More on entropy

$$S = k\ell nW = -k\Sigma P_i \ell nP_i$$

$$W = \frac{N!}{n_1!n_2!\ldots n_t!}$$

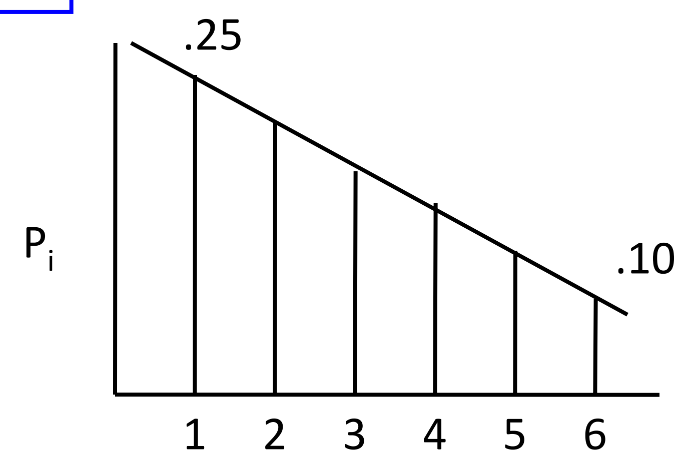
$$P_i = \frac{n_i}{N}$$

if no constraints: max entropy $\Rightarrow$ flat distribution

role dice: 1, 2, 3, 4, 5, 6 equally probable

constraints max entropy $\Rightarrow$ exponential distributions

unbiased dice avg score = 3.5
if biased so that avg score = 3.0 ⟶



$$S = -k\Sigma P_i \ell nP_i$$

only function for which all prob, = when no constraints and probabilities obey multiplication rule when there are constraints

Entropy is a way of dealing with incomplete information

ex: four-sided die: red 1; red 2; blue 1, blue 2

suppose red and blue occur 50% of time, 1 occurs ¾ of time, and 2 ¼ of time

	1	2
r	1/4	1/4
b	1/2	0

	1	2
r	3/8	1/8
b	3/8	1/8

	1	2
r	1/2	0
b	1/4	1/4

all are consistent with observations

least biased ← we have no reason to believe there are color differences

Partition functions – various degrees of freedom – single particle

translation

1D particle-in-box $\varepsilon_n = \frac{n^2 h^2}{8mL^2}$

$$\theta_{tr} = \frac{h^2}{8mL^2 k}$$

$$q_{tr} = \sum_{n=1}^{\infty} e^{-n^2 h^2/8mL^2 kT} = \sum_{n=1}^{\infty} e^{-n^2 \theta_{tr}/T}$$

In general, $\theta_{tr}/T << 1$

$$q_{tr} \sim \int_0^{\infty} e^{-n^2 \theta_{tr}/T} dn = \sqrt{\frac{2\pi mkT}{h^2}} L$$

For 3D $q_{tr} = q_x q_y q_z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \frac{V}{\Lambda^3}$

Argon, T = 273 K, V = 2.24 x 10^{-2} m^3 (standard state vol.)

q_{tr} =4.8 x 10^{30} states/atom

$$E_{tr} = \frac{3}{2} kT \qquad C_{v,tr} = \frac{3}{2} k$$

vibrations – assume harmonic oscillator

$$q_{vibr} = \sum_{v=0}^{\infty} e^{-\left(v+\frac{1}{2}\right)\frac{h\upsilon}{kT}} = e^{-\frac{h\upsilon}{2kT}}\left(1+e^{-\frac{h\upsilon}{kT}}+e^{-\frac{2h\upsilon}{kT}}+\ldots\right)$$

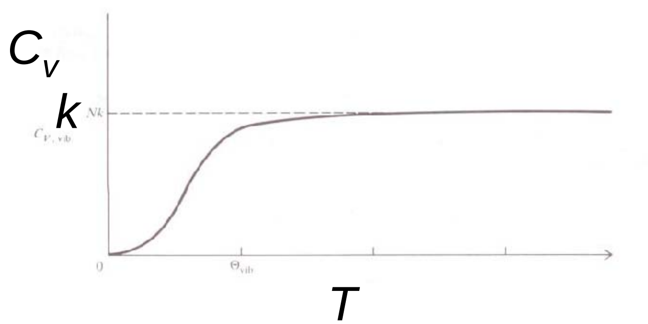
$$= e^{-\frac{h\upsilon}{2kT}}\left(1+x+x^2+\ldots\right) = \frac{e^{-h\upsilon/2kT}}{1-x}$$

$$q_{vibr} = \frac{1}{1-e^{-h\upsilon/kT}}$$

$T \to \infty$: $\frac{kT}{h\nu}$

$T \to 0$: 1

The ZPE contribution has been removed



O_2, T = 273 K , q_{vib} = 1.005
→ most molecules in ground state

In the high *T* limit, $E_{vib} = kT$, $C_v = k$ *(equipartition theorem: KE and PE contributions)*

Rotations – assume rigid rotor, diatomic

$$\varepsilon_\ell = \frac{\ell(\ell+1)h^2}{8\pi^2 I}, \quad \theta_{rot} = \frac{h^2}{k8\pi^2 I}$$

$$q_{rot} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\varepsilon_\ell/kT}$$

↑ degeneracy

for $T >> \theta_{rot}$, approx. as $\int$

$$q_{rot} = \frac{T}{\sigma\theta_{rot}} = \frac{8\pi^2 IkT}{\sigma h^2}$$

High T, $E_{rot} = kT$, $C_{v,rot} = k$: equipartition theorem

σ = symmetry #
1 – heteronuclear diatomic
2 – homonuclear diatomic
2 – H_2O
12 – C_6H_6

O_2, T = 273 K, q_{rot} = 72

nonlinear molecules

$$q_{rot} = \frac{\sqrt{\pi I_a I_b I_c}}{\sigma} \left(\frac{8\pi^2 kT}{h^2}\right)^{3/2}$$

Electronic partition function

$$q_{el} = g_0 + g_1 e^{-\Delta\varepsilon_1/kT} + g_z e^{-\Delta\varepsilon_2/kT} + \ldots$$

In general, at room temp:

$$q_{el} \approx g_0$$

H atom g_0 = 2 (↑ or ↓)
B atom g_0 = 6 (^2P)
NO g_0 = 2
O_2 g_0 = 3

$$q = q_{tr} q_{rot} q_{vib} q_{el}$$