CHEM2000

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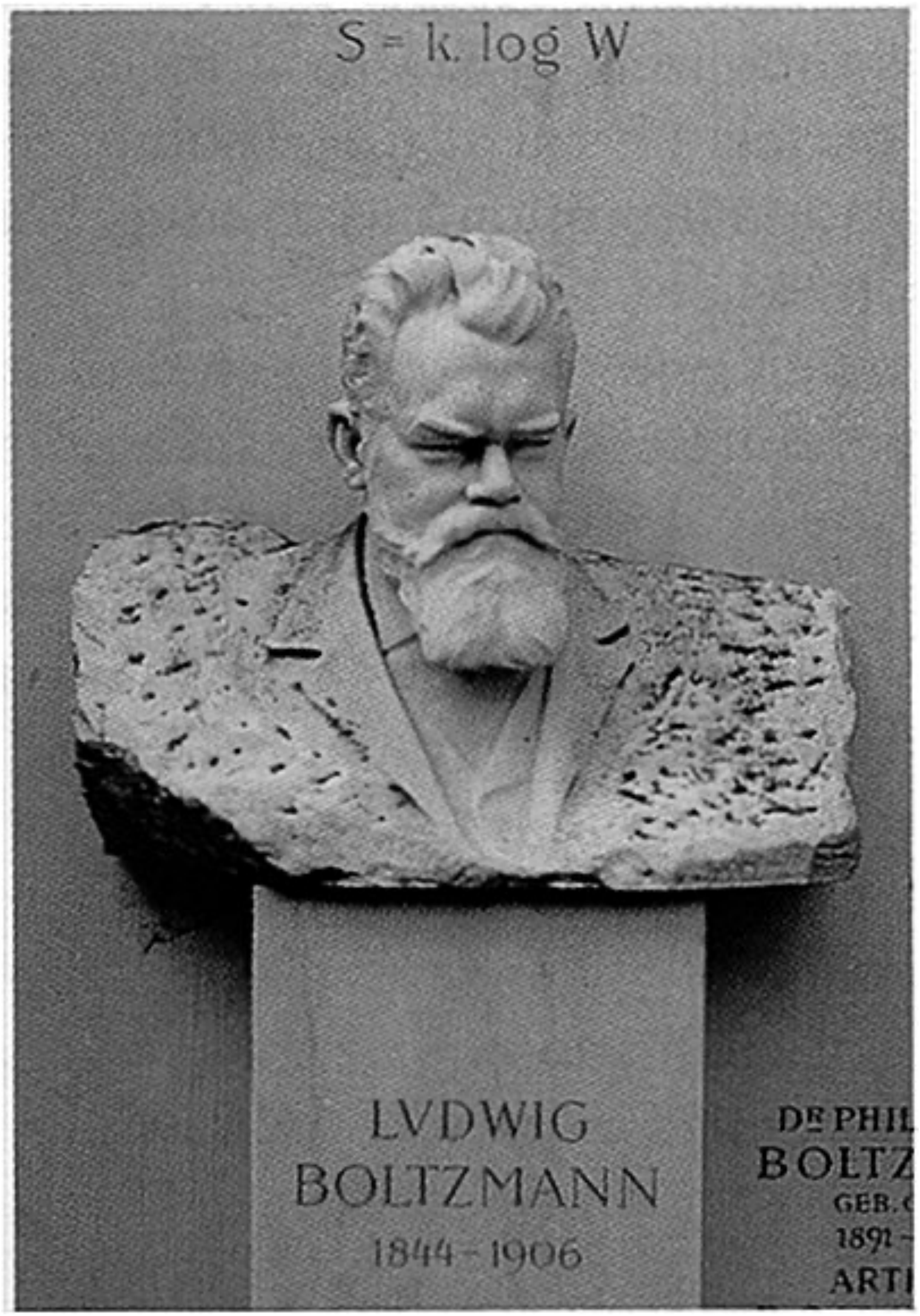
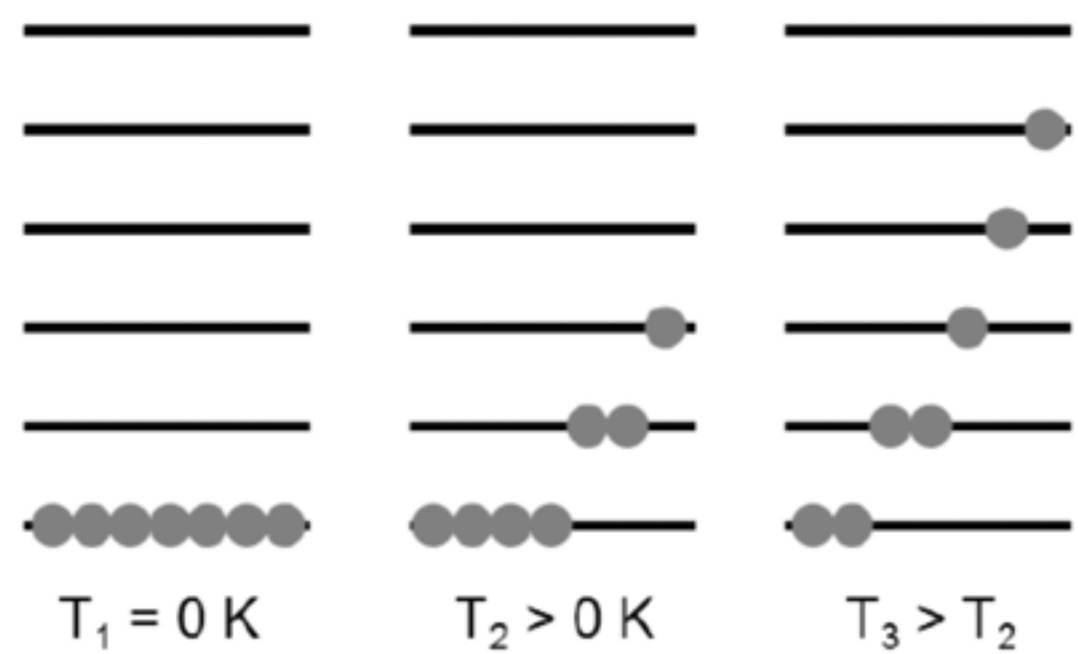
Boltzmann distribution



$$\mathrm{S} = \mathrm{k_B} \ln \mathrm{W}$$

It is a population distribution that maximises the entropy of a system, given the constraints of energy and mass conservation.



Boltzmann factor

The Boltzmann factor gives the probability of a system being in a state that has energy ε_i when the thermodynamic temperature is T.

$$\beta = \frac{1}{RT}$$

$$p_i \propto e^{-\beta \varepsilon_i}$$

$$R = N_a k_B$$

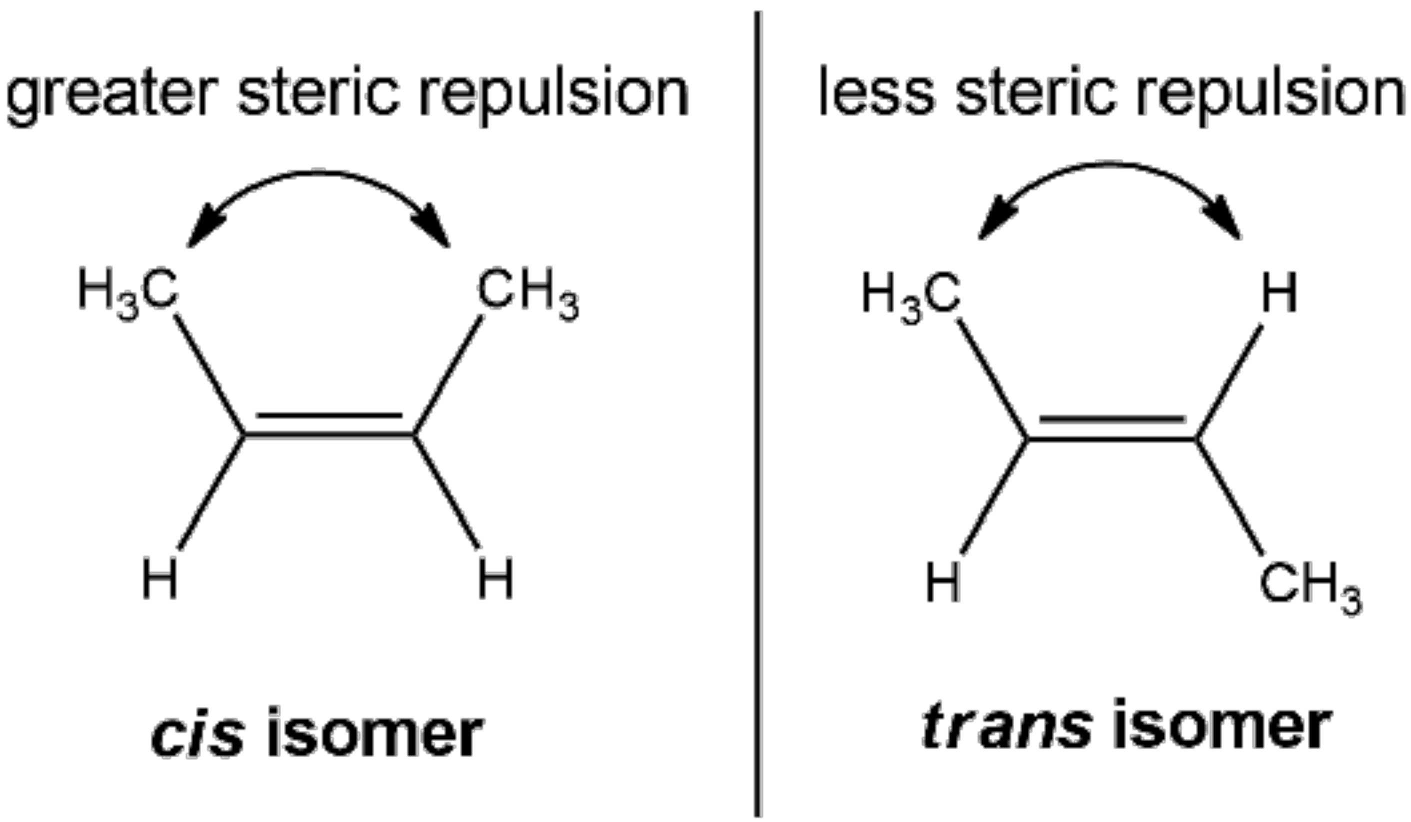
ε_i can be seen as a "generalised" energy. Depending on the system it can be replaced with potential energy, enthalpy, free energy...

Because it is difficult to compute the proportionality constant, the Boltzmann factor is most often used to discuss the relative population of two states separated in energy by $\Delta\varepsilon = (\varepsilon_i - \varepsilon_j)$

$$\frac{p_i}{p_j} = \frac{e^{-\beta \varepsilon_i}}{e^{-\beta \varepsilon_j}} = e^{-\beta \Delta \varepsilon}$$

Exercise

Although the kinetics for the transformation between the *cis*- and *trans*- isomers of 2-butene may be slow, at equilibrium (and in the gas phase) the relative population of the two isomers can be predicted using the Boltzmann factor



$$\frac{p_{trans}}{p_{cis}} = e^{-\beta\Delta\varepsilon} = \frac{N_{trans}}{N_{cis}}$$

Knowing that the standard free energy difference between the *cis*- and *trans*- isomers is -2.42 kJ/mol, compute the fraction of molecules in the *trans*- isomer at 400K.
What is the equilibrium constant at the same temperature?

$$\frac{N_{trans}}{N_{cis}} = e^{-\beta\Delta\varepsilon} = e^{2420/(8.314\times400)} = 2.07$$

$$\begin{aligned}
\%_{trans} &= \frac{N_{trans}}{N_{trans} + N_{cis}} \\
&= \frac{2.07N_{cis}}{2.07N_{cis} + N_{cis}} = \frac{2.07}{3.07} = 67.4\%
\end{aligned}$$

$$\%_{cis} = 32.6\%$$

$$cis \leftrightharpoons trans$$

$$\begin{aligned} K_{eq} &= \frac{c_{trans}}{c_{cis}} \\ &= \frac{x_{trans}}{x_{cis}} \\ &= \frac{0.674}{0.326} = 2.07 \end{aligned}$$

$$\begin{aligned} \Delta G^{\ominus} &= -RT \ln K_{eq} \\ -2.42\ [kJ/mol] &= -8.314[J/K\ mol]400[K] \ln K_{eq} \\ 0.727 &= \ln K_{eq} \\ K_{eq} &= 2.07 \end{aligned}$$

The equilibrium constant is the ratio between the probabilities of the system being in the products or reactants states

$$K_{eq} = \exp\left(-\frac{\Delta G^{\ominus}}{RT}\right)$$

Significance of the Arrhenius parameters

$$k_r = Ae^{-\frac{E_a}{RT}}$$

- The *activation energy* (E_a) is the minimum kinetic energy that the reactants must have to overcome the barrier and form the product

- The *pre-exponential factor* (A) is a measure of how often the system tries to overcome the barrier