### **CHEM2000**

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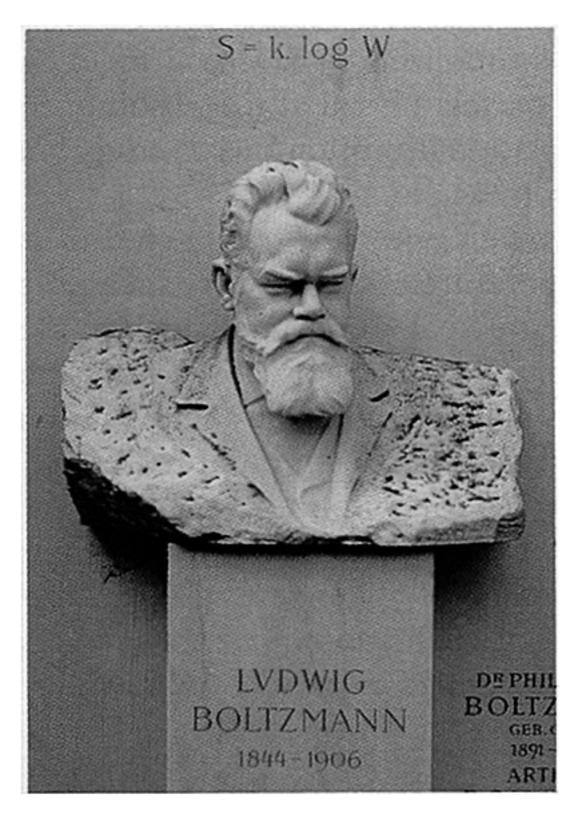
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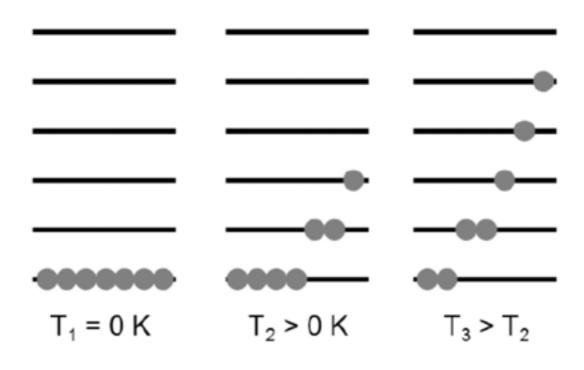
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# Boltzmann distribution



$$S = k_B \ln W$$

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  $\varepsilon_i$  when the thermodynamic temperature is T.

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

 $\varepsilon_i$  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  $\Delta \varepsilon = (\varepsilon_i - \varepsilon_j)$ 

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

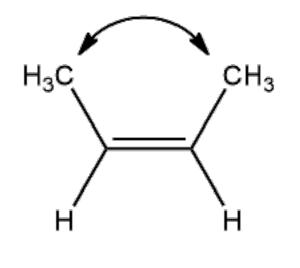
$$R = N_a k_B$$

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

# Exercise

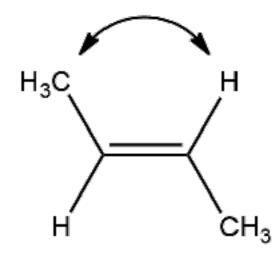
Although the kinetics for the transformation between the *cis*- and *trans*- isomers of 2-butene may be slow, at equilibrium (and in the gas phase) the relative population of the two isomers can be predicted using the Boltzmann factor

#### greater steric repulsion



cis isomer

#### less steric repulsion



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

trans isomer

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?

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

$$\%_{trans} = \frac{N_{trans}}{N_{trans} + N_{cis}}$$

$$= \frac{2.07N_{cis}}{2.07N_{cis} + N_{cis}} = \frac{2.07}{3.07} = 67.4\%$$

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

$$cis \leftrightharpoons trans$$

$$K_{eq} = \frac{c_{trans}}{c_{cis}}$$

$$= \frac{x_{trans}}{x_{cis}}$$

$$= \frac{0.674}{0.326} = 2.07$$

$$\Delta G^{\circ} = -RT \ln K_{eq}$$
 $-2.42 \; [kJ/mol] = -8.314 [J/K \; mol] 400 [K] \ln K_{eq}$ 
 $0.727 = \ln K_{eq}$  The equilibrium constant  $K_{eq} = 2.07$  between the probabil

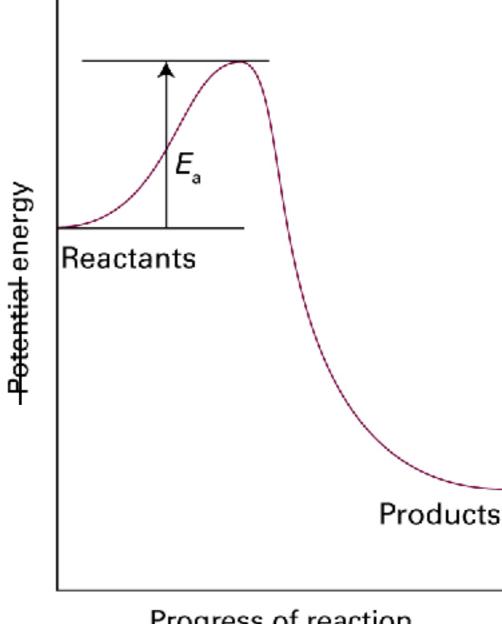
The equilibrium constant is the ratio between the probabilities of the system being in the products or reactants states

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

# 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



Progress of reaction