

Lecture 24

Monday, October 23, 2023 9:55 AM

Last Time = "Chain of Command"

$$W(E, V, \dots) \leftrightarrow E(S, V, \dots) \leftrightarrow \begin{cases} H(S, P) = E + PV \\ F(T, V) = E - TS \end{cases} \leftrightarrow \begin{cases} G(T, P) = E + PV - TS \\ = H - TS \\ = \mu N \end{cases}$$

↑
chemical potential
= molar free energy

Heat Capacity =

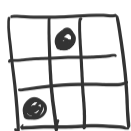
$$dE = C_v dT, \quad dS = \frac{dE}{T} = \frac{C_v dT}{T} \quad (\text{const. } V \ \& \ n)$$

$$dH = C_p dT, \quad dS = \frac{dH}{T} = \frac{C_p dT}{T} \quad (\text{const. } P \ \& \ n)$$

Deriving Laws: ① System equilibrium

② Postulates equation

③ Combine



$$S_{\text{gas}} \sim nR \ln W \quad \left. \begin{array}{l} \frac{dS}{dV} = \frac{nR}{V} \\ \frac{dS}{dT} = \frac{P}{T} \end{array} \right\} \begin{array}{l} PV = nRT \\ \text{"ideal" gas} \end{array}$$

Today: Reactions @ constant T (not const E, as in postulate 2)

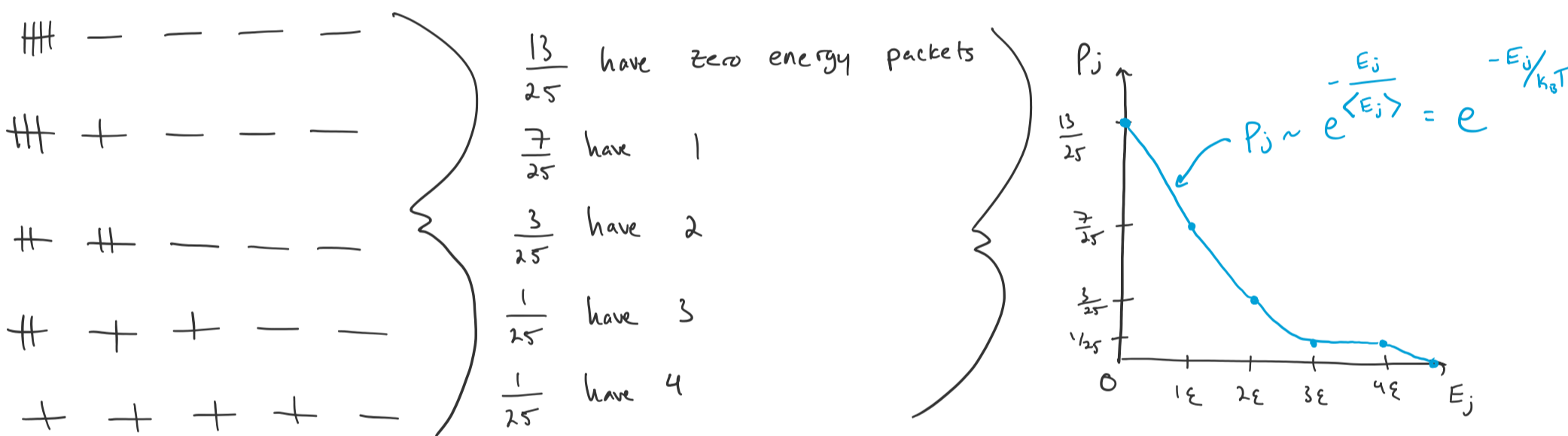
$P_j = \frac{1}{W_j}$ by Postulate 2 @ const. E. What about const T?

ex. pg 17 of notes in class exercise

$N = 5$ identical molecules

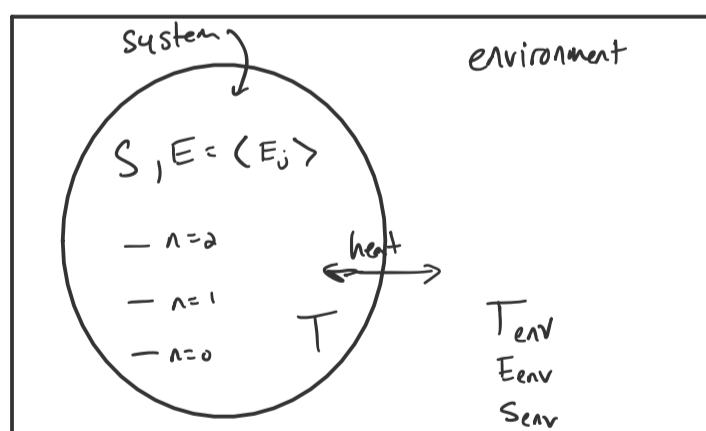
$K = 4$ identical energy packets, each of energy "E"

Distributed randomly among the molecules



⇒ higher E states are more likely @ higher T

"Ansatz" of the more rigorous derivation in the notes:



$$P_j = P(E_j)$$

↑
total isolated system

$$E_{\text{env}} + E = E_{\text{tot}}$$

① $W_{\text{tot}}(E_{\text{tot}})$ = total # of microstates in the total isolated system

② $W(E_j) \cdot W_{\text{env}}(E_{\text{tot}} - E)$ = # of microstates if the system has energy E_j

$$\Rightarrow P_j = \frac{W(E_j) W_{\text{env}}(E_{\text{tot}} - E)}{W(E_{\text{tot}})}$$

Need to replace "tot" & "env" by system variables

If we eliminate total/environment variables in favor of system variables,

$$P_j = W(E_j) e^{-E_j / k_B T} \cdot \frac{1}{Z}$$

← Boltzmann factor

$$Z = e^{-(E-TS)/k_B T} = e^{-F/k_B T}$$