Last Time: heat capacity and "laws"

Only valid in these special cases: $dE = C_v dT$; $dS = \frac{dE}{T} = C_v dT$ at const. V

$dH = C_p dT$; $dS = \frac{dH}{T} = \frac{C_p dT}{T}$ at const. P

$PV = nRT$ an example of a "law"

Always that: $dS = \frac{P}{T} dV + \dots \Rightarrow \frac{dS}{dV} = \frac{P}{T}$

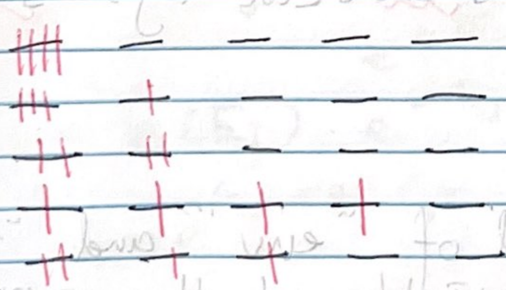
Only true for: $dS = nR \ln\frac{V}{n} + \dots \Rightarrow \frac{dS}{dV} = \frac{nR}{V}$ particle in a box when $M \gg N \gg 1$

Today: more on reaction at const. T

So far, $E(S) \rightarrow E(T)$, but $W(E) \rightarrow ?$ at const. T

$P_j = \frac{1}{W}$ (const E)$_j$ but $P_j = ?$ at const. T

ex: p. 17 includes exercise. $K = 4$ energy packet "ε" distributed randomly among $N = 5$ identical molecules



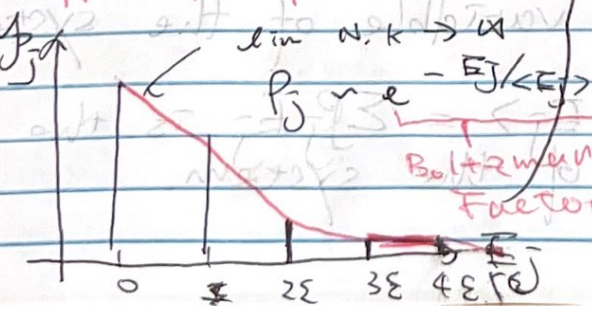
$P_j = \frac{13}{25}$ if $E = 0$

$P_j = \frac{7}{25}$ if $E = \varepsilon$

$P_j = \frac{3}{25}$ if $E = 2\varepsilon$

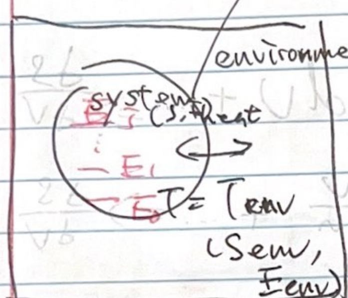
$\vdots$

$P_j = \frac{1}{25}$ if $E = 4\varepsilon$.



Higher E states are less likely at a given T.

Proof: $E = \langle E_j \rangle = \sum P_j E_j$.



$P_j = P(E_j)$? when $T =$ constant

① $W_{tot}(E_{tot}) = \#$ of microstates

② $\#$ of microstates when system is at energy E_j

$W(E_j) \cdot W_{env}(E_{tot} - E_j)$

Isolated system

$E_{tot} = \text{constant}$

By energy conservation:

③. $$P_j = \frac{W(E_j) \cdot W_{env}(E_{tot} - E_j)}{W_{tot}(E_{tot})} < 1.$$

use $S = k_B \ln W$

$W = e^{S/k_B}$

Not that useful → Prefer 1 variable in a function.

$$= W(E_j) \cdot e^{\{(S_{env}(E_{tot} - E_j) - S_{tot}(E_{tot})\}}$$

④ Want to get rid of "env" and "tot" and only have variable of the system left.

a). Let $E = \langle E_j \rangle = \sum P_j E_j$ is the average energy of the system.

$\Rightarrow S_{tot}(E_{tot}) = S(E) + S_{env}(E_{tot} - E)$.

so we get rid of ~~$S(E_{tot})$~~ $S_{tot}(E_{tot})$

$$\Rightarrow P_j = W_j\, e^{\{S_{env}(E_{tot}-E_j) - S(E) - S_{env}(E_{tot}-E)\}/k_B}$$

b). Trick: Taylor expansion S_{env} about E

$$y(x-x_0) = y(x_0) + \frac{dy}{dx}\Big|_{x_0}(x-x_0) + \dots$$

$$S_{env}(E_{tot}-E_j) = S_{env}(E_{tot}-E) + \frac{dS_{env}}{dE_j}(E_j - E) + \dots$$

$$= \cancel{S_{env}} \quad + \left(\frac{\partial S_{env}}{\partial E_{env}}\right)\left(\frac{\partial E_{env}}{\partial E_j}\right)(E_j - E) + \dots$$

$1/T$ $\quad = -1$

$$S_{env}(E_{tot}-E_j) = S_{env}(E_{tot}-E) + \frac{1}{T}(E_j - E)$$

Inserting S_{env}.

$$p_j = W(E_j)\cdot e^{\{-S - \frac{1}{T}(E-E_j)\}/k_B}$$

$$= W(E_j)\cdot \frac{e^{-E_j/k_BT}}{e^{-(E-TS)/k_BT}}$$

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

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

$$F = -k_BT\ln Z$$

$W(E)$ $\qquad$ $Z(T)$

$p_j = \frac{1}{W}$ $\qquad$ $p_j = \frac{1}{Z}W(E_i)\cdot e^{-E_j/k_BT}$.