} \right)_y, \quad (\text{A.0.7})$$

which you should be able to prove.

Lastly, we also have that the order of differentiation does not matter,

$$\frac{\partial^2 u(x, y)}{\partial x \partial y} = \frac{\partial^2 u(x, y)}{\partial y \partial x}, \quad (\text{A.0.8})$$

which you have encountered in your mathematics courses.

## B Legendre Transformations

An alternative approach to determine the thermodynamic potentials is to apply Legendre transformations. These are a more abstract mathematical idea that are a consequence of how we could define a function. Typically, for some curve  $y(x)$ , we represent this through sets of  $(x, y)$  points [ $y_1 = y(x_1)$ ,  $y_2 = y(x_2)$ , etc.]. However, for a convex curve, we could also represent this via sets of tangents, defined by slopes,  $P$ , and intercepts,  $\Psi$ , see figure B.1. If the relationship  $\Psi = \Psi(P)$  is known, then the curve can be drawn.

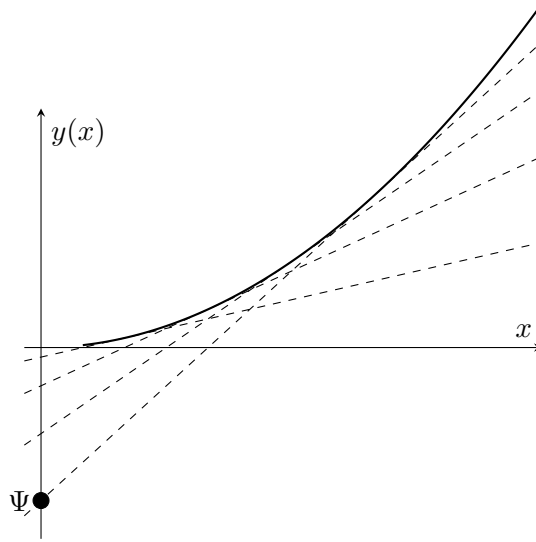


Figure B.1: Illustration of how  $y(x) = x^2$  can also be represented through intercepts  $\Psi$  and tangents  $P$ , such that  $\Psi(P) = -\frac{P^2}{4}$ .

The tangent through a point  $(x, y)$  on the curve has a slope

$$P = \frac{y - \Psi}{x - 0}, \quad (\text{B.0.1})$$

where  $\Psi$  is the intercept of the tangent. Rearranging, we have

$$\Psi(P) = y - xP. \quad (\text{B.0.2})$$

We must now write  $x$  and  $y$  as a function of  $P$ . This is where it is important that the curve is convex, such that any slope is unique to a single value of  $x$ , such that  $P = y'(x)$ , where  $y' = dy/dx$ . Then, for a given  $x = x_P$ , we can find  $y_P = y(x_P)$ , and have

$$\Psi(P) = y_P - x_P P, \quad (\text{B.0.3})$$

where  $x_P$  and  $y_P$  are now constants associated with each value of  $P$ .

As an example, we can find the Legendre transformation of  $y(x) = x^2$ .  $y'(x) = 2x$ , so particular slope is given by,

$$P = 2x_P. \quad (\text{B.0.4})$$

We then have

$$y_P = y(x_P) = (x_P)^2 = \left(\frac{P}{2}\right)^2 = \frac{P^2}{4}. \quad (\text{B.0.5})$$

This leaves us with

$$\begin{aligned}\Psi(P) &= y_P - x_P P, \\ &= \frac{P^2}{4} - \frac{P}{2}P, \\ &= -\frac{P^2}{4}.\end{aligned}\tag{B.0.6}$$

So  $\Psi(P) = -\frac{P^2}{4}$  is the Legendre transform of  $y(x) = x^2$ .

**Exercise:** show that the Legendre transform of  $y(x) = e^x$  is  $\Psi(P) = P(1 - \ln P)$ .

In thermodynamics, it allows us to remove an unwanted state variable in favour of another. For example, from  $E(S, V)$  we could replace the entropy dependence with temperature  $T = (\frac{\partial E}{\partial S})_V$ . Applying this Legendre transformation on energy with respect to entropy, at fixed volume, yields the Helmholtz energy:

$$F(T, V) = E - \left(\frac{\partial E}{\partial S}\right)_V S = E - TS.\tag{B.0.7}$$

As shown in subsubsection 4.5.3, we find the entropy dependence is removed,

$$dF = dE - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT.\tag{B.0.8}$$

Identically, we could apply a Legendre transform on  $E$  with respect to  $V$ , at fixed  $S$ , to obtain the enthalpy,  $H$ ;

$$H(S, P) = E - \left(\frac{\partial E}{\partial V}\right)_S V = E + PV.\tag{B.0.9}$$

**Exercise:** Find the Gibbs free energy by applying the appropriate Legendre transform on  $F(T, V)$ .

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**Further reading:**

- Chapter 3 & chapter 4 up to and including 4.3 in [Modern Thermodynamics with Statistical Mechanics by C. S. Helrich](#).