FREE ENERGY

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

$$F = U - TS$$

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

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T} \longrightarrow F = -kT \ln Z \text{ FITS}$$

$$\Downarrow$$

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

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

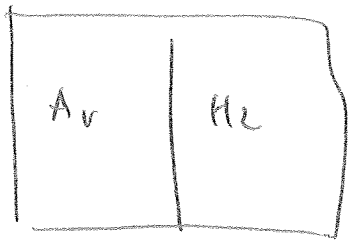
$$\frac{\partial}{\partial T} \ln Z = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \ln Z = -\frac{1}{kT^2} \frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

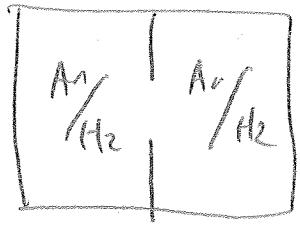
$$= \frac{U}{kT^2}$$

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

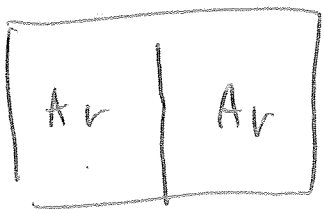
6.6 DISTINGUISHABLE AND INDISTINGUISHABLE PARTICLES

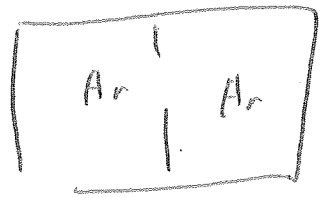
E_1 E_2





$\Delta S = 2Nk \ln 2$





$\Delta S = 0$

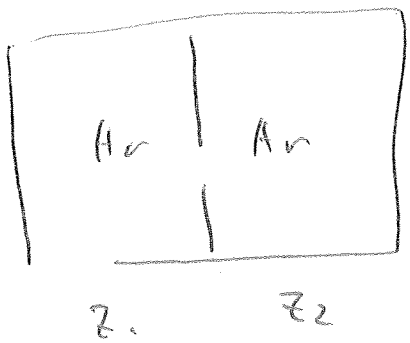
?

$Z_{TOTAL} = Z_1 Z_2$

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

$$F = -kT \ln Z$$

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



$$Z_1 = \sum_s e^{-\beta \varepsilon_s} \qquad Z_2 = \sum_s e^{-\beta \varepsilon_{2s}}$$

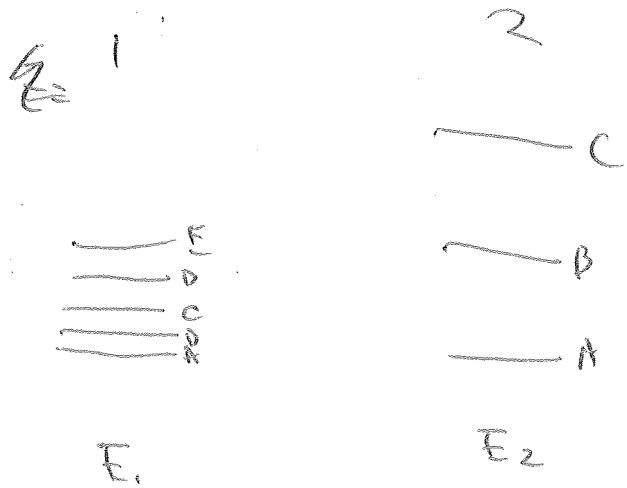
---

1 2

E_1 E_2

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

$$E_1 + E_2 = E_T \qquad Z_{TOTAL} = \sum_s e^{-(E_1+E_2)/\beta}$$

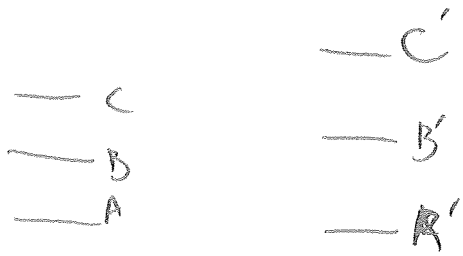


$$Z_{TOTAL} = \sum_{S} e^{-(E_1 + E_2)/\beta}$$

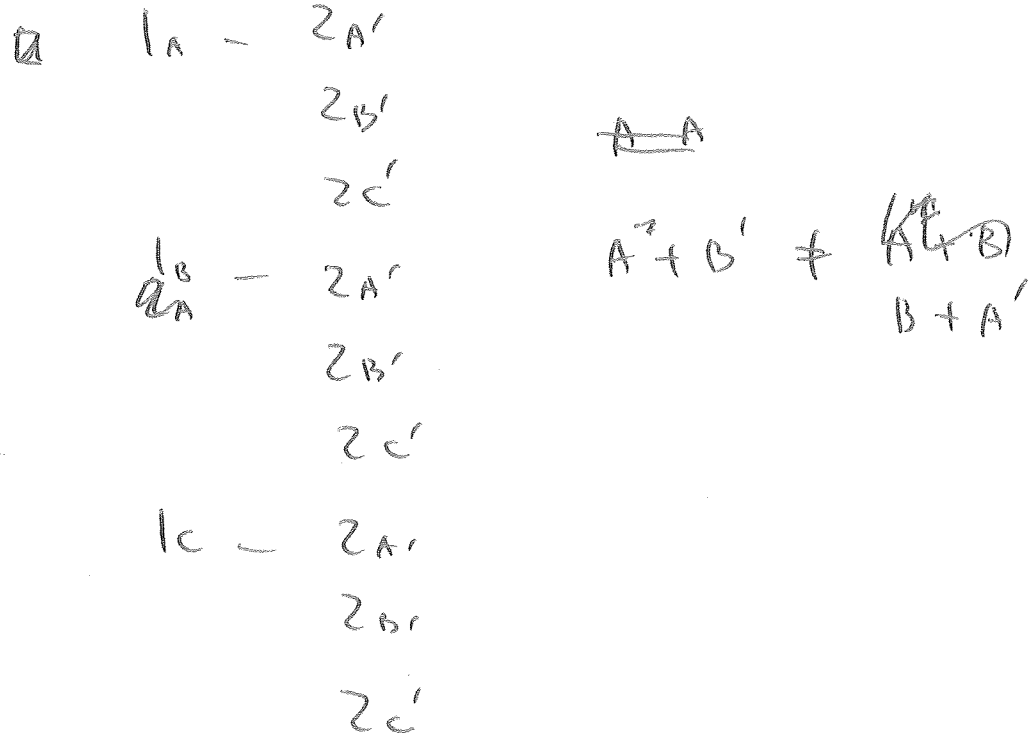
$$Z_1 = \sum_{S_1} e^{-E_1(S_1)/\beta} \qquad Z_2 = \sum_{S_2} e^{-E_2(S_2)/\beta}$$

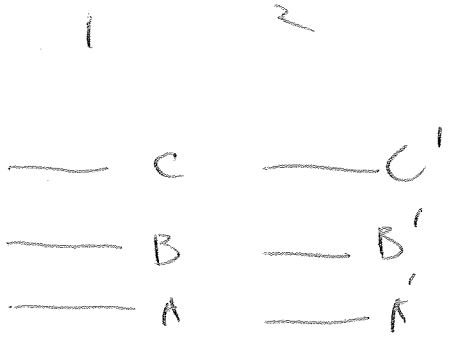
1	2
A	A
A	B
A	C
B	A
B	B
B	C

$$Z_T = Z_1 Z_2$$



$$Z_1 = e^{-E_A/\beta} + e^{-E_B/\beta} + e^{-E_C/\beta} \cdots$$





A - A'
, - B'
- C'

B A'
B'
C'

C - A'
B'
C'

BUT $E_{A-B'}$ = ~~$E_{B'-A}$~~ B - A' DOUBLE COUNT

IDEAL GAS

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