

~~Free~~

FREE ENERGY

$$\bar{F} = -kT \ln Z \quad Z = e^{-F/kT}$$

$$F = U - TS$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T} \quad \longleftrightarrow \quad F = -kT \ln Z - TS$$

↓

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)$$

$$\frac{\partial F}{\partial T} = \frac{\partial}{\partial T} (-kT \ln Z) = -k \ln Z - kT \frac{\partial}{\partial T} \ln Z$$

$$\begin{aligned} \frac{\partial}{\partial T} \ln Z &= \frac{\partial \ln Z}{\partial T} = \frac{1}{Z} \frac{\partial Z}{\partial T} = \frac{1}{kT^2} \frac{\partial}{\partial T} \left(\sum_i e^{-\beta \epsilon_i} \right) \\ &= \frac{U}{kT^2} \end{aligned}$$

$$\frac{\partial F}{\partial T} = -k \ln Z - kT \frac{U}{kT^2} = \frac{F}{T} - \frac{U}{T} \quad \checkmark$$

DISTINGUISHABLE AND IN DISTINGUISHABLE PARTICLES

6.6

~~PARTITION~~ Fun



1

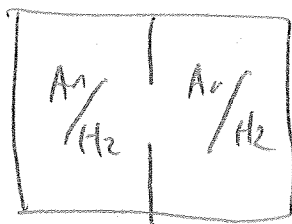
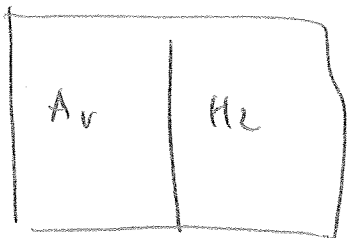
E_1



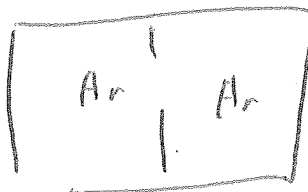
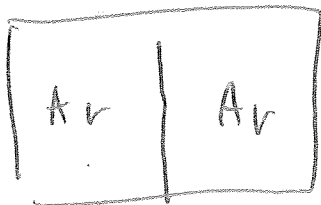
2

E_2

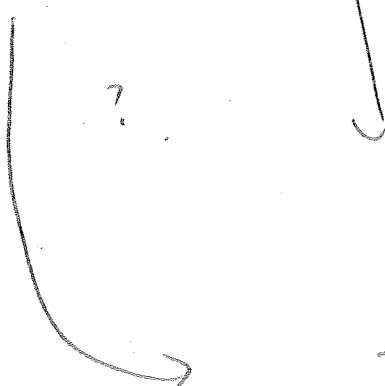
$$Z_{TOTAL} = Z_1 + Z_2$$



$$\Delta S = 2Nk_B \ln 2$$



$$\Delta S = 0$$

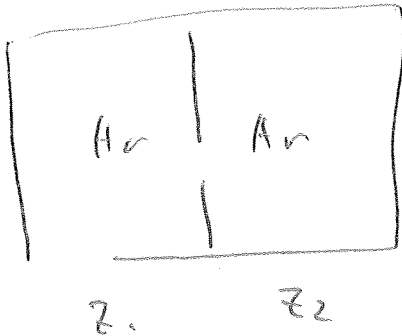


$$Z_{TOTAL} = Z_1 Z_2$$

$$Z_{TOTAL} = \frac{1}{2} Z Z$$

$$F = -kT \ln Z$$

$$S = \frac{\partial F}{\partial T} = -k \ln Z = \frac{F - U}{T}$$



$$z_1 = \sum_s e^{-\beta E_s} \quad z_2 = \sum_s e^{-\beta E_s}$$



~~$$z_1 = \sum_s e^{-\beta E_s}$$~~

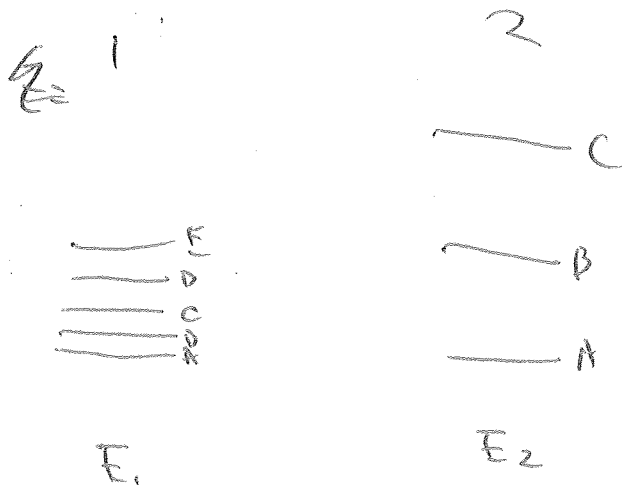
$$z_1 = \sum_{s_1} e^{-\beta E_1(s_1)}$$

$$E_1 \quad E_2$$

$$z_2 = \sum_{s_2} e^{-\beta E_2(s_2)}$$

$$E_1 + E_2 = E_T$$

$$z_{\text{TOTAL}} = \sum_s e^{-\beta (E_1 + E_2)}$$

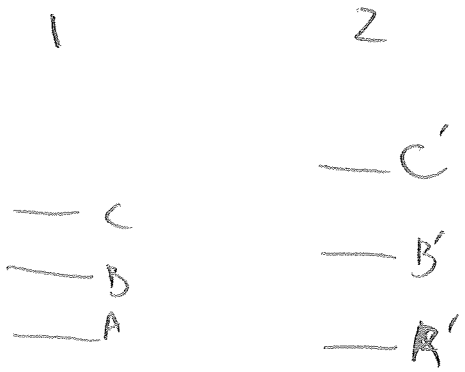


$$Z_{\text{TOTAL}} = \sum_s e^{-(E_1 + E_2) / kT}$$

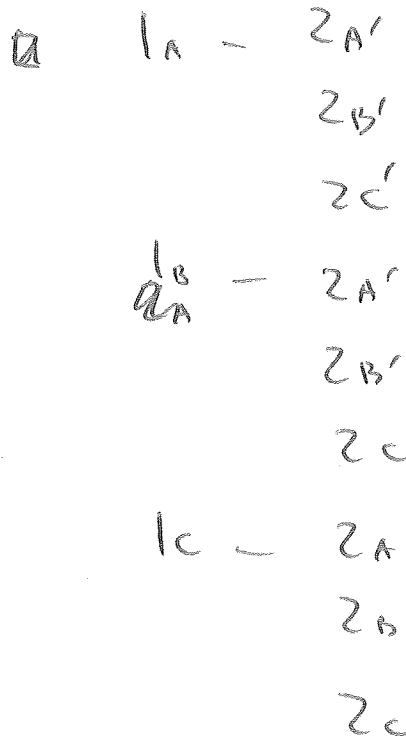
$$Z_1 = \sum_{s_1} e^{-E_1(s_1) / kT} \quad Z_2 = \sum_{s_2} e^{-E_2(s_2) / kT}$$

1	2
A	A
A	B
A	C
B	A
B	B
B	C

$$Z_T = Z_1 Z_2$$



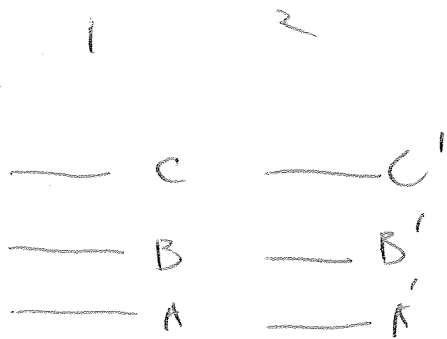
$$Z_1 = e^{-E_A/\beta} + \frac{1}{2} e^{-E_B/\beta} + e^{-E_C/\beta}$$



~~A A~~

$$A^2 + B' \neq \frac{1}{2}(A+B)$$

$$B + A'$$



A - A'
 - B'
 - C'

DUT E A - B' -

~~E~~
 B - A'

DOUBLE CENTER

B A'
 B'
 C'

C - A'
 B'
 C'

IDEAL GAS

$$Z = \frac{1}{N!} Z_1^N$$
