

SM part 1. thermodynamics:

part 1. several conditions:

- ① slowly move
- ② release sth.
- ③ indistinguishable
- ④ when to use TAS \Rightarrow sd to give direction?
- ⑤ classical.
- ⑥ thermo engine. (multi-processes)

Tricks \Rightarrow math, Maxwell, state variables
must be consistent!!!

① joule effect, $\Delta f(H) = 0$

② ✓

state equation!!!

③ $p \cdot V = \text{const}$, yet $p = p_{\text{total}}$, $V = V_{\text{part}}$ or $p = p_{\text{part}}$, $V = V_{\text{total}}$
use different.

④ ✓

⑤ ✓

⑥ multi-process

① + ② + ④ + ⑤ = single process.

adiabatic? slow enough?

reversible \rightarrow conserved XXX energy

irreversible \rightarrow not

XXX energy

yet ⑥ is different, because

it is not a single process!!!

main point is sth.

is fixed. e.g. S.T.P.V. fixed.

choose either two. ✓

the strategy (for ^{thermodynamic} ~~microscopic~~ derivations)

(1) Summarize all of the microscopic quantities:

$N, \mu, T, S, V, p, \dots, \mathcal{J}, \mathcal{E}, \mathcal{F}, H, G.$

their definition, and their power. (what does their change mean).
and relation to other quantity (if needed more from definition).

(2) ~~In order to read~~ based on professor's talks.
then read the book ~~of~~ from Landau.

S, V, T, P. $C_4^2 \times 2 = 12$. $C_4^2 = 6$.

1) $\left(\frac{\partial a}{\partial b}\right)_c = \left(\frac{\partial a}{\partial b}\right)_d + \left(\frac{\partial a}{\partial d}\right)_b \cdot \left(\frac{\partial d}{\partial b}\right)_c$ (2) Maxwell (3) revert $\frac{1}{x}$.
 (4) chain?

already know:

$$\left(\frac{\partial V}{\partial P}\right)_T = -k_T V \quad \left(\frac{\partial V}{\partial P}\right)_S = -k_S V \quad \left(\frac{\partial V}{\partial T}\right)_P = \alpha V$$

could know =

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

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial T}{\partial P}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_P \cdot \left(\frac{\partial V}{\partial P}\right)_T = \frac{k_T}{\alpha}$$

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

up to now: revert + Maxwell (partial) \rightarrow total 12.

(V, P; T) (V, T; P) (P, T; V)

(V, P; S) (S, P; T) (S, V; T) ✓ (6)

2 x Maxwell.

and also define:

$$C_V = \left(\frac{\partial S}{\partial T}\right)_V = \frac{R}{T} C_V \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{R}{T} C_V$$

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

yet $\left\{ \begin{array}{l} C_P/C_V = k_T/k_S \\ C_P - C_V = \alpha^2 \cdot \frac{T \cdot V}{k_T} \end{array} \right.$

assume (S, T; V), (S, T; P), ✓ (2)

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_S \Rightarrow \left(\frac{\partial V}{\partial T}\right)_S = -\frac{R C_V / T}{\frac{R C_V k_T}{\alpha T}} = -\frac{R C_V k_T}{\alpha T}$$

(V, T; S) ✓

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_S \Rightarrow \left(\frac{\partial P}{\partial T}\right)_S = +\frac{R \cdot C_P \cdot \frac{R}{T}}{V \alpha T}$$

(P, T; S) ✓ (4)

$$\Rightarrow \left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S = \frac{\alpha T \cdot R}{R C_V k_T} (S, P; V)$$

$$\Rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S = \frac{\alpha T \cdot R}{R C_P} (S, V; P)$$

finish!

$$\left(\frac{\partial V}{\partial S}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_S \cdot \left(\frac{\partial P}{\partial S}\right)_V = -(-k_S V) \cdot \frac{\alpha T V}{C_P} = \frac{R \alpha k_T}{R C_V k_S}$$

The following table shows the results of the experiment. The first column is the time taken for the reaction to occur, the second column is the volume of gas produced, and the third column is the rate of reaction.

Time (s)	Volume of Gas (cm ³)	Rate of Reaction (cm ³ /s)
0	0	0
10	10	1.0
20	20	1.0
30	30	1.0
40	40	1.0
50	50	1.0
60	60	1.0
70	70	1.0
80	80	1.0
90	90	1.0
100	100	1.0

The rate of reaction is constant at 1.0 cm³/s. This is because the concentration of the reactants is constant throughout the experiment.

The volume of gas produced is directly proportional to the time taken for the reaction to occur. This is because the rate of reaction is constant.

The graph shows a straight line passing through the origin. This indicates that the reaction is first order with respect to the reactants.

The equation of the line is $V = t$, where V is the volume of gas produced and t is the time taken for the reaction to occur.

The gradient of the line is 1.0, which is equal to the rate of reaction.

Statistical mechanics partition function and thermodynamics.

Quantity in thermodynamics:


- $SQ \rightarrow$ environment E_m to system E .
- $E \rightarrow$ inner energy of E system.
- $P \rightarrow$ the outside pressure to E . $\delta W = -pdV$
- $V \rightarrow$ size of volume of E .
- $T \rightarrow$ thermodynamic quantity, equilibrium.
- $S \rightarrow$ entropy, degree of freedom's free-level.


$$\begin{cases} H \\ M \end{cases} \begin{cases} \sigma \\ A \end{cases} \begin{cases} V \\ q \end{cases} = \begin{cases} -P \\ V \end{cases} = \begin{cases} \sigma \\ Y \end{cases}$$

\Rightarrow $F = E - TS$ $H = E + pV$ $G = E - TS + pV$

micro systems: $E = \sum E_i$, $N = \sum N_i$, ...

11. $p = \sum P_i p_i$, $S = \sum -P_i \ln P_i = -\ln(p \ln p)$ □

12. $\frac{dP}{dE}$  $\frac{dP}{dE} \cdot dE$

$w(E)$  $\Rightarrow W(E) = \frac{dP}{dE} \cdot w(E)$ is "non-degenerate" for E .

i.e. after degeneracy averaged non-degenerate state. \checkmark
 $w(E) \Delta E = 1$ the broadness of this distribution are how much "uniform energy" are required.
 $w(\bar{E}) \Delta T = 1$ how much "uniform states" are required.

$\Delta T = \Delta p \Delta q / (2\pi\hbar)^5$ exactly how many "states" required.
 $S = \ln \Delta T \Rightarrow$ give us the size of linear expansion" □

grand distribution function:

$$w(E) = \frac{1}{Z} \cdot \exp[\beta(\mu - E)]$$

$$Z = \sum \exp[\beta(\mu - E)]$$

$$\langle N \rangle = +T \cdot \partial \ln Z$$

$$\langle E \rangle = +T^2 \partial_T \ln Z$$

$$\langle Y \rangle = -T \partial_Y \ln Z$$

$$S = \ln Z + \frac{\mu \langle N \rangle}{T} + \frac{\langle E \rangle}{T}$$

$$\left(= \sum \frac{e^{-\alpha N}}{N! h^{3N}} \int e^{-\beta E} d\Omega \right)$$

$$d\Omega = (dp dq)^N$$

Canonical distribution:

$$Z = \sum e^{-E/T} \quad F = -T \ln Z$$

$$S = (\partial F / \partial T)_V \quad E = T^2 \partial \ln Z / \partial T$$

$$Z_N = \frac{1}{N!} Z_1^N \quad F_N = TN [\ln N - 1 - \ln Z_1 - p]$$

$$G_N = \dots \quad \mu = \dots$$

? distinguishable?
indistinguishable?

Relations = (1). $dE = Tds - pdV$. (F. G. H ...)

$$\mu = \frac{1}{N} G \quad !!! \text{ most amazing solution!}$$

(2). $p = p(T, V)$ state relation

? conditions : (1). $\left\{ \begin{array}{l} \text{reversible} \cdot dE = Tds - pdV \text{ conserved xxx energy } S \rightarrow \text{max?} \\ \text{irreversible } dE \leq Tds - pdV \text{ min/max xxx energy or } S \rightarrow \text{max?} \end{array} \right.$

(2). single process \rightarrow fix two. change 1.

multi process \rightarrow complicated, ~~remember~~ remember the thermo engine !!

3. ~~different~~ ^{same} species : $p = \text{const}$ yet $V \propto$ ratio
different species : $p \propto$ ratio. yet $V = \text{const}$.