# 1 Simple Applications of macroscopic thermodynamics

## 1.1 General relationship of thermodynamics

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

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

where

$$\dbar Q = dE + \dbar W = dE + pdV$$

The only external parameter of change is $V$

$$\implies dE = TdS - pdV$$

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

$$dE = TdS - pdV$$

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

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

so

$$dE = TdS - d(pV) + Vdp$$

or

$$d(E + pV) = TdS + Vdp$$

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

$$dE = d(TS) - SdT - pdV$$
$$d(E - TS) = -SdT - pdV$$

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

$$dF = dE - (TdS + SdT)$$
$$= TdS - pdV - Tds - SdT$$
$$= -SdT - pdV$$

2. So $F = F(T, V)$ the 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 $dV \to dp$ so from chain rule

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

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

$$dE = (d(TS) - SdT) - (d(pV) - Vdp)$$
$$d(E - TS + pV) = -SdT + VdP$$

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**

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

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

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

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

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

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

which can be derived from the Thermodynamic functions

$$E = E(S, V)$$
$$H = H(S, p) = E + pV$$
$$F = F(T, V) = E - TS$$
$$G = G(T, p) = E - TS + pV$$

## 1.2   Specific Heats

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

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

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

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

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

$$đQ = dE + pdV = nC_V dT + pdV$$

- For an ideal gas

$$pV = nRT$$
$$pdV = nRdT$$
$$\implies \left(\frac{dV}{dT}\right) = \frac{nR}{p}$$

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 diatomimc molecule there are 2 extra degrees of freedom for rotaion so

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

## 1.3   Adiabatic expansion or compression

Some definitions:

- "Isothermal": $T$ is constant $\implies pV = $ Constant.

- "Adiabatic": $đQ = 0$

$$\implies 0 = dE + pdV$$
$$= nC_V dT + pdV$$

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

$$VdP + pdV = nRdT$$

and substituting $dT$ into the adiabatic expression

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

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 ge

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

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 or 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

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

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 $p_i V_i^\gamma = 1 \implies p = \frac{1}{V^\gamma}$

$$W = \int_{V_i}^{V_f} pdV = \int_{V_i}^{V_f} \frac{1}{V^\gamma}dV$$
$$= \frac{1}{1-\gamma}\left(V_f^{1-\gamma} - V_i^{1-\gamma}\right)$$

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

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

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

**General case:**

$$C_V = \left(\frac{\dstrok Q}{dT}\right)_V = T(\frac{\partial S}{\partial T})_V$$
$$C_p = \left(\frac{\dstrok Q}{dT}\right)_p = T(\frac{\partial S}{\partial T})_p$$

## 1.4　Entropy

Consider $S = S(T, P)$

$$\dstrok Q = TdS = T\left[\left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP\right]$$
$$= C_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

## 1.5 Specifc heats again

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

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

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

where

$$\text{đ}Q = TdS = T\left[\left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP\right]$$

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

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

$$C_V = \left(\frac{\text{đ}Q}{dT}\right)_V = C_p + T\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

where we can replace the entropy term wit 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 due (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 $\alpha$ and $\kappa$ then see if the above equation gives us the relation $C_P - C_V = R$

## 1.6   Entropy and Internala energy

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

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

etc.
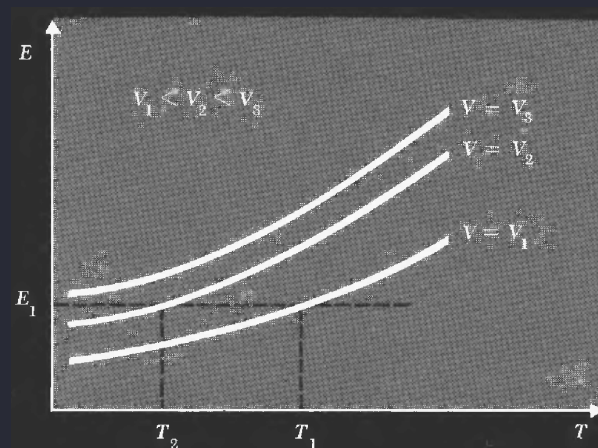
## 1.7   Free expansion of a gas

For the general case

$$dE = 0$$
$$E = E(T, V)$$



Figure 1.1: Free expansion of a gas

**Van de Waals Gas**

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

## 1.8   Heat Engine

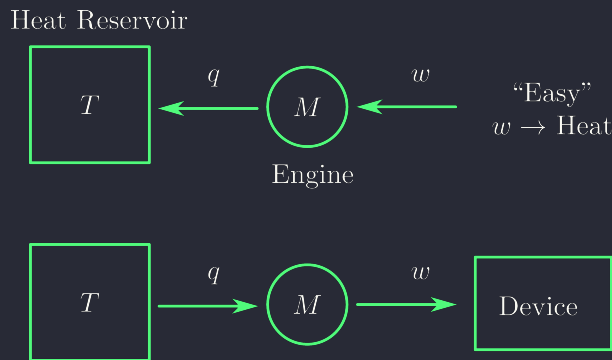What is a heat engine? Heat $\rightarrow$ Work.

Heat Reservoir



Figure 1.2: (top) reverse "easy" process converting work to heat. (botton) 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 hea reservoir $\Delta S = -q/T$ thus

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

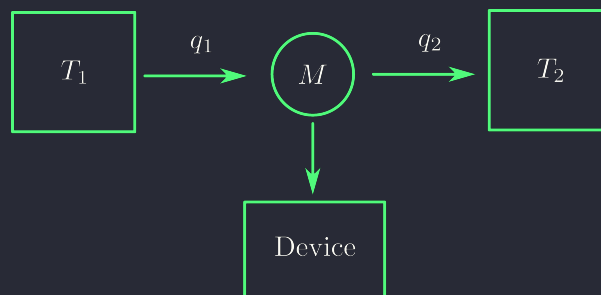Building a heat engine: Using two heat reservoirs



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

$$\Delta S_{\text{tot}} = -\frac{q_1}{T_1} - \frac{q_2}{T_2} \geq 0$$

$$= -\frac{q_1}{T_1} + \frac{q_1 - W}{T_2}$$

$$\implies \frac{W}{T_2} \leq q_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

thus the efficiency of the engine

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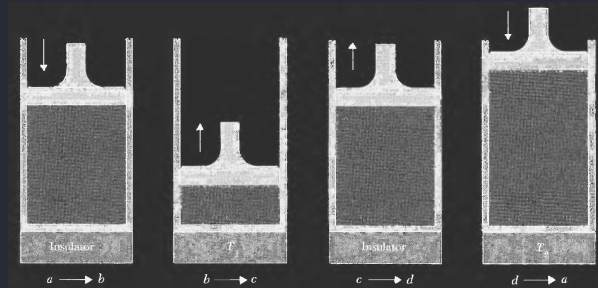$$= 1 - \frac{T_2}{T_1}$$

**Carnot Engine**



Figure 1.4: 4 stages of Carnot Engine

- $a \to b$: adiabatic (no heat exchange) bringing colder $T_2 \to T_1$

- $b \to c$: isothermal (constant temp) adding heat $q_1$ from hot reservoir

- $c \to d$: adiabatic (no heat exchange) cooling down $T_1 \to T_2$ as work is done through expansion

- $d \to a$: isothermal (constant temp) releasing heat $q_2$ to cold reservoir

**Worksheet**   Carnot Engine using an ideal gas:
The work done is

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

so using the ideal gas law $PV = nRT$