

20<sup>th</sup> February 2019

Clausius inequality  $\rightarrow$

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

$\rightarrow$  Equality holds for reversible processes.

$$(*) \int_i^f \frac{\delta Q_{rev}}{T} \Big|_1 = \int_i^f \frac{\delta Q_{rev}}{T} \Big|_2$$

This allows us to introduce a state function —

$$dS = \frac{\delta Q_{rev}}{T}$$

$$\Rightarrow S_2 - S_1 = \Delta S = \int_1^2 \frac{\delta Q_{rev}}{T}$$

↑  
Entropy (State fn.)

$$(*) S(f) - S(i) > \int_i^f \frac{\delta Q_{irrev}}{T}$$

$$\Rightarrow \Delta S \geq \frac{\delta Q}{T}$$

↕  
□ Clarify this step.

◦ Process adiabatic  $\rightarrow$

$$S(f) \geq S(i)$$

(2nd Law entropic version)

Here we note that this is limited to adiabatic process only. — but that is not entirely true. It is equivalent to all other versions of the statement.

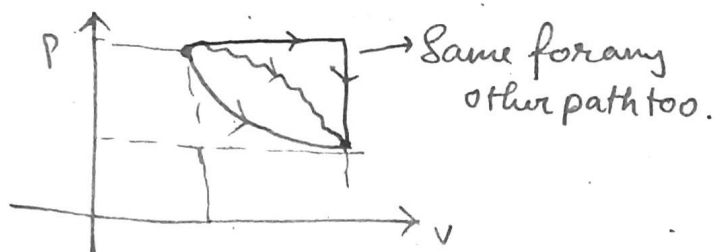
(\*) We can always consider a process adiabatic if we consider system + surroundings.

# 0 Calculations of entropy ~~case~~ change →

## 0. Joule's Free Expansion →

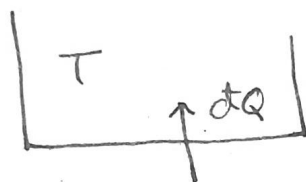
→ Process is irreversible  $(P_0, V_0, T_0) \rightarrow (\frac{P_0}{2}, 2V_0, T_0)$

→ Consider hypothetical 'isothermal process'.



Connect same initial and final state.

## ② Entropy change of a reservoir →



(\*) Marker for reservoir is internal energy.

(\*) If you add water to the ocean, the height of ocean remains unchanged, but the amount of water does change.

$$\Delta S = \int_i^f \frac{dQ_{\text{rev}}}{T}$$

$$\text{or } dS = \frac{dQ_{\text{rev}}}{T} = \frac{dQ}{T}$$

??  
It is the only marker of the reservoir (only state func)  
so it does not matter if the heat was transferred reversibly or irreversibly.

③ Reservoir ( $T_R$ ) and small system ( $T_S$ )

$$\Delta S_{\text{system}} = \int \frac{\delta Q_{\text{rev}}}{T} \quad (T_R > T_S, \text{ say})$$

$$\delta Q = C dT \Rightarrow C \equiv \frac{\delta Q}{dT} \quad (\text{polytropic process})$$

$$\therefore \Delta S_{\text{system}} = \int_{T_S}^{T_R} \frac{C dT}{T} = C \ln \left( \frac{T_R}{T_S} \right)$$

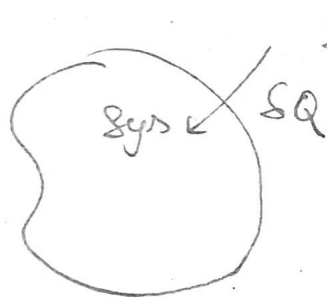
$$\therefore \Delta S_{\text{reservoir}} = \int \frac{\delta Q}{T_R} = \frac{\Delta Q}{T_R} = \frac{C(T_S - T_R)}{T_R}$$

Now, we add these,

$$\Delta S_{\text{universe}} = \Delta S_{\text{reservoir}} + \Delta S_{\text{system}} \rightarrow ?$$

We will find that ~~it~~ it is +ve.

○ Principle of entropy increase  $\rightarrow$



$$\Delta S_{\text{surr}} = - \frac{\delta Q}{T_{\text{surr}}}$$

This is the case where surroundings is so large that it acts like a reservoir, making this true.

$$\Delta S_{\text{sys}} \geq \frac{\delta Q}{T_{\text{sys}}} \rightarrow \text{Clausius ineq.}$$

$$\therefore \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\geq \frac{\delta Q}{T_{\text{sys}}} - \frac{\delta Q}{T_{\text{surr}}}$$

$$= \delta Q \left( \frac{1}{T_{\text{sys}}} - \frac{1}{T_{\text{surr}}} \right) \geq 0$$

as  $T_{\text{surr}} > T_{\text{sys}}$

## Internal Energy for Ideal and Vander Waals gas. $\rightarrow$

\* We have used thus far the fact that  $\left(\frac{du}{dv}\right) = 0$  for ideal gas as experimental fact. Now we derive it.

$$\delta Q = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[p + \left(\frac{\partial u}{\partial v}\right)\right] dv$$

(1st law of thermodynamics)

$$\Rightarrow \frac{\delta Q}{T} = dS = \frac{1}{T} \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\frac{1}{T} \left(\frac{\partial u}{\partial v}\right)_T + \frac{p}{T}\right] dv$$

(2nd law added)  $\rightarrow$  State function.

RHS must be exact differential.

•  $M(x, y) dx + N(x, y) dy$  is exact if  $\frac{\partial M}{\partial y}|_x = \frac{\partial N}{\partial x}|_y$

$$\left[\frac{\partial}{\partial v} \left\{ \frac{1}{T} \left(\frac{\partial u}{\partial T}\right)_v \right\}\right]_T = \left[\frac{\partial}{\partial T} \left\{ \frac{1}{T} \left(\frac{\partial u}{\partial v}\right)_T + \frac{p}{T} \right\}\right]_v$$

then  $dS$  is an exact differential.

$$\Rightarrow \frac{1}{T} \frac{\partial^2 u}{\partial T \partial v} = \frac{1}{T} \frac{\partial^2 u}{\partial T \partial v} + \frac{1}{T^2} \left(\frac{\partial u}{\partial v}\right)_T + \left[\frac{\partial}{\partial T} \left(\frac{p}{T}\right)\right]_v$$

$\swarrow \quad \searrow$   
Cancel

$$\Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T^2 \left[\frac{\partial}{\partial T} \left(\frac{p}{T}\right)\right]_v$$

$$= T \left(\frac{\partial p}{\partial T}\right)_v - p$$

$$\Rightarrow \boxed{\frac{1}{T} \left(\frac{\partial u}{\partial v}\right)_T + \frac{p}{T} = \left(\frac{\partial p}{\partial T}\right)_v} \quad \begin{matrix} (*) \\ \text{Imp} \end{matrix} \quad \begin{matrix} (*) \\ \text{No assumption of} \\ \text{system} \end{matrix}$$

Take entropy expression,  $\left(\frac{\partial S}{\partial v}\right)_T = 0 + \left(\frac{1}{T} \left(\frac{\partial u}{\partial v}\right)_T + \frac{p}{T}\right)$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v}$$

One of Maxwell's equations.

• Ideal gas →

$$P = \frac{nRT}{V} \Rightarrow \left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}$$

$$\therefore \frac{1}{T} \left( \frac{\partial u}{\partial V} \right)_T + \frac{P}{T} = \frac{nR}{V}$$

$$\Rightarrow \frac{1}{T} \left( \frac{\partial u}{\partial V} \right)_T + \frac{P}{T} = \frac{P}{T} \quad (\text{for IG})$$

$$\Rightarrow \boxed{\left( \frac{\partial u}{\partial V} \right)_T = 0}$$

Ideal gas internal energy does not depend on volume.

$$\Rightarrow U = f(T) = \frac{3}{2} nRT$$

→ Thermodynamics cannot tell you - KTG does.

• Van der Waals gas →

□ Do calculation yourself.

$$\Rightarrow \boxed{\left( \frac{\partial u}{\partial V} \right)_T = \frac{n^2 a}{V^2}}$$

Integrating,

$$U = g(T) - \frac{n^2 a}{V}$$

↓

Thermodynamics cannot calculate this.

22<sup>nd</sup> Feb 2022

$$du = \delta Q + \delta w$$

$$\Rightarrow \delta Q = du - \delta w$$

→ Reversible quasi-static (hydrostatic) process,

$$\delta w = -p dv$$

Now,

$$\delta Q_{rev} = T dS \Rightarrow dS = \left( \frac{1}{T} \right) \delta Q_{rev}$$

□ Read about this  
(side comment -  
no exam ques)

integrating factor  
that makes  $\delta Q_{rev}$  exact  
differential.

$$\therefore T dS = du + p dv$$

We may think this only for reversible processes. — but that is not the case.

$$T dS = du + p dv$$

↓                      ↓                      ↘  
Exact (state)      Exact (state)      Exact (state)

If we change,  $(S_1, u_1, v_1) \rightarrow (S_2, u_2, v_2)$   
it does not depend on the process/path, as this is  
change in state variables only.

⇒ This expression is true in general.

\* Note that  $\delta w = -p dv$  can be done when we have  
assumed quasi-static process.

$$\therefore Tds = C_v dT + p dv$$

↙ Ideal gas

$$\Rightarrow Tds = C_p dT - v dp$$

Now,  $pV = RT \Rightarrow p dv + v dp = R dT$

$$\therefore Tds = (C_p p dv + C_v v dp) \frac{1}{R}$$

⊗ We can use these formulae to calculate change in entropy

always pick the path along which integration is the easiest.

$$\therefore S_2 - S_1 = C_p \ln\left(\frac{v_2}{v_1}\right) + C_v \ln\left(\frac{p_2}{p_1}\right)$$

$$\begin{aligned} (p_1, v_1) &\rightarrow (p_2, v_2) \\ \Rightarrow S_2 - S_1 &= C_v \ln\left(\frac{p_2}{p_1}\right) + \gamma C_v \ln\left(\frac{v_2}{v_1}\right) \\ &= C_v \ln\left(\frac{p_2 v_2^\gamma}{p_1 v_1^\gamma}\right) \end{aligned}$$

○ Entropy change for Van der Waals gas →

$$\begin{aligned} S_2 - S_1 &= \int \frac{dQ}{T} \\ &= \int C_v dT + \int \frac{1}{T} \left( p + \left( \frac{\partial u}{\partial v} \right)_T \right) dv \end{aligned}$$

↗ probably wrong

$$\Rightarrow u = u_0 + C T - u^2 \frac{a}{v^2}$$

↓  
cannot be derived  
in thermodynamics.

$$\Rightarrow \left( \frac{\partial u}{\partial v} \right)_T = \frac{n^2 a}{v^2}$$

$$\begin{aligned} p + \left( \frac{\partial u}{\partial v} \right)_T &= \frac{nRT}{v-nb} - \frac{n^2 a}{v^2} + \frac{n^2 a}{v^2} \\ &= \frac{nRT}{v-nb} \end{aligned}$$

$$\therefore \frac{\delta Q}{T} = C_v \frac{dT}{T} + \frac{nRT}{(v-nb)^2} dv$$

$$\Rightarrow \frac{\delta Q}{T} = C_v \frac{dT}{T} + \frac{nR}{(v-nb)} dv$$

$$\begin{aligned} \therefore S_2 - S_1 &= \int \frac{\delta Q}{T} \\ &= C_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2 - nb}{v_1 - nb} \right) \end{aligned}$$

Other ~~part~~ change,  $(T_1, v_1) \rightarrow (T_2, v_2)$

$$\text{In isothermal: } S_2 - S_1 = R \ln \left( \frac{v_2 - b}{v_1 - b} \right)$$

(\*) You can ~~also~~ calculate this by calculating total heat exchanged and dividing that by T.

□ HW: Calculate  $dW$ , calculate  $du$ ;  
calculate  $dQ$ .



$$\therefore dQ = T dS$$

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

$$\Rightarrow C_v = T \left( \frac{\partial S}{\partial T} \right)_v$$

Now,

$$S = S(V, T)$$

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

$$\Rightarrow \left( \frac{\partial S}{\partial T} \right)_p = \left( \frac{\partial S}{\partial T} \right)_v + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p$$

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

Now using maxwell equation,

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

$$\Rightarrow C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_p$$

True in general

Ideal gas,  $PV = nRT$

$$\Rightarrow C_p - C_v = \frac{nR}{V} \cdot \frac{nR}{P} T$$

$$= nR$$

⊗ In older derivation, we had to assume  $U$  is not a function of  $V$ . — so 2nd law input required.

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

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

Using maxwell eqn again

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

Using that -1 PD formula

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

another one of maxwells  
equations.