

1 Simple Applications of macroscopic thermodynamics

1.1 General relationship of thermodynamics

Fundamental thermodynamic relation for a *quasi-static process*:

$$dS = \frac{\delta Q}{T}$$

where

$$\delta Q = dE + \delta W = dE + p dV$$

The only external parameter of change is V

$$\implies dE = T dS - p dV$$

This specifies certain relationship between T, S, p, V i.e. S & V are independent variables

$$E = E(S, V)$$

So we have a pure mathematical relationship

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

where

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

which we already know! Because dE is an exact differential

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

this is known as the first Maxwell relation ([wiki](#)).

How about S, P ?

From our favorite starting point

$$dE = T dS - p dV$$

we need to change $dV \rightarrow dp$ so from chain rule

$$d(pV) = p dV + V dp \implies p dV = d(pV) - V dp$$

so

$$dE = T dS - d(pV) + V dp$$

or

$$d(E + pV) = T dS + V dp$$

lets call this new parameter $H = E + pV$ the **enthalpy** i.e.

$$H = H(S, p)$$

So

$$\begin{cases} T = \left(\frac{\partial H}{\partial S} \right)_p \\ V = \left(\frac{\partial H}{\partial p} \right)_S \end{cases}$$

where dH is an exact differential

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

or the second Maxwell relation!

Worksheet We can derive the Helmholtz free energy $F = F(T, V)$ by starting with

$$d(TS) = TdS + SdT \implies TdS = d(TS) - SdT$$

so

$$\begin{aligned} dE &= d(TS) - SdT - pdV \\ d(E - TS) &= -SdT - pdV \end{aligned}$$

1. Thus the Helmholtz free energy $F \equiv E - TS$ so

$$\begin{aligned} dF &= dE - (TdS + SdT) \\ &= TdS - pdV - TdS - SdT \\ &= -SdT - pdV \end{aligned}$$

2. So $F = F(T, V)$ then we know that

$$\begin{cases} -S = \left(\frac{\partial F}{\partial T}\right)_V \\ -p = \left(\frac{\partial F}{\partial V}\right)_T \end{cases}$$

and dF is an exact differential

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

Finally for independent parameters T, p :

$$dE = TdS - pdV$$

we need to change $dV \rightarrow dp$ so from chain rule

$$d(pV) = pdV + Vdp \implies pdV = d(pV) - Vdp$$

so also using $TdS = d(TS) - SdT$

$$\begin{aligned} dE &= (d(TS) - SdT) - (d(pV) - Vdp) \\ d(E - TS + pV) &= -SdT + Vdp \end{aligned}$$

where $G = E - TS + pV$ is the Gibbs free energy $G = G(T, p)$

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

and dG is an exact differential

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

Summary of Maxwell relations

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial V}{\partial T}\right)_p &= -\left(\frac{\partial S}{\partial p}\right)_T \end{aligned}$$

or in box form Where the components are horizontal (TS) and vert (pV) give us the relations.
e.g. something

$$\begin{array}{c|c} E & F \\ \hline H & G \end{array}$$

Review of Maxwell relations the DoS and external parameters of the system

$$(T, S) \quad \text{and} \quad (p, V)$$

are not independent, but related through

$$dE = Tds - pdV$$

From this we can get the Maxwell relations

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial V}{\partial T}\right)_p &= -\left(\frac{\partial S}{\partial p}\right)_T \end{aligned}$$

which can be derived from the Thermodynamic functions

$$\begin{aligned} E &= E(S, V) \\ H &= H(S, p) = E + pV \\ F &= F(T, V) = E - TS \\ G &= G(T, p) = E - TS + pV \end{aligned}$$

1.2 Specific Heats

- Molar specific heat at constant volume $dV = 0$

$$C_V = \frac{1}{n} \left(\frac{dQ}{dT} \right)_V \quad dE = dQ = nC_V dT$$

- Molar specific heat for constant pressure $dp = 0$

$$C_p = \frac{1}{n} \left(\frac{dQ}{dT} \right)_p = C_V + \frac{1}{n} p \left(\frac{dV}{dT} \right)_p$$

When comparing the two specific heats we can infer that $C_p > C_V$ because the heat dQ has to both increase the internal energy and do mechanical work to expand the volume:

$$dQ = dE + pdV = nC_V dT + pdV$$

- For an ideal gas

$$\begin{aligned} pV &= nRT \\ pdV &= nRdT \\ \Rightarrow \left(\frac{dV}{dT} \right) &= \frac{nR}{p} \end{aligned}$$

thus

$$C_p = C_V + R$$

where we define

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{R}{C_V}$$

For the idea gas molecule the energy is given by

$$E(T) = \frac{3}{2}nRT$$

where there is 3 degrees of freedom thus

$$C_V = \frac{1}{n} \frac{dE}{dT} = \frac{3}{2}R$$

$$C_p = C_V + R = \frac{5}{2}R$$

For a diatomic molecule there are 2 extra degrees of freedom for rotation so

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3}$$

1.3 Adiabatic expansion or compression

Some definitions:

- “Isothermal”: T is constant $\implies pV = \text{Constant}$.
- “Adiabatic”: $dQ = 0$

$$\implies 0 = dE + pdV$$

$$= nC_V dT + pdV$$

So from the ideal gas law $pV = nRT$ we can get

$$VdP + pdV = nRdT$$

and substituting dT into the adiabatic expression

$$dQ = 0 = V \frac{C_V}{R} dP + \frac{C_V P}{R} dV + pdV$$

which can be rewritten as

$$0 = (C_V + R)pdV + C_V VdP = C_p pdV + C_v Vdp$$

or dividing by $C_V PV$ we get

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0$$

Integration then gives

$$\gamma \ln V + \ln P = \text{Constant} \implies \ln(PV^\gamma) = \text{Constant}$$

or

$$PV^\gamma = \text{Constant}$$

Worksheet

- Pumping a bike tire, a liter of air at 1 atm is compressed *adiabatically* to 7 atm. (Air is mostly diatomic gas)

- For diatomic gas

$$E(T) = \frac{5}{2}nRT$$

So the specific heats are

$$C_V = \frac{1}{n} \frac{dE}{dT} = \frac{5}{2}RC_p = C_V + R = \frac{7}{2}R$$

which gives us

$$\gamma = \frac{C_p}{C_V} = \frac{7}{5}$$

- The final volume after compression is

$$p_i V_i^\gamma = p_f V_f^\gamma$$

or

$$(1 \text{ atm})(1 \text{ L})^{7/5} = (7 \text{ atm})V_f^{7/5} \implies V_f = 0.25 \text{ L}$$

- Work done compressing air: using $p_i V_i^\gamma = 1 \implies p = \frac{1}{V^\gamma}$

$$\begin{aligned} W &= \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{1}{V^\gamma} dV \\ &= \frac{1}{1-\gamma} (V_f^{1-\gamma} - V_i^{1-\gamma}) \end{aligned}$$

- If initial temp is 300 K, the final temp is

$$\begin{aligned} P_i V_i &= nRT_i \quad P_f V_f = nRT_f \\ \implies \frac{P_f V_f}{P_i V_i} &= \frac{T_f}{T_i} \end{aligned}$$

- If the compression is isothermal (pumping very slowly) how does the answers change?

General case:

$$\begin{aligned} C_V &= \left(\frac{dQ}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \\ C_P &= \left(\frac{dQ}{dT} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P \end{aligned}$$

1.4 Entropy

Consider $S = S(T, P)$

$$\begin{aligned} dQ &= T dS = T \left[\left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \right] \\ &= C_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP \end{aligned}$$

1.5 Specific heats again

General relation between C_v and C_p for non-ideal gas ($C_p - C_v = R$),

$$C_V = \left(\frac{dQ}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$C_P = \left(\frac{dQ}{dT} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

where

$$\begin{aligned} dQ = TdS &= T \left[\left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \right] \\ &= C_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP \end{aligned}$$

The pressure $P(T, V)$ with temp and volume dependence has a differential

$$dP = \left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV$$

and since C_V acknowledges fixed volume $dV = 0$ we get

$$C_V = \left(\frac{dQ}{dT} \right)_V = C_P + T \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V$$

where we can replace the entropy term with the Maxwell relation

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

We define the “volume coefficient of expansion”

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

so

$$\left(\frac{\partial S}{\partial P} \right)_T = -\alpha V$$

The second term is not well defined since fixing volume while increasing pressure is hard to do (e.g. filling a water bottle with more and more water). Now using the volume dependence $V(P, T)$ i.e.

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP = 0$$

and moving thing around we get

$$\left(\frac{dP}{dT} \right)_V = - \frac{\left(\frac{\partial V}{\partial T} \right)_P}{\left(\frac{\partial V}{\partial P} \right)_T}$$

where we define another term

$$\kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

AKA the “isothermal compressibility” thus

$$\boxed{C_P - C_V = VT \frac{\alpha^2}{\kappa}}$$

One check we can do is use the Ideal gas law to calculate α and κ then see if the above equation gives us the relation $C_P - C_V = R$

1.6 Entropy and Internal energy

$S(T, V)$ doing the same thing

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \\ &= \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_N dV \end{aligned}$$

etc.

1.7 Free expansion of a gas

For the general case

$$\begin{aligned} dE &= 0 \\ E &= E(T, V) \end{aligned}$$

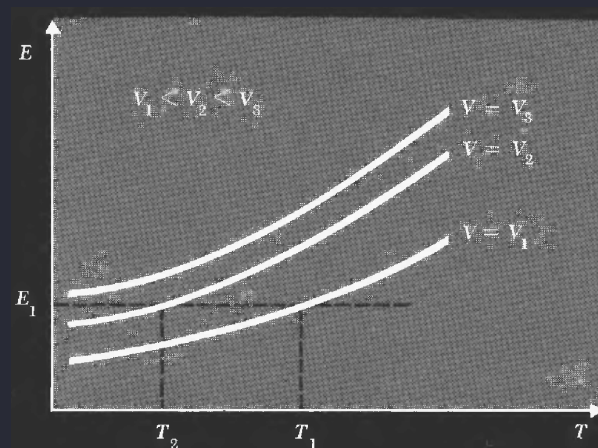


Figure 1.1: Free expansion of a gas

Van de Waals Gas

$$\begin{aligned} \left(P + \frac{a}{v^2} \right) (v - b) &= RT \quad E = E(T, V) \\ v &= \frac{V}{n} \end{aligned}$$

1.8 Heat Engine

What is a heat engine? Heat \rightarrow Work.

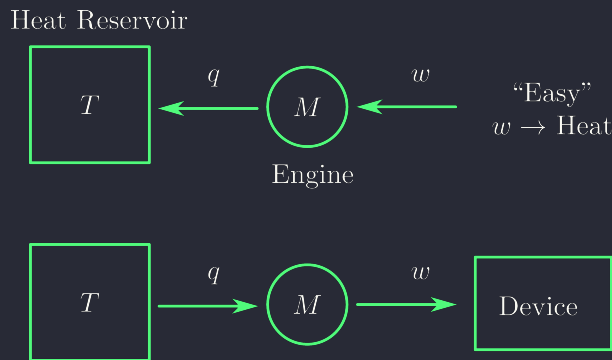


Figure 1.2: (top) reverse “easy” process converting work to heat. (bottom) Heat Engine converting heat from a reservoir into work.

- For a heat engine: whatever mechanisms needed to retune to the same original condition; go through a cycle; otherwise, engine cannot continuously operate.
- Ideally perfect engine: $q = w$ or 100% efficiency

A perfect engine *violates* the 2nd law of thermodynamics $\Delta S \geq 0$.

- entropy change for engine and external device $\Delta S = 0$
- entropy change for heat reservoir $\Delta S = -q/T$ thus

$$\Delta S_{\text{tot}} = -\frac{q}{T} < 0$$

Building a heat engine: Using two heat reservoirs

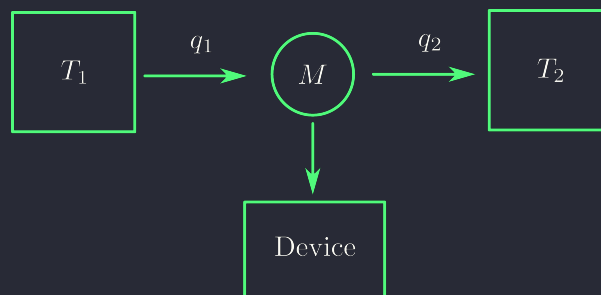


Figure 1.3: Heat engine using two heat reservoirs

Where we make $q_1 > q_2$ so that heat flows from $T_1 \rightarrow T_2$ so that

$$W = q_1 - q_2 \implies q_2 = q_1 - W$$

so the total entropy change is

$$\begin{aligned} \Delta S_{\text{tot}} &= -\frac{q_1}{T_1} - \frac{q_2}{T_2} \geq 0 \\ &= -\frac{q_1}{T_1} + \frac{q_1 - W}{T_2} \\ \implies \frac{W}{T_2} &\leq q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \end{aligned}$$

thus the efficiency of the engine

$$\begin{aligned}\eta &= \frac{W}{q_1} \leq T_2 \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ &= 1 - \frac{T_2}{T_1}\end{aligned}$$

Carnot Engine

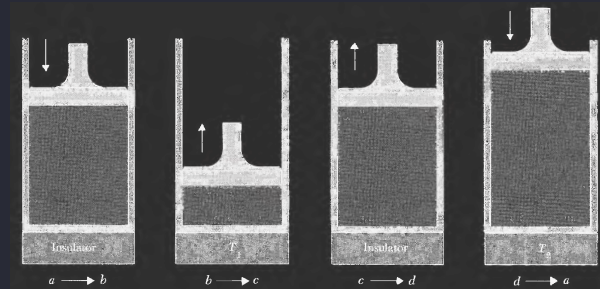


Figure 1.4: 4 stages of Carnot Engine

- $a \rightarrow b$: adiabatic (no heat exchange) bringing colder $T_2 \rightarrow T_1$
- $b \rightarrow c$: isothermal (constant temp) adding heat q_1 from hot reservoir
- $c \rightarrow d$: adiabatic (no heat exchange) cooling down $T_1 \rightarrow T_2$ as work is done through expansion
- $d \rightarrow a$: isothermal (constant temp) releasing heat q_2 to cold reservoir

Worksheet Carnot Engine using an ideal gas:

The work done is

$$W = \int_a^b P dV + \int_b^c P dV + \int_c^d P dV + \int_d^a P dV$$

- $b \rightarrow c$: Using the ideal gas law $PV = nRT$ we get

$$W = \int P dV = \int_{V_b}^{V_c} \frac{nRT_1}{V} dV = nRT_1 \ln \frac{V_c}{V_b}$$

and since $\Delta E = 0$ we know that

$$q_1 = W = nRT_1 \ln \frac{V_c}{V_b}$$

- $d \rightarrow a$: Same as above

$$q_2 = nRT_2 \ln \frac{V_a}{V_d}$$

so

$$W = q_1 - q_2$$

where the work done should be the total heat of the system as we go from $a \rightarrow b \rightarrow c \rightarrow d \rightarrow a$, i.e.

$$\Delta E = 0 \implies W = \Delta Q$$

The efficiency of the Carnot engine is by definition

$$\eta = \frac{W}{q_1} = \frac{q_1 - q_2}{q_1} = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2 \ln(V_d/V_a)}{T_1 \ln(V_c/V_b)}$$

Argument:

$$\frac{V_d}{V_a} = \frac{V_c}{V_b}$$

From the adiabatic process

$$PV^\gamma = \text{Constant}$$

so

$$\begin{aligned} P_a V_a^\gamma &= P_b V_b^\gamma \\ P_d V_d^\gamma &= P_c V_c^\gamma \\ \implies \frac{P_a V_a^\gamma}{P_d V_d^\gamma} &= \frac{P_b V_b^\gamma}{P_c V_c^\gamma} \end{aligned}$$

And from the Isothermal process

$$PV = \text{Constant} \implies \frac{P_a V_a}{P_b V_b} = \frac{P_d V_d}{P_c V_c}$$

From the former equation we can rewrite it as

$$\frac{P_a V_a V_a^{\gamma-1}}{P_d V_d V_d^{\gamma-1}} = \frac{P_b V_b V_b^{\gamma-1}}{P_c V_c V_c^{\gamma-1}}$$

which cancels out some terms

$$\frac{V_a^{\gamma-1}}{V_d^{\gamma-1}} = \frac{V_b^{\gamma-1}}{V_c^{\gamma-1}} \implies \frac{V_d}{V_a} = \frac{V_c}{V_b}$$

1.9 Refrigerators

[insert figure of 2 fridges]

From the Thermo Laws

- 1st law:

$$W + q_2 + q_1$$

- 2nd law:

$$\Delta S = \frac{q_1}{T_1} + \frac{-q_2}{T_2} \geq 0$$

or

$$\frac{q_1}{q_2} \geq \frac{T_1}{T_2}$$

We define the “coefficient of performance”

$$CoP \equiv \frac{q_2}{W} = \frac{q_2}{q_1 - q_2} = \frac{1}{\frac{q_1}{q_2} - 1} \leq \frac{1}{\frac{T_1}{T_2} - 1} = \frac{T_2}{T_1 - T_2}$$

Case:

- Room temp: $T_1 = 300K$
- Freezer: $T_2 = 255K$

so the CoP is roughly

$$\frac{255}{45} \approx 5.67$$

since less work is required to move heat rather than converting into heat, the number is greater than one $CoP > 1$.

	$-TS \rightarrow$	
$+pV \downarrow$	E	F
	H	G

Recap: Classical thermodynamics only focuses on macroscopic parameters and their measures.

Key Points:

- $dE = dQ + dW$ from 1st law.
- $dE = TdS - PdV$, and from 2nd law $dS = dQ/T$
- Relationship between (T, S) and (P, V) where F is the Hemholtz, G is Gibbs, and H is enthalpy.