

This is the fourth take-home quiz: Q4

Make another max-5-min video in which you use the following slides (or another selection of slides of your choice, from the ones I used in class) to explain:

- (A) the key assumptions and observations that underlie our modeling the properties of a chemically reacting mixture even when it is not at chemical equilibrium;
- (B) the key assumptions and observations that underlie our kinetic model of the chemical reaction rates.

As usual, avoid spending time on the mathematical derivations and, rather, focus on the physical meaning that the mathematical relations are designed to capture.

Hatsopoulos-Keenan statement of the Second Law of Thermodynamics

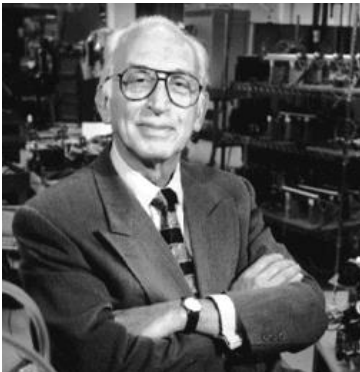
For a system with r constituents subject to a set of z chemical reactions $\sum_{i=1}^r \nu_i^{(j)} A_i = 0$, for $j = 1, \dots, z$, a composition \mathbf{n} is **compatible with a given composition** \mathbf{n}_a if there exists a solution $\boldsymbol{\epsilon}$ to the system of z proportionality relations

$$n_i = n_{ia} + \sum_{j=1}^z \sum_{i=1}^r \nu_i^{(j)} \epsilon_j \quad (\text{equivalent compact notation } \mathbf{n} = \mathbf{n}_a + \boldsymbol{\nu} \cdot \boldsymbol{\epsilon})$$

Second Law:

Assertion 1: in the subset of states of a system **compatible with given values of the amounts of constituents** \mathbf{n} and of the parameters $\boldsymbol{\beta}$, there is always one and only one SES for each value of the energy E .

Assertion 2: Starting from any state of the system, it is always possible, through a reversible weight process, to reach a SES with arbitrarily fixed, **compatible values of the amounts of constituents** and the parameters.



Collisions

At $T = 0\text{ K}$, the molecules of the reactants and products lack kinetic energy and their bond configurations are situated at the bottom of their respective valleys on the potential energy surface.

At $T > 0\text{ K}$, part of the energy is kinetic, and the molecules are subject to continuous collisions, resulting in the conversion of some kinetic energy into deformation of the bonds that hold them together. Consequently, reactants and products explore configurations of higher potential energy.

As the temperature increases, the probability also grows that the configuration of some or all of the interatomic bonds surpasses the saddle point separating the two valleys, thereby transforming the reactants into products or vice versa.

The bonds act like vibrating springs. Collisions excite these vibrations and random redistribution of this energy among the bonds may end up weakening some bonds.

If this happens when the collision occurs at particular angles, the weakened bonds can break to form other bonds, and the collision is chemically effective.

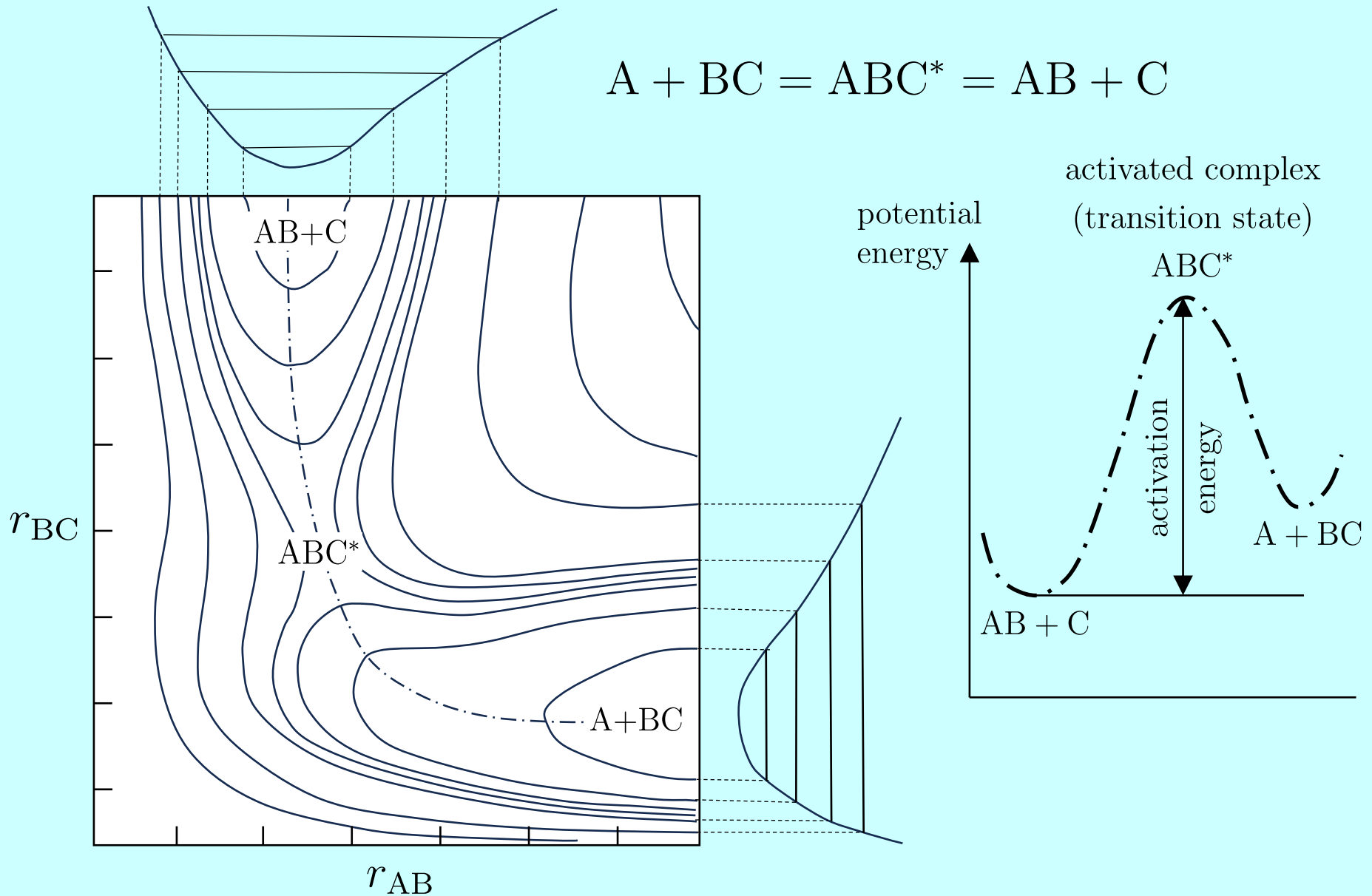
Otherwise, the collision results only in the redistribution of the energy among the various degrees of freedom (translational, rotational, vibrational, electronic) without changing the composition.



Photo exposed on the 4th floor of MIT building 10, by H.E. Edgerton around 1935. Contact between golf ball and club head lasts only 6 ms.

Take a look also at this YouTube video of golf ball bouncing on a hard wall
https://www.youtube.com/watch?v=JcVEW2X_Nus

Potential energy surface and the role of the activated complex



Forward and backward half-reactions

Rename the positive stoichiometric coefficients as ν_i^- and the negative ones as ν_i^+ , so that

$$\sum_i \nu_i A_i = 0 \quad \text{rewrites as} \quad \sum_i \nu_i^+ A_i = A^* = \sum_i \nu_i^- A_i \quad \text{with} \quad \nu_i = \nu_i^- - \nu_i^+$$

where we also identify the **transition state** as an unstable intermediate species we call the **activated complex** A^* . This way, the half reactions can be viewed as producing the **activated complex** A^* from either the reactants or the products

$$\sum_i \nu_i^+ A_i = A^* \quad \text{forward half-reaction} \quad \text{in our notation} \quad -\sum_i \nu_i^+ A_i + A^* = 0$$

$$\sum_i \nu_i^- A_i = A^* \quad \text{backward half-reaction} \quad \text{in our notation} \quad -\sum_i \nu_i^- A_i + A^* = 0$$

Properties of reaction can be written in terms of those of these reaction, e.g.,

$$\Delta h^\circ(T) = \sum_i \nu_i h_{ii}^\circ(T) = \Delta h_+^\circ(T) - \Delta h_-^\circ(T)$$

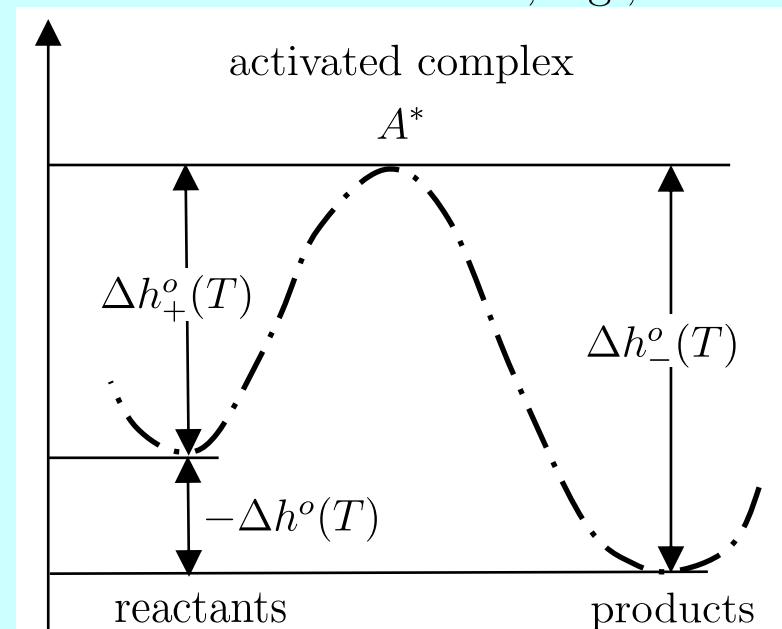
where

$$\Delta h_+^\circ(T) = -\sum_i \nu_i^+ h_{ii}^\circ(T) + h_*^\circ(T)$$

(activation energy of the forward path)

$$\Delta h_-^\circ(T) = -\sum_i \nu_i^- h_{ii}^\circ(T) + h_*^\circ(T)$$

(activation energy of the backward path)



Turning reactions “on” and “off” does not affect the local properties

Given the instantaneous composition (\mathbf{n}, n^*) :

- Neglect the contribution of the activated complex A^* to the mixtures properties (indeed, for large n , we can assume $n^* \ll n$ because A^* is highly unstable and hence very short lived).
- Assume that the rate at which **non-chemical collisions** redistribute the excesses or defects in local kinetic energy caused by the chemical reactions, is much faster than the rate at which **chemically effective collisions** produce them. Thus, if we suddenly turn reactions “off”, the mixture relaxes almost instantly to SE, and even when reactions are “on” the state (all the properties) is very close to the SES it would relax to if we turned them “off”.
- Therefore, the instantaneous properties can be assumed equivalent to the SE properties of a mixture with the composition but with no active chemical reaction mechanisms, i.e., with reactions **turned “off”**. In particular,

$$S_{\epsilon}^{\text{on}} = S_{\text{off}}(U, V, \mathbf{n}) = S_{\text{off}}(U, V, \mathbf{n}_a + \boldsymbol{\nu} \cdot \boldsymbol{\epsilon})$$

Family of partial SES's and chemical SES

The extended simple system model, assumes:

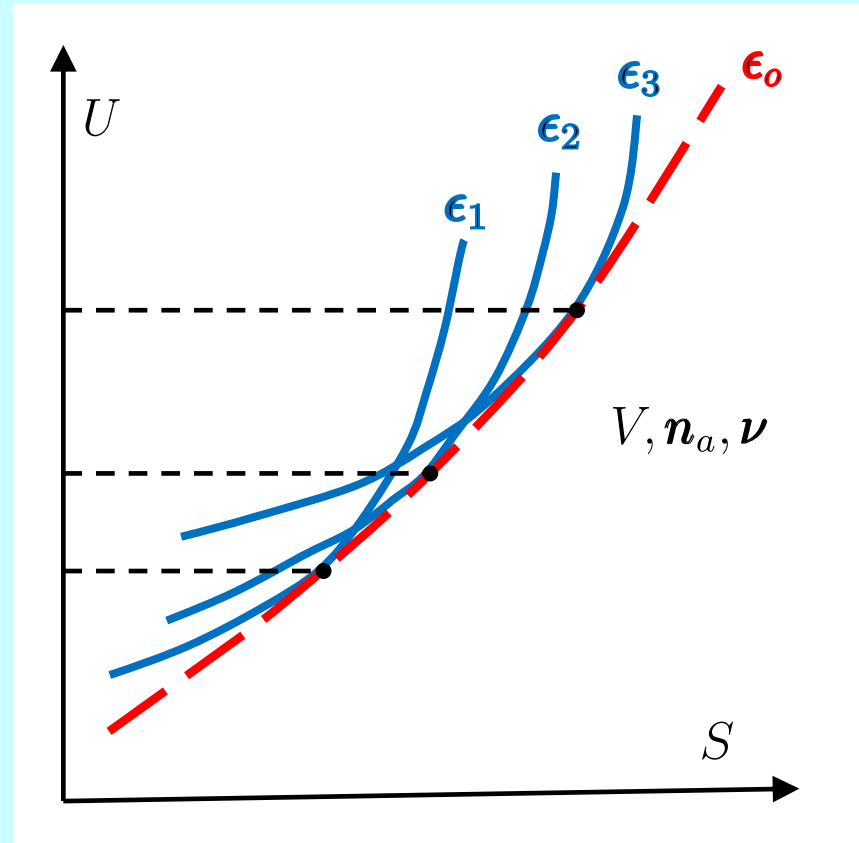
$$S_{\epsilon}^{\text{on}} = S_{\text{off}}(U, V, \mathbf{n}(\mathbf{n}_a, \boldsymbol{\nu}, \boldsymbol{\epsilon})) \quad \text{with} \quad \mathbf{n}(\mathbf{n}_a, \boldsymbol{\nu}, \boldsymbol{\epsilon}) = \mathbf{n}_a + \boldsymbol{\nu} \cdot \boldsymbol{\epsilon}$$

This represents a z-parameter family of SES curves (z is the number of independent reaction coordinates) which spans the range of allowed energy and entropy values.

The maximum entropy principle requires that at SE, the system chooses the set of values of the reaction coordinates, $\boldsymbol{\epsilon}_o$ that satisfies

$$Y_j = \left(\frac{\partial S_{\boldsymbol{\epsilon}}^{\text{on}}}{\partial \epsilon_j} \right)_{U, V, \mathbf{n}_a, \boldsymbol{\nu}, \boldsymbol{\epsilon}'_j} = 0 \quad \forall j$$

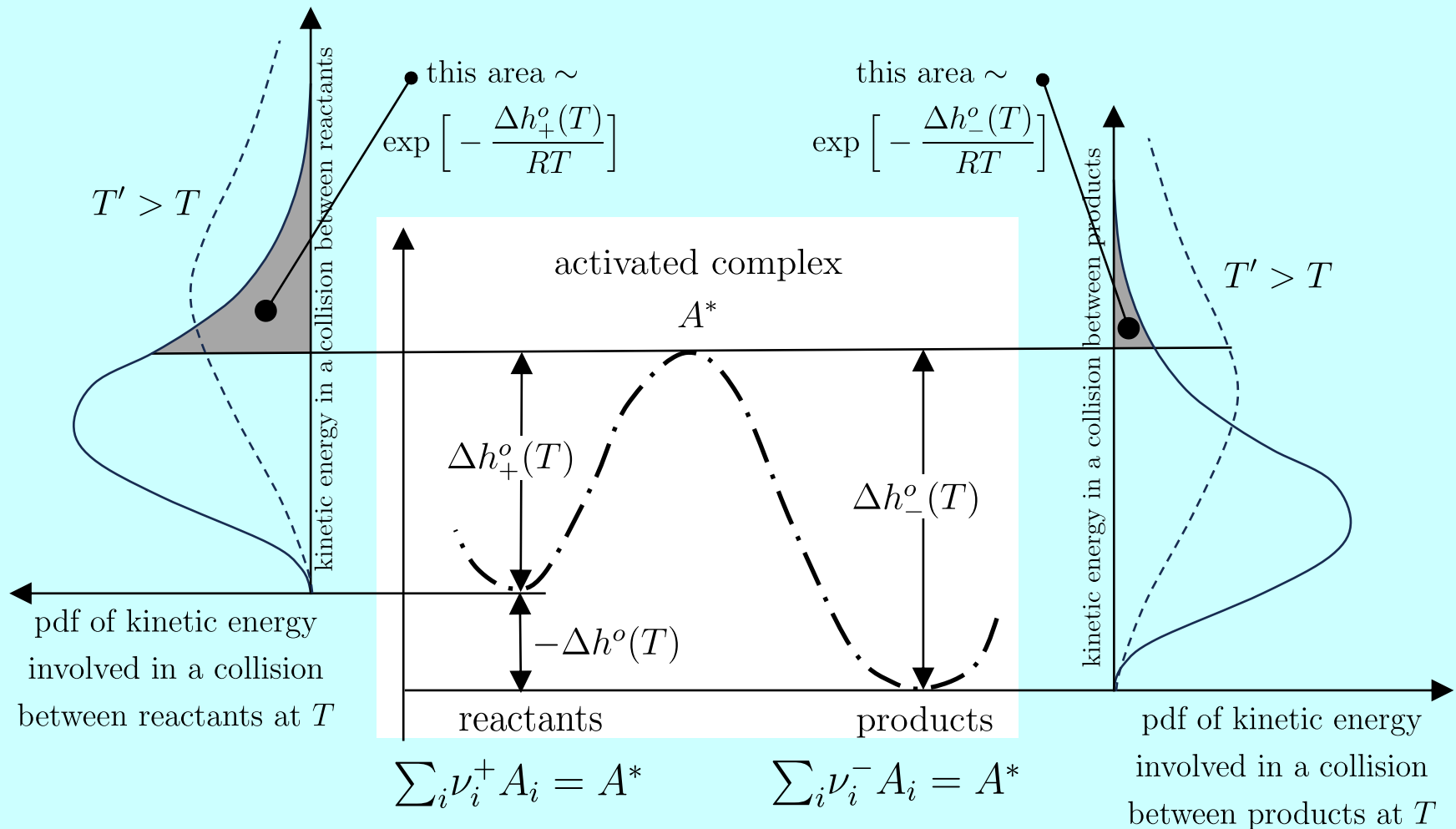
Y_j is called the **affinity of the j-th reaction**. It is zero at equilibrium.



Arrhenius activation barrier

From kinetic theory of collisions and the Maxwell-Boltzmann distribution of velocities at stable equilibrium, the pdf at temperature T of a collision with kinetic energy greater than E_{kin} is

$$\int_{E_{\text{kin}}}^{\infty} \text{pdf}_T(E_{\text{kin}}) dE_{\text{kin}} \sim \exp\left[-\frac{E_{\text{kin}}}{RT}\right] \quad \text{Arrhenius law}$$



Forward and backward reaction rates

model based on collision probabilities considerations

Forward
half-reaction:

$$\sum_i \nu_i^+ A_i = A^*, \nu_i^+ > 0$$

$$\exp \left[-\frac{\Delta h_+^o(T)}{RT} \right]$$

Arrhenius probability of a collision with overall $E_{\text{kin}} > \Delta h_+^o(T)$.

$$A^+(T)$$

Probability of decay of A^* towards the products.

$$\prod_i y_i^{\nu_i^+}$$

Probability that the collision involves the necessary molecules.

$$\prod_i y_i^{\nu_i^+} = \frac{1}{[N]^{\nu^+}} \prod_i [N_i]^{\nu_i^+}$$

$$\dot{\epsilon}^+ = \underbrace{\frac{A^+(T)}{[N]^{\nu^+}} \exp \left[-\frac{\Delta h_+^o(T)}{RT} \right]}_{k_o^+(T) \text{ forward rate constant}} \prod_i [N_i]^{\nu_i^+}$$

Backward
half-reaction:

$$\sum_i \nu_i^- A_i = A^*, \nu_i^- > 0$$

$$\exp \left[-\frac{\Delta h_+^o(T)}{RT} \right]$$

Arrhenius probability of a collision with overall $E_{\text{kin}} > \Delta h_+^o(T)$.

$$A^-(T)$$

probability of decay of A^* towards the reactants.

$$\prod_i y_i^{\nu_i^-}$$

Probability that the collision involves the necessary molecules.

$$\prod_i y_i^{\nu_i^-} = \frac{1}{[N]^{\nu^-}} \prod_i [N_i]^{\nu_i^-}$$

$$\dot{\epsilon}^- = \underbrace{\frac{A^-(T)}{[N]^{\nu^-}} \exp \left[-\frac{\Delta h_-^o(T)}{RT} \right]}_{k_o^-(T) \text{ backward rate constant}} \prod_i [N_i]^{\nu_i^-}$$

net reaction rate of $\sum_i \nu_i A_i = 0$ with $\nu_i = \nu_i^- - \nu_i^+$: $\dot{\epsilon} = \dot{\epsilon}^+ - \dot{\epsilon}^-$ $\dot{n}_i = \nu_i \dot{\epsilon} = (\nu_i^- - \nu_i^+) (\dot{\epsilon}^+ - \dot{\epsilon}^-)$

Forward and backward reaction rates

model based on hypothetical half-equilibrium concentrations of the activated complex

Recall the nonequilibrium law of mass action (in terms of concentrations)

$$\prod_i [N_i]^{\nu_i} = K^c(T) \exp \left[-\frac{Y}{R} \right] \quad \text{where } Y = -\frac{1}{T} \sum_i \nu_i \mu_i = Y^+ - Y^- \quad \text{for reaction } \sum_i \nu_i A_i = 0$$

we may write it also for the half-reactions of formation of the activated complex A_* ($\nu_i = \nu_i^- - \nu_i^+$)

$$\frac{[N_*]}{\prod_i [N_i]^{\nu_i^\pm}} = K_\pm^c(T) \exp \left[-\frac{Y_\pm}{R} \right] \quad \text{where } Y_\pm = -\frac{1}{T} \left[\mu_* - \sum_i \nu_i^\pm \mu_i \right] \quad \text{for reactions } -\sum_i \nu_i^\pm A_i + A_* = 0$$

Denote by $[N_*]_\pm^{\text{eq}}$ the hypothetical concentrations that would obtain if $Y_\pm = 0$, respectively, i.e.,

$$[N_*]_\pm^{\text{eq}} = K_\pm^c(T) \prod_i [N_i]^{\nu_i^\pm} \quad \text{therefore we can rewrite the above as } [N_*] = [N_*]_\pm^{\text{eq}} \exp \left[-\frac{Y_\pm}{R} \right]$$

$$\Rightarrow \frac{[N_*]_-^{\text{eq}}}{[N_*]_+^{\text{eq}}} = \exp \left[-\frac{Y}{R} \right] \quad \text{or} \quad \text{DoD} = \frac{Y}{R} = \ln \frac{[N_*]_+^{\text{eq}}}{[N_*]_-^{\text{eq}}} \quad \left(\text{at equil. } [N_*]_+^{\text{eq}}|_o = [N_*]_-^{\text{eq}}|_o = [N_*]_o \right)$$

Assume that the forward and backward reaction rates are proportional to the hypothetical equilibrium concentrations $[N_*]_\pm^{\text{eq}}$ of the activated complex

$$\dot{\epsilon}^\pm = \kappa_\pm [N_*]_\pm^{\text{eq}} \quad \kappa_\pm = \text{frequency of forward/backward decay of } A_*$$

$$\Rightarrow \dot{\epsilon}^\pm = \underbrace{\kappa_\pm K_\pm^c(T)}_{k_o^\pm(T)} \prod_i [N_i]^{\nu_i^\pm} \quad \frac{\dot{\epsilon}^-}{\dot{\epsilon}^+} = \frac{\kappa^- [N_*]_-^{\text{eq}}}{\kappa^+ [N_*]_+^{\text{eq}}} = \frac{\kappa^-}{\kappa^+} \exp \left[-Y/R \right]$$

This holds also at chemical equilibrium, where we have $Y = 0$ and $\dot{\epsilon}_o^- = \dot{\epsilon}_o^+$, therefore, the **principle of detailed balance** takes the form $\kappa^- = \kappa^+$, so that $\dot{\epsilon} = \kappa [K_+^c(T) - K_-^c(T)]$.

Image Credits

Slide 2:

- Portrait of George N. Hatsopoulos courtesy of Jim Harrison (MIT News).
- Portrait of Joseph H. Keenan courtesy of the MIT Museum.

Slide 3:

Photo of golf ball compression during collision with club head © The Museum of Fine Arts, Houston. All rights reserved. This content is excluded from our Creative Commons license. For more information, see <https://ocw.mit.edu/help/faq-fair-use>.

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2.43 Advanced Thermodynamics

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