Chapter 5
Simple applications of macroscopic thermodynamics

Speaker: Yufeng Lu
Supervisor: Dr. Jun Fan

City University of Hong Kong

Oct. 17, 2014

Line

Macro parameters $(E, T \ldots)$

$\downarrow$ Thermodynamic laws

Basic relations $(TdS = dE + pdV \ldots)$

$\downarrow$ Thermodynamic functions

Maxwell relations

$\downarrow$

General relations $(C_p - C_V$ from V, T, p...)

Line

Macro parameters $(E, T \ldots)$

$\downarrow$ Thermodynamic laws

Basic relations $(TdS = dE + pdV \ldots)$

$\downarrow$ Thermodynamic functions

Maxwell relations

$\downarrow$

General relations $(C_p - C_V \text{ from } V, T, p...)$

Why the last step?

experimental measurements $\rightarrow$ theoretical properties.

Outline

1. **An example: $TdS = dE + pdV$.**
2. **A special case: for ideal gases**
   - Energy: $E = E(T)$
   - Heat capacities: $c_p = c_V + R$
   - Quasi-static adiabatic process: $pV^\gamma =$constant
3. **Maxwell relations and thermodynamic functions**
4. **General cases**
   - Heat capacities, after Maxwell relations
   - Energy, after Maxwell relations
5. **Applications**
   - Heat engines
   - Refrigerators
   - Equivalence of Kelvin and Clausius statements

Outline

1. **An example:** $TdS = dE + pdV$.
2. **A special case: for ideal gases**
   - Energy: $E = E(T)$
   - Heat capacities: $c_p = c_V + R$
   - Quasi-static adiabatic process: pV^{γ} =constant
3. **Maxwell relations and thermodynamic functions**
4. **General cases**
   - Heat capacities, after Maxwell relations
   - Energy, after Maxwell relations
5. **Applications**
   - Heat engines
   - Refrigerators
   - Equivalence of Kelvin and Clausius statements

An example

An example..

An example

An example..

Examples

An example

An example..

Examples are always useful.

An example

To an infinitesimal process,

An example

To an infinitesimal process, the first law yields

An example

To an infinitesimal process, the first law yields

$$dQ = dE + dW. \tag{1.1}$$

An example

To an infinitesimal process, the first law yields

$$dQ = dE + dW. \tag{1.1}$$

If the process is also quasi-static,

An example

To an infinitesimal process, the first law yields

$$dQ = dE + dW. \tag{1.1}$$

If the process is also quasi-static, the second law says

$$dQ = TdS. \tag{1.2}$$

An example

To an infinitesimal process, the first law yields

$$dQ = dE + dW. \tag{1.1}$$

If the process is also quasi-static, the second law says

$$dQ = TdS. \tag{1.2}$$

As well known,

An example

To an infinitesimal process, the first law yields

$$dQ = dE + dW. \tag{1.1}$$

If the process is also quasi-static, the second law says

$$dQ = TdS. \tag{1.2}$$

As well known, the work done by the system is given by

$$dW = pdV. \tag{1.3}$$

An example

To an infinitesimal process, the first law yields

$$dQ = dE + dW. \tag{1.1}$$

If the process is also quasi-static, the second law says

$$dQ = TdS. \tag{1.2}$$

As well known, the work done by the system is given by

$$dW = pdV. \tag{1.3}$$

Combining (1.1) to (1.3), one may get that

$$TdS = dE + pdV. \tag{5.1.5}$$

The aim of this chapter

The whole chapter will be based on

The aim of this chapter

The whole chapter will be based on $\boxed{\text{only}}$ the thermodynamic laws

The aim of this chapter

The whole chapter will be based on only the thermodynamic laws to derive important relationships between macroscopic quantities.

The aim of this chapter

The whole chapter will be based on $\boxed{\text{only}}$ the thermodynamic laws to derive important $\boxed{\text{relationships}}$ between macroscopic quantities. Those conclusions are $\boxed{\text{completely}}$ $\boxed{\text{independent}}$ of

The aim of this chapter

The whole chapter will be based on $\boxed{\text{only}}$ the thermodynamic laws to derive important $\boxed{\text{relationships}}$ between macroscopic quantities. Those conclusions are $\boxed{\text{completely}}$ $\boxed{\text{independent}}$ of any specific models assumed to describe

The aim of this chapter

The whole chapter will be based on **only** the thermodynamic laws to derive important **relationships** between macroscopic quantities. Those conclusions are **completely independent** of any specific models assumed to describe **the microscopic constituents of a system.**

Outline

1. **An example:** $TdS = dE + pdV$.
2. **A special case: for ideal gases**
   - Energy: $E = E(T)$
   - Heat capacities: $c_p = c_V + R$
   - Quasi-static adiabatic process: pV^γ =constant
3. **Maxwell relations and thermodynamic functions**
4. **General cases**
   - Heat capacities, after Maxwell relations
   - Energy, after Maxwell relations
5. **Applications**
   - Heat engines
   - Refrigerators
   - Equivalence of Kelvin and Clausius statements

Energy

Energy

Theorem

For an ideal gas, its internal energy does not depend on its volume, but only on its temperature, which is

$$E = E(T).$$

Energy

Theorem

For an ideal gas, its internal energy does not depend on its volume, but only on its temperature, which is

$$E = E(T).$$

proof. Suppose that there are ν mole ideal gas.

Energy

Theorem

For an ideal gas, its internal energy does not depend on its volume, but only on its temperature, which is

$$E = E(T).$$

proof. Suppose that there are ν mole ideal gas. The equation of states and (5.1.5) tell us,

$$\left.\begin{aligned} T dS = dE + p dV; \\ \frac{p}{T} = \frac{\nu R}{V}; \end{aligned}\right\} \Rightarrow dS = \frac{1}{T} dE + \frac{\nu R}{V} dV. \tag{2.1}$$

Energy

Theorem

For an ideal gas, its internal energy does not depend on its volume, but only on its temperature, which is

$$E = E(T).$$

proof. Suppose that there are ν mole ideal gas. The equation of states and (5.1.5) tell us,

$$\left.\begin{aligned} T dS = dE + p dV; \\ \frac{p}{T} = \frac{\nu R}{V}; \end{aligned}\right\} \Rightarrow dS = \frac{1}{T} dE + \frac{\nu R}{V} dV. \tag{2.1}$$

From the exact differential of E, one may obtain that

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV. \tag{2.2}$$

Energy

Combining (2.1) and (2.2), one gets that

Energy

Combining (2.1) and (2.2), one gets that

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \left[\frac{\nu R}{V} + \left(\frac{\partial E}{\partial V}\right)_T\right] dV.$$

Energy

Combining (2.1) and (2.2), one gets that

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \left[\frac{\nu R}{V} + \left(\frac{\partial E}{\partial V}\right)_T\right] dV.$$

Compared with

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,$$

Energy

Combining (2.1) and (2.2), one gets that

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \left[\frac{\nu R}{V} + \left(\frac{\partial E}{\partial V}\right)_T\right] dV.$$

Compared with

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,$$

one has

$$\begin{aligned}\left(\frac{\partial S}{\partial T}\right)_V &= \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V;\\ \left(\frac{\partial S}{\partial V}\right)_T &= \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}.\end{aligned}$$

Energy

Combining (2.1) and (2.2), one gets that

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \left[\frac{\nu R}{V} + \left(\frac{\partial E}{\partial V}\right)_T\right] dV.$$

Compared with

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,$$

one has

$$\begin{aligned}
\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial S}{\partial T}\right)_V &= \left(\frac{\partial}{\partial V}\right)_T \left[\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V\right];\\
\left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial}{\partial T}\right)_V \left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right].
\end{aligned}$$

Energy

By the equality of the second derivatives for $S(T, V)$,

Energy

By the equality of the second derivatives for $S(T, V)$,

$$\left(\frac{\partial}{\partial V}\right)_T \left[\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V\right] = \left(\frac{\partial}{\partial T}\right)_V \left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right],$$

Energy

By the equality of the second derivatives for $S(T, V)$,

$$\left(\frac{\partial}{\partial V}\right)_T \left[\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V\right] = \left(\frac{\partial}{\partial T}\right)_V \left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right],$$

which further implies

$$\cancel{\frac{1}{T}\frac{\partial^2 E}{\partial V \partial T}} = \left(\frac{\partial}{\partial T}\right)_V \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \cancel{\frac{1}{T}\frac{\partial^2 E}{\partial T \partial V}} + 0.$$

Energy

By the equality of the second derivatives for $S(T, V)$,

$$\left(\frac{\partial}{\partial V}\right)_T \left[\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V\right] = \left(\frac{\partial}{\partial T}\right)_V \left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right],$$

which further implies

$$= \left(\frac{\partial}{\partial T}\right)_V \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T \qquad .$$

Energy

By the equality of the second derivatives for $S(T, V)$,

$$\left(\frac{\partial}{\partial V}\right)_T \left[\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V\right] = \left(\frac{\partial}{\partial T}\right)_V \left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right],$$

which further implies

$$= \left(\frac{\partial}{\partial T}\right)_V \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T \qquad .$$

Therefore,

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

Energy

By the equality of the second derivatives for $S(T, V)$,

$$\left(\frac{\partial}{\partial V}\right)_T \left[\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V\right] = \left(\frac{\partial}{\partial T}\right)_V \left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right],$$

which further implies

$$= \left(\frac{\partial}{\partial T}\right)_V \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T \qquad .$$

Therefore,

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

which means the internal energy of an ideal gas is not dependent on its volume.

Heat capacities

Heat capacities

Consider a system $A = A(T, y)$.

Heat capacities

Consider a system $A = A(T, y)$. y probably be V or p.

Heat capacities

Consider a system $A = A(T, y)$. y probably be V or p. Recall that,

$$C_y := \left(\frac{dQ}{dT}\right)_y, \tag{2.3}$$

and

Heat capacities

Consider a system $A = A(T, y)$. y probably be V or p. Recall that,

$$C_y := \left(\frac{dQ}{dT}\right)_y, \tag{2.3}$$

and

$$c_y := \frac{1}{\nu} C_y = \frac{1}{\nu}\left(\frac{dQ}{dT}\right)_y. \tag{2.4}$$

Heat capacities

In an infinitesimal process,

Heat capacities

In an infinitesimal process, the first law tells us

$$dQ = dE + pdV.$$

Heat capacities

In an infinitesimal process, the first law tells us

$$dQ = dE + pdV.$$

In any case, for ν mole an ideal gas, (should be in an infinitesimal process) by the definition of *heat capacity with constant volume*,

$$\nu c_V = C_V := \left(\frac{dQ}{dT}\right)_V = \frac{dE}{dT}.$$

Heat capacities

In an infinitesimal process, the first law tells us

$$dQ = dE + pdV.$$

In any case, for ν mole an ideal gas, (should be in an infinitesimal process) by the definition of *heat capacity with constant volume*,

$$\nu c_V = C_V := \left(\frac{dQ}{dT}\right)_V = \frac{dE}{dT}.$$

Thus,

$$dE = \nu c_V dT.$$

Heat capacities

Similar, in any case, for an ideal gas, by the definition of *heat capacity with constant pressure*,

$$\begin{aligned} \nu c_p := \left(\frac{dQ}{dT}\right)_p &= \left(\frac{dE + pdV}{dT}\right)_p \\ &= \left(\frac{dE}{dT}\right)_p + \left(\frac{pdV}{dT}\right)_p \end{aligned}$$

Heat capacities

Similar, in any case, for an ideal gas, by the definition of *heat capacity with constant pressure*,

$$
\begin{aligned}
\nu c_p := \left(\frac{dQ}{dT}\right)_p &= \left(\frac{dE + pdV}{dT}\right)_p \\
&= \left(\frac{dE}{dT}\right)_p + \left(\frac{pdV}{dT}\right)_p = \nu c_V + \nu R.
\end{aligned}
$$

Heat capacities

Similar, in any case, for an ideal gas, by the definition of *heat capacity with constant pressure*,

$$\begin{aligned} \nu c_p := \left(\frac{dQ}{dT}\right)_p &= \left(\frac{dE + pdV}{dT}\right)_p \\ &= \left(\frac{dE}{dT}\right)_p + \left(\frac{pdV}{dT}\right)_p = \nu c_V + \nu R. \end{aligned}$$

Thus,

$$c_p = c_V + R.$$

Heat capacities

Similar, in any case, for an ideal gas, by the definition of *heat capacity with constant pressure*,

$$\nu c_p := \left(\frac{dQ}{dT}\right)_p = \left(\frac{dE + pdV}{dT}\right)_p$$
$$= \left(\frac{dE}{dT}\right)_p + \left(\frac{pdV}{dT}\right)_p = \nu c_V + \nu R.$$

Thus,

$$c_p = c_V + R.$$

$c_p \rightarrow$ more easily to get by experiment.

Heat capacities

Similar, in any case, for an ideal gas, by the definition of *heat capacity with constant pressure*,

$$\begin{aligned}\nu c_p := \left(\frac{dQ}{dT}\right)_p &= \left(\frac{dE + pdV}{dT}\right)_p \\ &= \left(\frac{dE}{dT}\right)_p + \left(\frac{pdV}{dT}\right)_p = \nu c_V + \nu R.\end{aligned}$$

Thus,

$$c_p = c_V + R.$$

$c_p \to$ more easily to get by experiment.
$c_V \to$ more easily to get by theoretic calculation.

Quasi-static adiabatic process

Quasi-static adiabatic process

- For an ideal gas, T is keeping constant $\Rightarrow$

$$pV = const. \Rightarrow p\downarrow = \frac{const.}{V\uparrow}$$

decreases when the gas expands.

Quasi-static adiabatic process

- For an ideal gas, T is keeping constant $\Rightarrow$

$$pV = const. \Rightarrow p\downarrow = \frac{const.}{V\uparrow}$$

  decreases when the gas expands.
- For an ideal gas, when it expands under an adiabatic ($dQ = 0$) condition,

$$0 = dQ = dE\downarrow + dW\uparrow \Rightarrow T\downarrow = 2E\downarrow/3Nk.$$

Quasi-static adiabatic process

- For an ideal gas, T is keeping constant $\Rightarrow$

$$pV = const. \Rightarrow p\downarrow = \frac{const.}{V\uparrow}$$

decreases when the gas expands.

- For an ideal gas, when it expands under an adiabatic ($dQ = 0$) condition,

$$0 = dQ = dE\downarrow + dW\uparrow \Rightarrow T\downarrow = 2E\downarrow/3Nk.$$

- Question: How is the pressure p related to V in a kind of the second process?

Quasi-static adiabatic process

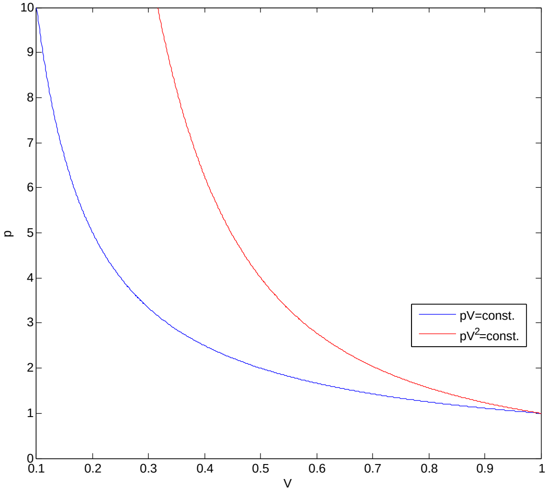
Theorem

In the second process,

$$pV^{\gamma} = const. \tag{2.5}$$

where $\gamma := \frac{c_p}{c_V} > 1.$

Quasi-static adiabatic process



Outline

1. An example: $TdS = dE + pdV$.
2. A special case: for ideal gases
   - Energy: $E = E(T)$
   - Heat capacities: $c_p = c_V + R$
   - Quasi-static adiabatic process: pV^γ =constant
3. **Maxwell relations and thermodynamic functions**
4. General cases
   - Heat capacities, after Maxwell relations
   - Energy, after Maxwell relations
5. Applications
   - Heat engines
   - Refrigerators
   - Equivalence of Kelvin and Clausius statements

Maxwell relations

Consider a quasi-static infinitesimal process with a system

Maxwell relations

Consider a quasi-static infinitesimal process with a system having only V as an external parameter.

Maxwell relations

Consider a quasi-static infinitesimal process with a system having only V as an external parameter. one should have

$$dQ = TdS = dE + pdV. \tag{3.1}$$

$E = E(S, V)$

From (3.1), one can find $dE = TdS - pdV$.

$E = E(S, V)$

From (3.1), one can find $dE = TdS - pdV$. Further,

$E = E(S, V)$

From (3.1), one can find $dE = TdS - pdV$. Further,

$$\left.\begin{aligned} \left(\frac{\partial E}{\partial S}\right)_V = T(S,V); \\ \left(\frac{\partial E}{\partial V}\right)_S = -p(S,V); \\ \frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V} \end{aligned}\right\} \tag{3.2}$$

$E = E(S, V)$

From (3.1), one can find $dE = TdS - pdV$. Further,

$$\left.\begin{aligned} \left(\frac{\partial E}{\partial S}\right)_V &= T(S, V); \\ \left(\frac{\partial E}{\partial V}\right)_S &= -p(S, V); \\ \frac{\partial^2 E}{\partial V \partial S} &= \frac{\partial^2 E}{\partial S \partial V} \end{aligned}\right\} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V. \tag{3.2}$$

$E = E(S, V)$

From (3.1), one can find $dE = TdS - pdV$. Further,

$$\left.\begin{aligned} \left(\frac{\partial E}{\partial S}\right)_V &= T(S,V); \\ \left(\frac{\partial E}{\partial V}\right)_S &= -p(S,V); \\ \frac{\partial^2 E}{\partial V \partial S} &= \frac{\partial^2 E}{\partial S \partial V} \end{aligned}\right\} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V. \tag{3.2}$$

Note: here, dE is used as an exact differential.

$H = H(S, p)$

Again, consider the same process and the same system as previous.

$H = H(S, p)$

Again, consider the same process and the same system as previous. Let $V = V(p)$. Then

$$\frac{d(pV(p))}{dp} = V(p) + p\frac{V(p)}{dp}.$$

Equivalently,

$$pdV = d(pV) - Vdp.$$

$H = H(S, p)$

Again, consider the same process and the same system as previous. Let $V = V(p)$. Then

$$\frac{d(pV(p))}{dp} = V(p) + p\frac{V(p)}{dp}.$$

Equivalently,

$$pdV = d(pV) - Vdp.$$

From again (3.1),

$H = H(S, p)$

Again, consider the same process and the same system as previous. Let $V = V(p)$. Then

$$\frac{d(pV(p))}{dp} = V(p) + p\frac{V(p)}{dp}.$$

Equivalently,

$$pdV = d(pV) - Vdp.$$

From again (3.1), i.e. $TdS = dE + pdV$,

$H = H(S,p)$

Again, consider the same process and the same system as previous. Let $V = V(p)$. Then

$$\frac{d(pV(p))}{dp} = V(p) + p\frac{V(p)}{dp}.$$

Equivalently,

$$pdV = d(pV) - Vdp.$$

From again (3.1), i.e. $TdS = dE + pdV$, one has

$$\begin{aligned} TdS &= dE + d(pV) - Vdp \\ \Rightarrow d(E+pV) &= TdS + Vdp. \end{aligned} \tag{3.3}$$

$H = H(S, p)$

Therefore, one can find $d(E + pV)$ is another exact differential.

$H = H(S, p)$

Therefore, one can find $d(E + pV)$ is another exact differential. Define

$$H := E + pV$$

and call it

$H = H(S, p)$

Therefore, one can find $d(E + pV)$ is another exact differential. Define

$$H := E + pV$$

and call it “enthalpy”.

$H = H(S, p)$

Therefore, one can find $d(E + pV)$ is another exact differential. Define

$$H := E + pV$$

and call it "enthalpy". As you can imagine,

$H = H(S, p)$

Therefore, one can find $d(E + pV)$ is another exact differential. Define

$$H := E + pV$$

and call it "enthalpy". As you can imagine, something should be done to H as treated to E before.

$H = H(S, p)$

By definition of H, one has $dH = TdS + Vdp$ and further,

$H = H(S, p)$

By definition of H, one has $dH = TdS + Vdp$ and further,

$$\left.\begin{array}{r}\left(\frac{\partial H}{\partial S}\right)_p = T(S,p);\\ \left(\frac{\partial H}{\partial p}\right)_S = V(S,p);\\ \frac{\partial^2 H}{\partial p \partial S} = \frac{\partial^2 H}{\partial S \partial p}\end{array}\right\} \quad \left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_p. \tag{3.4}$$

$F = F(T, V)$

Again and again, consider the same system and process as before.

$F = F(T, V)$

Again and again, consider the same system and process as before. Very similarly, one can find $d(E - TS)$ should be an exact differential. So define a quantity

$$F := E - TS,$$

where E and S are treated as functions of T and V.

$F = F(T, V)$

Again and again, consider the same system and process as before. Very similarly, one can find $d(E - TS)$ should be an exact differential. So define a quantity

$$F := E - TS,$$

where E and S are treated as functions of T and V.
F then is usually called the "Helmholtz free energy".

$F = F(T, V)$

Again and again, consider the same system and process as before. Very similarly, one can find $d(E - TS)$ should be an exact differential. So define a quantity

$$F := E - TS,$$

where E and S are treated as functions of T and V.
F then is usually called the "Helmholtz free energy".
And, by using the equality of the cross derivatives, one may obtain that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V . \tag{3.5}$$

$G = G(T, p)$

Again and again and again, the same system and process are under considered.

$G = G(T, p)$

Again and again and again, the same system and process are under considered. One can also find $d(E - TS + pV)$ is another exact differential. Define

$$G := E - TS + pV$$

and call it "Gibbs free energy".

$G = G(T, p)$

Again and again and again, the same system and process are under considered. One can also find $d(E - TS + pV)$ is another exact differential. Define

$$G := E - TS + pV$$

and call it "Gibbs free energy". Again, the equality of the cross derivatives tells us

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p . \tag{3.6}$$

Summarize

Maxwell relations

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

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

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

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

Thermodynamic functions

$$dE = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dF = -SdT - pdV$$

$$dG = -SdT + Vdp$$

Outline

1. **An example: $TdS = dE + pdV$.**
2. **A special case: for ideal gases**
   - Energy: $E = E(T)$
   - Heat capacities: $c_p = c_V + R$
   - Quasi-static adiabatic process: pV^{γ} =constant
3. **Maxwell relations and thermodynamic functions**
4. **General cases**
   - Heat capacities, after Maxwell relations
   - Energy, after Maxwell relations
5. **Applications**
   - Heat engines
   - Refrigerators
   - Equivalence of Kelvin and Clausius statements

Heat capacities

One can use the Maxwell relations for some substance to deduce the relation between the heat capacity under constant volume and the heat capacity under constant pressure.

Heat capacities

One can use the Maxwell relations for some substance to deduce the relation between the heat capacity under constant volume and the heat capacity under constant pressure.

Theorem

Let

$$\alpha := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p ;$$
$$\kappa := -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T .$$

Then,

$$C_p - C_V = VT\frac{\alpha^2}{\kappa}. \tag{4.1}$$

Energy

One can also use the Maxwell relations to deduce the internal energy of some substance as a function of volume and temperature.

Energy

One can also use the Maxwell relations to deduce the internal energy of some substance as a function of volume and temperature.

Theorem

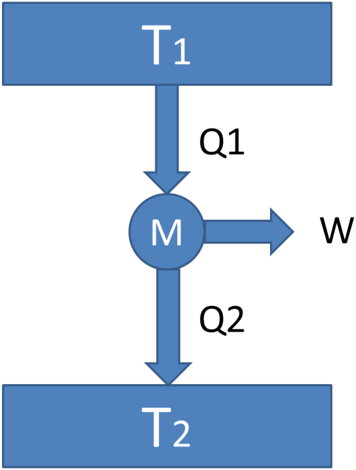
Treat E as a function of V and T. Then,

$$\begin{aligned} \left(\frac{\partial E}{\partial T}\right)_V &= C_V; \\ \left(\frac{\partial E}{\partial V}\right)_T &= T\left(\frac{\partial p}{\partial T}\right)_V - p. \end{aligned}$$

Outline

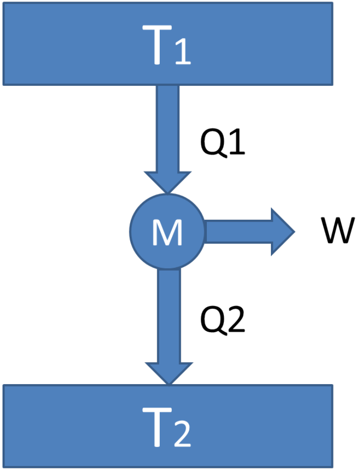
1. **An example:** $TdS = dE + pdV$.
2. **A special case: for ideal gases**
   - Energy: $E = E(T)$
   - Heat capacities: $c_p = c_V + R$
   - Quasi-static adiabatic process: pV^γ =constant
3. **Maxwell relations and thermodynamic functions**
4. **General cases**
   - Heat capacities, after Maxwell relations
   - Energy, after Maxwell relations
5. **Applications**
   - Heat engines
   - Refrigerators
   - Equivalence of Kelvin and Clausius statements

What is a heat engine?



$$T_1 > T_2$$

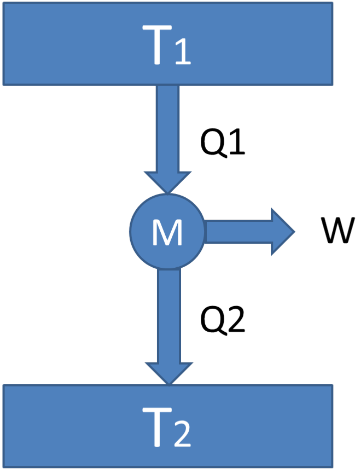
What is a heat engine?



Energy conservation $\Rightarrow$

$$Q_1 = W + Q_2.$$

What is a heat engine?



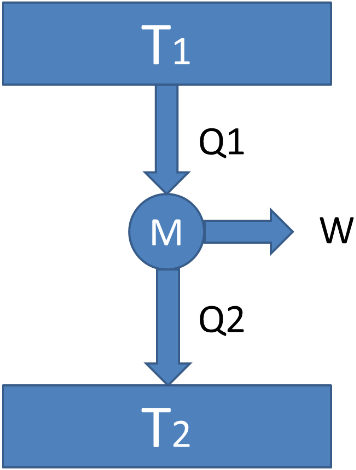
Energy conservation $\Rightarrow$

$$Q_1 = W + Q_2.$$

Define

$$\eta := \frac{W}{Q_1} \leq 1.$$

What is a heat engine?



Energy conservation $\Rightarrow$

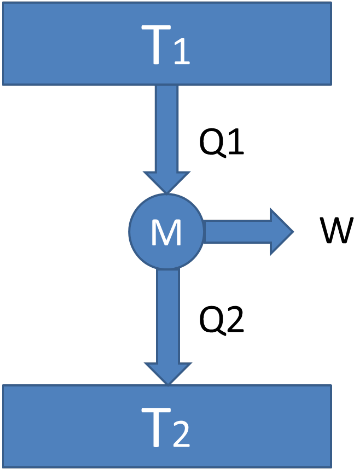
$$Q_1 = W + Q_2.$$

Define

$$\eta := \frac{W}{Q_1} \leq 1.$$

$$\eta = 1 \Rightarrow W = Q_1$$

What is a heat engine?



Energy conservation $\Rightarrow$

$$Q_1 = W + Q_2.$$

Define

$$\eta := \frac{W}{Q_1} \leq 1.$$

$$\eta = 1 \Rightarrow W = Q_1$$

Perfect!

Kelvin statement

Kelvin: Impossible to construct a device, operating in circle, that produce no effect other than the extraction of heat from a reservoir and do equivalent amount of work. [1]

[1]

Kelvin statement

Kelvin: Impossible to construct a device, operating in circle, that produce no effect other than the extraction of heat from a reservoir and do equivalent amount of work. [1]

[1] P. Jacobs, *Thermodynamics,* Imperial College Press, 2013.

Why not?

- Remember $Q_1 = W + Q_2$ and $W > 0$.

Why not?

- Remember $Q_1 = W + Q_2$ and $W > 0$.
- Perfect requires $Q_1 = W$.

Why not?

- Remember $Q_1 = W + Q_2$ and $W > 0$.
- Perfect requires $Q_1 = W$.
- Circle means no entropy change to the device.

Why not?

- Remember $Q_1 = W + Q_2$ and $W > 0$.
- Perfect requires $Q_1 = W$.
- Circle means no entropy change to the device.
- No effect means no entropy change to the outside.

Why not?

- Remember $Q_1 = W + Q_2$ and $W > 0$.
- Perfect requires $Q_1 = W$.
- Circle means no entropy change to the device.
- No effect means no entropy change to the outside.
- So that

$$\Delta S = -\frac{\Delta Q_1}{T_1} = -\frac{W}{T_1} < 0,$$

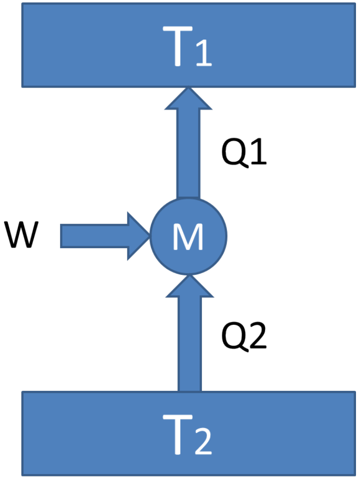
Why not?

- Remember $Q_1 = W + Q_2$ and $W > 0$.
- Perfect requires $Q_1 = W$.
- Circle means no entropy change to the device.
- No effect means no entropy change to the outside.
- So that

$$\Delta S = -\frac{\Delta Q_1}{T_1} = -\frac{W}{T_1} < 0,$$

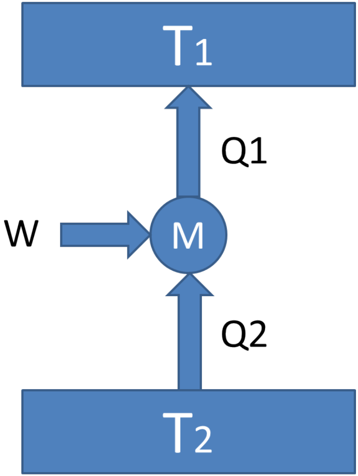
which is a contradiction with the second law.

What is a refrigerator?



$$T_1 > T_2$$

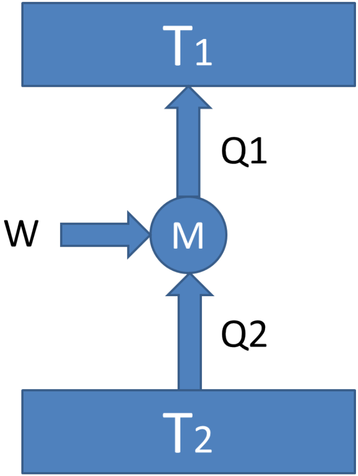
What is a refrigerator?



Energy conservation $\Rightarrow$

$$Q_1 = W + Q_2.$$

What is a refrigerator?



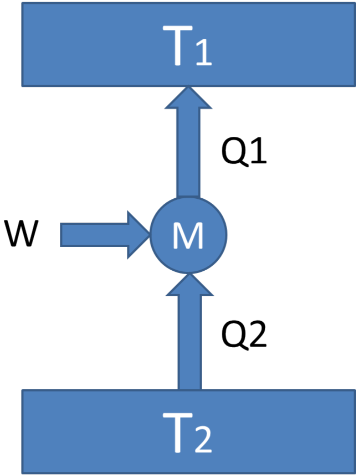
Energy conservation $\Rightarrow$

$$Q_1 = W + Q_2.$$

Define

$$\eta' := \frac{Q_2}{Q_1} \leq 1.$$

What is a refrigerator?



Energy conservation $\Rightarrow$

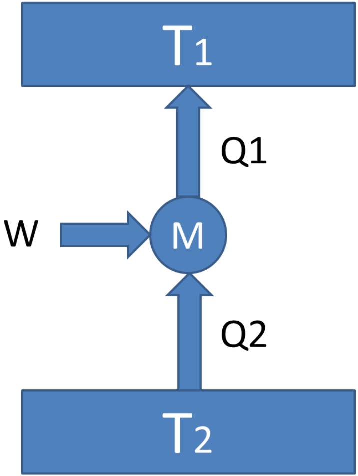
$$Q_1 = W + Q_2.$$

Define

$$\eta' := \frac{Q_2}{Q_1} \leq 1.$$

$$\eta' = 1 \Rightarrow Q_2 = Q_1$$

What is a refrigerator?



Energy conservation $\Rightarrow$

$$Q_1 = W + Q_2.$$

Define

$$\eta' := \frac{Q_2}{Q_1} \leq 1.$$

$$\eta' = 1 \Rightarrow Q_2 = Q_1$$

Perfect!

Clausius statement

Clausius: Impossible to construct a device, operating in circle, that produce no effect other than flowing heat from a colder to a hotter body. [2]

[2] P. Jacobs, *Thermodynamics*, Imperial College Press, 2013.

Why not?

- Remember $Q_1 = W + Q_2$ and $T_1 > T_2$.

Why not?

- Remember $Q_1 = W + Q_2$ and $T_1 > T_2$.
- Perfect requires $Q_1 = Q_2$.

Why not?

- Remember $Q_1 = W + Q_2$ and $T_1 > T_2$.
- Perfect requires $Q_1 = Q_2$.
- Circle means no entropy change to the device.

Why not?

- Remember $Q_1 = W + Q_2$ and $T_1 > T_2$.
- Perfect requires $Q_1 = Q_2$.
- Circle means no entropy change to the device.
- No effect means no entropy change to the outside.

Why not?

- Remember $Q_1 = W + Q_2$ and $T_1 > T_2$.
- Perfect requires $Q_1 = Q_2$.
- Circle means no entropy change to the device.
- No effect means no entropy change to the outside.
- So that

$$\Delta S = \frac{\Delta Q_1}{T_1} - \frac{\Delta Q_2}{T_2} = Q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) < 0,$$

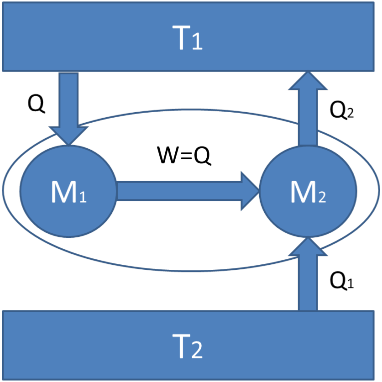
Why not?

- Remember $Q_1 = W + Q_2$ and $T_1 > T_2$.
- Perfect requires $Q_1 = Q_2$.
- Circle means no entropy change to the device.
- No effect means no entropy change to the outside.
- So that

$$\Delta S = \frac{\Delta Q_1}{T_1} - \frac{\Delta Q_2}{T_2} = Q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) < 0,$$

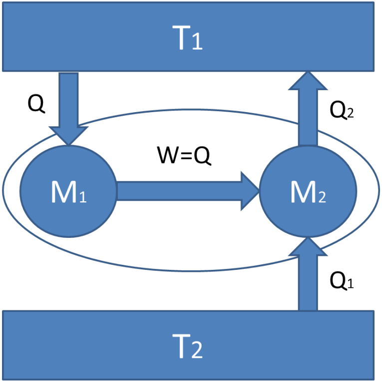
which is a contradiction with the second law.

Equivalence



"Clausius $\Rightarrow$ Kelvin":

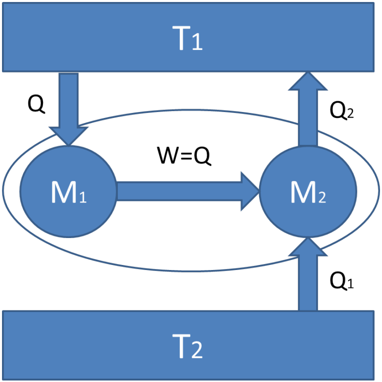
Equivalence



"Clausius $\Rightarrow$ Kelvin":

- Kelvin is wrong $\Rightarrow$ M_1 possible ($W = Q$).

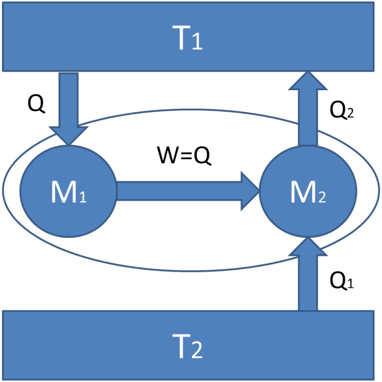
Equivalence



"Clausius $\Rightarrow$ Kelvin":

- Kelvin is wrong $\Rightarrow$ M_1 possible ($W = Q$).
- For M_2, $\Rightarrow$ $Q_2 = W + Q_1 = Q + Q_1$.

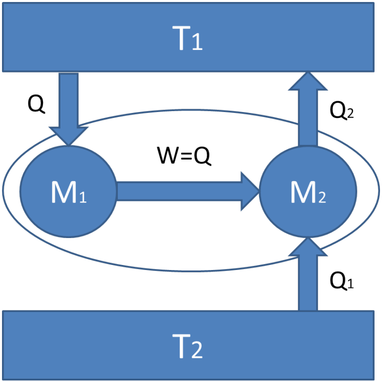
Equivalence



"Clausius $\Rightarrow$ Kelvin":

- Kelvin is wrong $\Rightarrow$ M_1 possible ($W = Q$).
- For M_2, $\Rightarrow$ $Q_2 = W + Q_1 = Q + Q_1$.
- For $M_1 + M_2$, it is possible to absorb Q_1 from T_2;

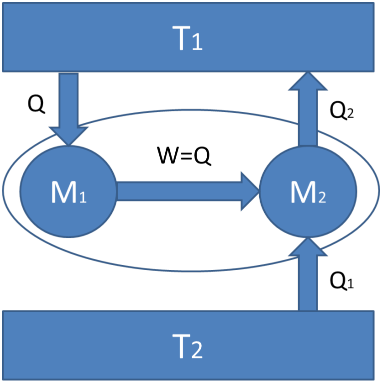
Equivalence



"Clausius $\Rightarrow$ Kelvin":

- Kelvin is wrong $\Rightarrow$ M_1 possible ($W = Q$).
- For M_2, $\Rightarrow$ $Q_2 = W + Q_1 = Q + Q_1$.
- For $M_1 + M_2$, it is possible to absorb Q_1 from T_2;
- while to eject $Q_2 - Q = Q_1$ to T_1;

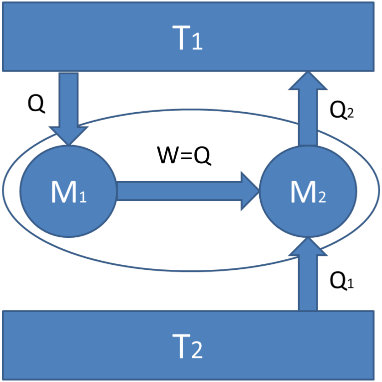
Equivalence



"Clausius $\Rightarrow$ Kelvin":

- Kelvin is wrong $\Rightarrow$ M_1 possible ($W = Q$).
- For M_2, $\Rightarrow$ $Q_2 = W + Q_1 = Q + Q_1$.
- For $M_1 + M_2$, it is possible to absorb Q_1 from T_2;
- while to eject $Q_2 - Q = Q_1$ to T_1;
- Remember $T_1 > T_2$.

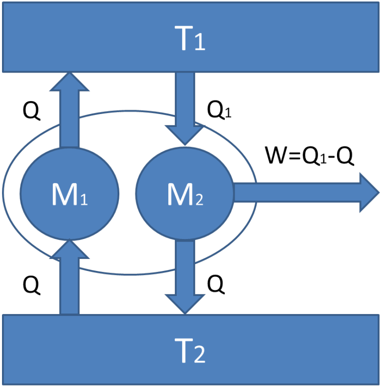
Equivalence



"Clausius $\Rightarrow$ Kelvin":

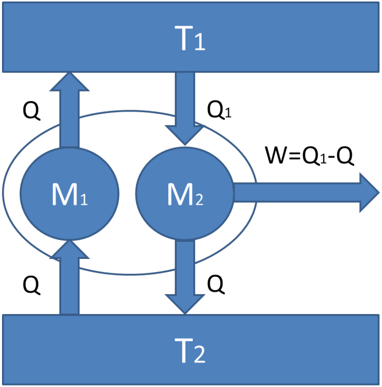
- Kelvin is wrong $\Rightarrow$ M_1 possible ($W = Q$).
- For M_2, $\Rightarrow$ $Q_2 = W + Q_1 = Q + Q_1$.
- For $M_1 + M_2$, it is possible to absorb Q_1 from T_2;
- while to eject $Q_2 - Q = Q_1$ to T_1;
- Remember $T_1 > T_2$.
- This contradicts with Clausius statement.

Equivalence



"Kelvin $\Rightarrow$ Clausius":

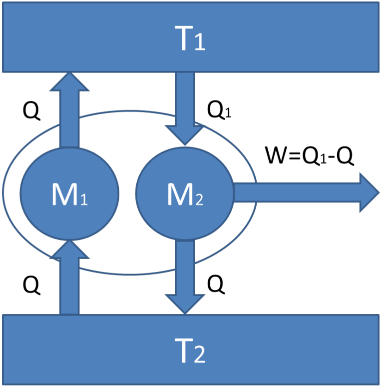
Equivalence



"Kelvin ⇒ Clausius":

- Clausius is wrong ⇒ M_1 possible.

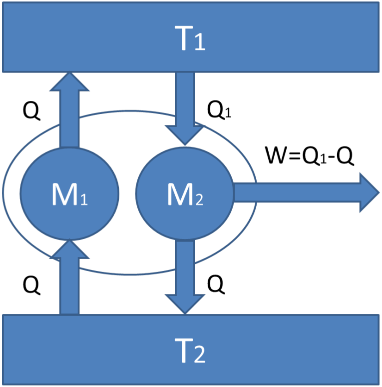
Equivalence



"Kelvin $\Rightarrow$ Clausius":

- Clausius is wrong $\Rightarrow$ M_1 possible.
- For M_2, $\Rightarrow$ $W = Q_1 - Q$.

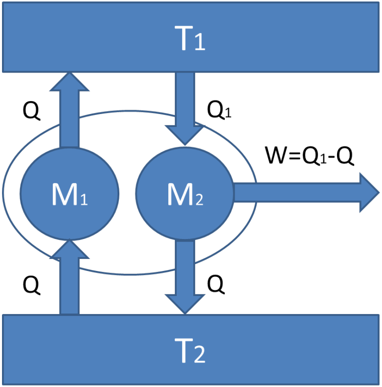
Equivalence



"Kelvin $\Rightarrow$ Clausius":

- Clausius is wrong $\Rightarrow$ M_1 possible.
- For M_2, $\Rightarrow$ $W = Q_1 - Q$.
- For $M_1 + M_2$, it is possible to absorb $Q_1 - Q$ from T_1;

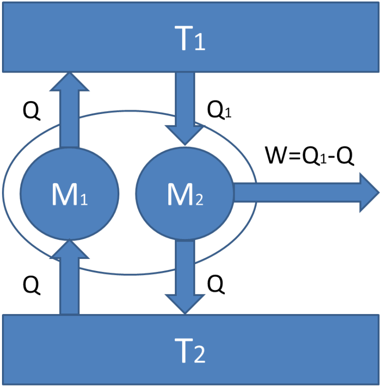
Equivalence



“Kelvin $\Rightarrow$ Clausius”:

- Clausius is wrong $\Rightarrow$ M_1 possible.
- For M_2, $\Rightarrow$ $W = Q_1 - Q$.
- For $M_1 + M_2$, it is possible to absorb $Q_1 - Q$ from T_1;
- while to do $W = Q_1 - Q$ to the outside;

Equivalence



"Kelvin $\Rightarrow$ Clausius":

- Clausius is wrong $\Rightarrow$ M_1 possible.
- For M_2, $\Rightarrow$ $W = Q_1 - Q$.
- For $M_1 + M_2$, it is possible to absorb $Q_1 - Q$ from T_1;
- while to do $W = Q_1 - Q$ to the outside;
- This contradicts with Kelvin statement.

References

- F. Reif, *Fundamentals of Statistical And Thermal Physics*, 1st version.
- P. Jacobs, *Thermodynamics,* Imperial College Press, 2013.

Acknowledgement

Thank you for your attention!