2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 19

Room 3-442
Tuesday, April 16, 2:30pm - 4:30pm

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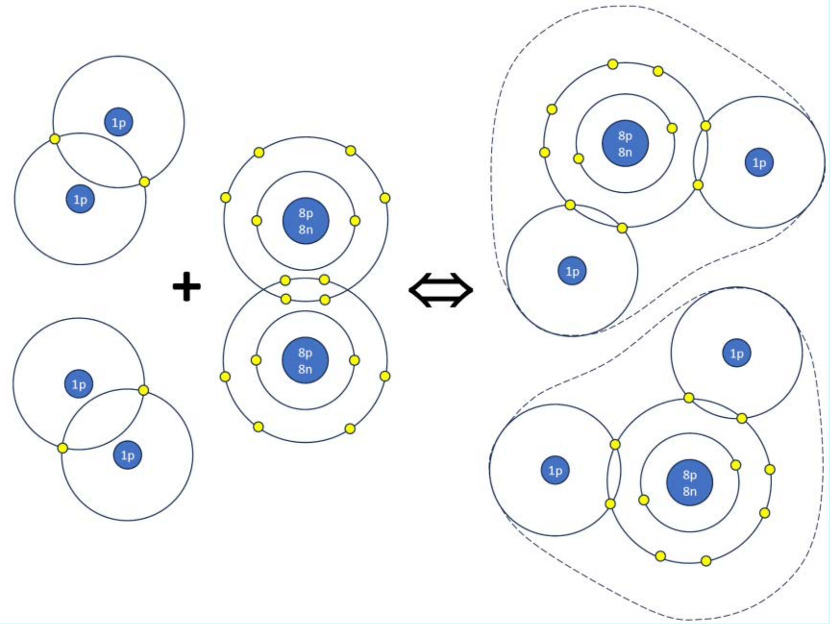
Systems with chemical reactions

Second law and state principle

Transition state model of chemical kinetics
Activated complex
Extension of the simple system model for large *n*

Notation and stoichiometry:

proportionality relations, reaction coordinates



chemical reaction mechanism

$$2H_2 + O_2 = 2H_2O \quad \text{or} \quad -2H_2 - O_2 + 2H_2O = 0$$

composition: $n_{H_2},\ n_{O_2},\ n_{H_2O}$

changes in composition: $\Delta n_{H_2},\ \Delta n_{O_2},\ \Delta n_{H_2O}$

proportionality relations

$$\frac{\Delta n_{H_2}}{-2} = \frac{\Delta n_{O_2}}{-1} = \frac{\Delta n_{H_2O}}{2} = \Delta\epsilon$$

$\epsilon =$ reaction coordinate

chemical symbols

$$A_1 = H_2,\ A_2 = O_2,\ A_3 = H_2O$$

stoichiometric coefficients

$$\nu_1 = -2,\ \nu_2 = -1,\ \nu_3 = 2$$

rewrite the mechanism as

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 = 0$$

$$\sum_i \nu_i A_i = 0$$

proportionality relations

$$\frac{\Delta n_1}{\nu_1} = \frac{\Delta n_2}{\nu_2} = \frac{\Delta n_3}{\nu_3} = \Delta\epsilon$$

$$\Delta n_i = \nu_i\,\Delta\epsilon \quad \forall i$$

$$n_{iP} = n_{iR} + \nu_i\,\epsilon$$

where $\epsilon = \epsilon_P - \epsilon_R$

$$\dot n_i = \nu_i \dot\epsilon \quad \forall i$$

$$\dot n_{iP} = \dot n_{iR} + \nu_i\,\dot\epsilon$$

Hatsopoulos-Keenan statement of the
Second Law of Thermodynamics

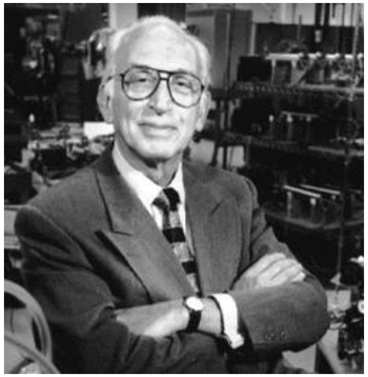
For a system with r constituents subject to a set of z chemical reactions $\sum_{i=1}^{r} \nu_i^{(j)} A_i = 0$, for $j = 1, \dots, \mathrm{z}$, a composition $\boldsymbol{n}$ is **compatible with a given composition** $\boldsymbol{n}_a$ if there exists a solution $\boldsymbol{\epsilon}$ to the system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

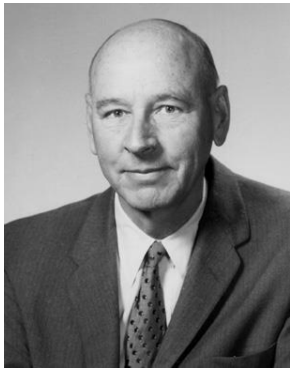
$$n_i = n_{ia} + \sum_{j=1}^{\mathrm{z}} \sum_{i=1}^{r} \nu_i^{(j)} \epsilon_j \qquad \text{(equivalent compact notation} \quad \boldsymbol{n} = \boldsymbol{n}_a + \boldsymbol{\nu} \cdot \boldsymbol{\epsilon} \text{)}$$

Second Law:

Assertion 1: in the subset of states of a system compatible with given values of the amounts of constituents $\boldsymbol{n}$ 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.





Direct consequences of the Second Law in the presence of chemical reactions:

State principle and maximum entropy principle

State principle: the value of any property **at stable equilibrium** is uniquely determined by the **set of compatible amounts** $\{\boldsymbol{n}\}_{\boldsymbol{n}_a,\boldsymbol{\nu}}$, the energy E and the parameters (for simplicity, assume volume V as the only parameter)

$$P = P(E, V, \boldsymbol{n}_a, \boldsymbol{\nu})$$

In particular, the entropy S as well as the **equilibrium composition**

$$\boldsymbol{n}_o = \boldsymbol{n}_a + \boldsymbol{\nu}\cdot\boldsymbol{\epsilon}_o$$

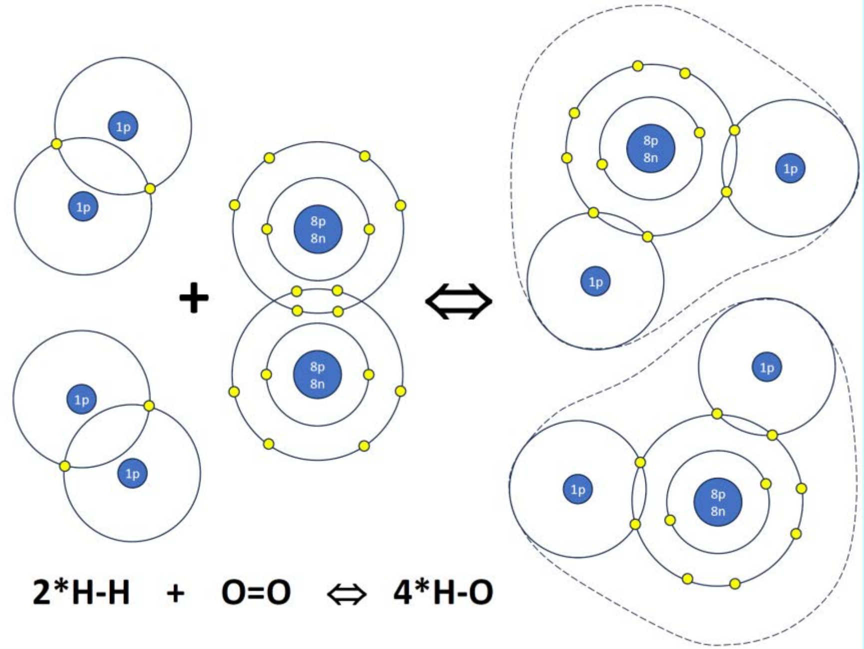
are properties, therefore, the following SES fundamental relations hold

$$S = S(E, V, \boldsymbol{n}_a, \boldsymbol{\nu}) \qquad \boldsymbol{n}_o = \boldsymbol{n}_o(E, V, \boldsymbol{n}_a, \boldsymbol{\nu}) \qquad \boldsymbol{\epsilon}_o = \boldsymbol{\epsilon}_o(E, V, \boldsymbol{n}_a, \boldsymbol{\nu})$$

compatible

Maximum entropy principle: among all the states with the same given values of the amounts of constituents, the parameters, and the energy, only the stable equilbrium state has the maximum value of the entropy.
(it is a direct consequence of the definition of s.e.s. and the statement of the Second Law; it holds in general for all systems)

Enthalpy of formation and bond energies

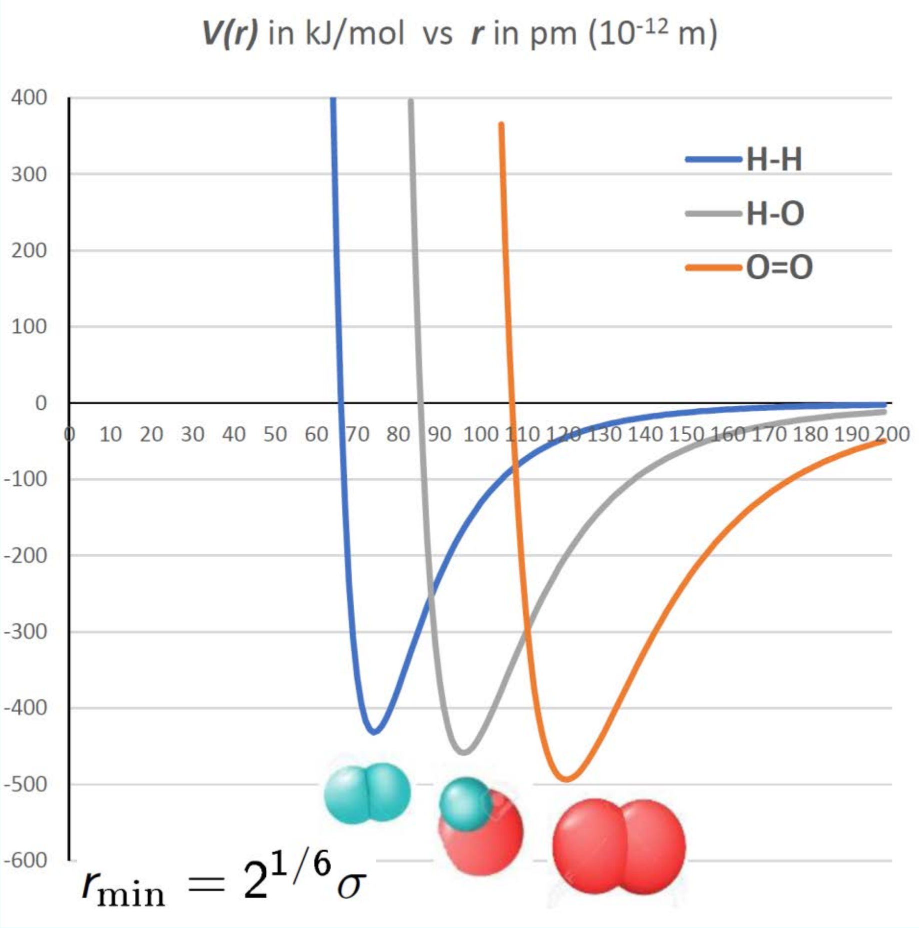


2*H-H + O=O ⇔ 4*H-O

$$V_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$
$$= \epsilon\left[\left(\frac{r_{\min}}{r}\right)^{12} - 2\left(\frac{r_{\min}}{r}\right)^{6}\right]$$

Bond parameters	Lennard Jones		**H-H**	**O=O**	**H-O**
Strength	**ε**	kJ/mol	**432**	**494**	**459**
Length	**r_min**	10^{-12} m	**74.1**	**120.8**	**95.8**

2*ε(H-H) + ε(O=O) - 4*ε(H-O)	**-478**
Enthalpy of formation of 2 moles of water	**-484**


V(r) in kJ/mol vs ***r*** in pm (10^{-12} m)

$$r_{\min} = 2^{1/6}\sigma$$

Collisions

At $T = 0\,\mathrm{K}$, 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 $T > 0\,\mathrm{K}$, 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.

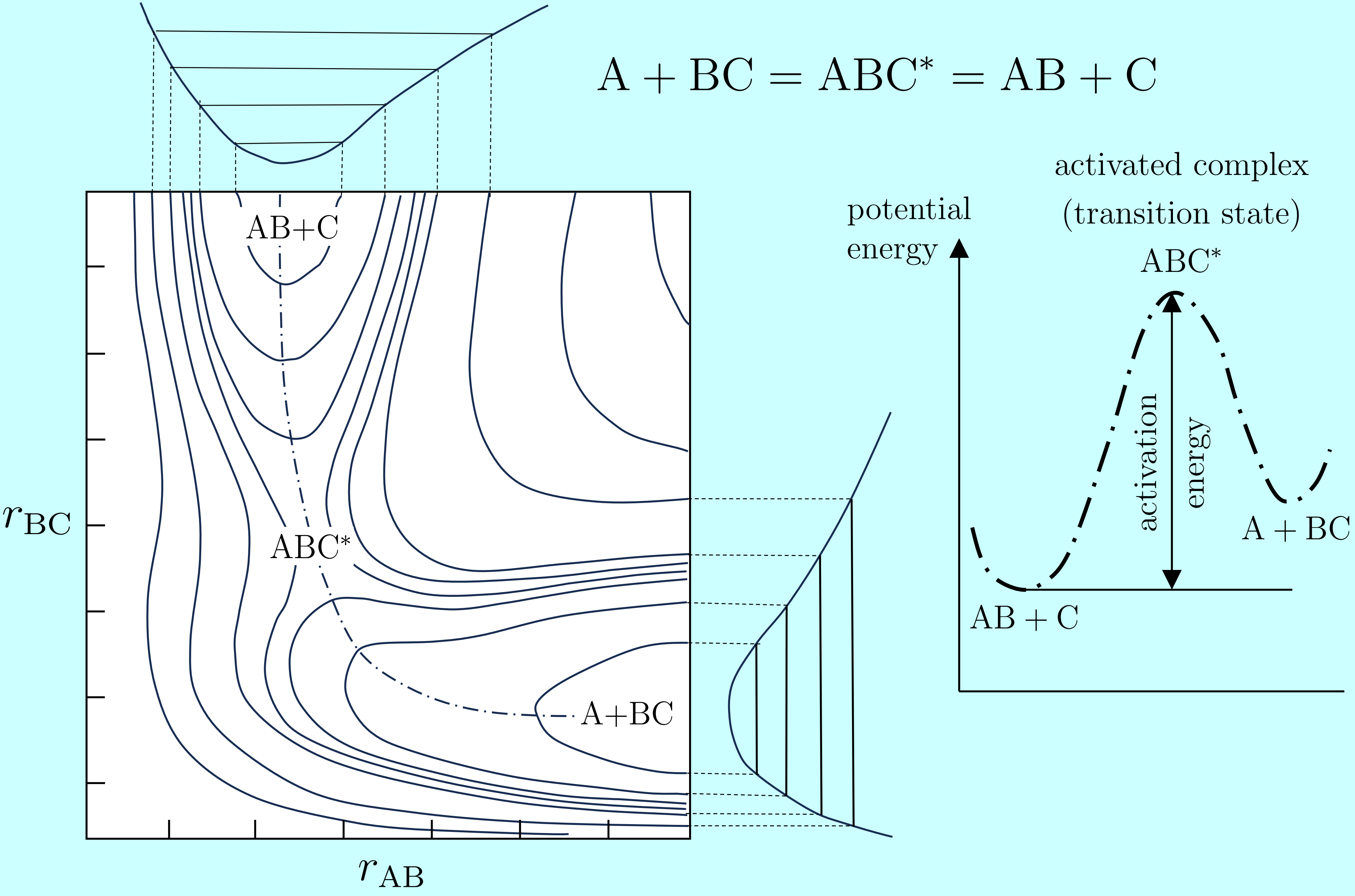
Otherwise, the collision results only in the redistribution of the energy among the various degrees of freedom (translational, rotational, vibrational, electronic) without changing the composition.

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

$$A + BC = ABC^* = AB + C$$



Forward and backward half-reactions

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

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

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

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

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

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

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

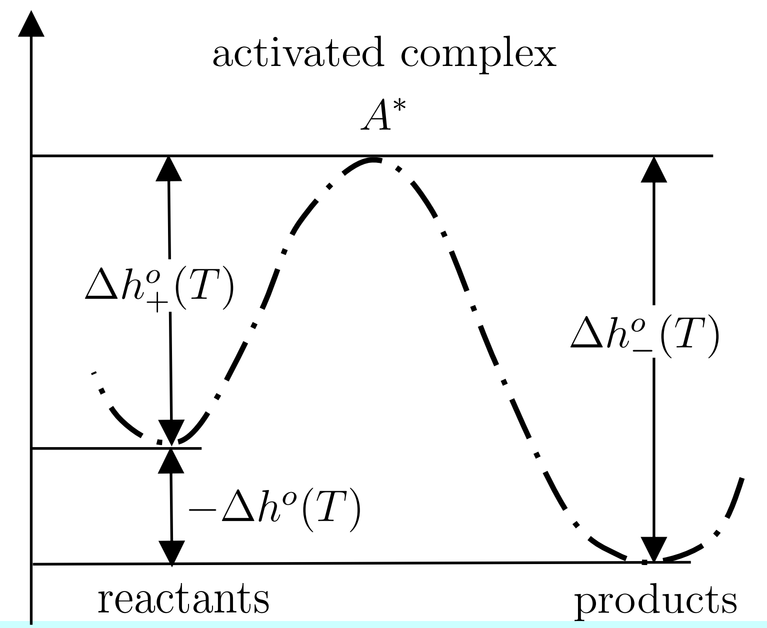
where

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

(activation energy of the forward path)

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

(activation energy of the backward path)



Extension of the simple system model + local equilibrium assumption:

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

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

- **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,

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

Extension of the simple system model:

Family of partial SES's and chemical SES

The extended simple system model, assumes:

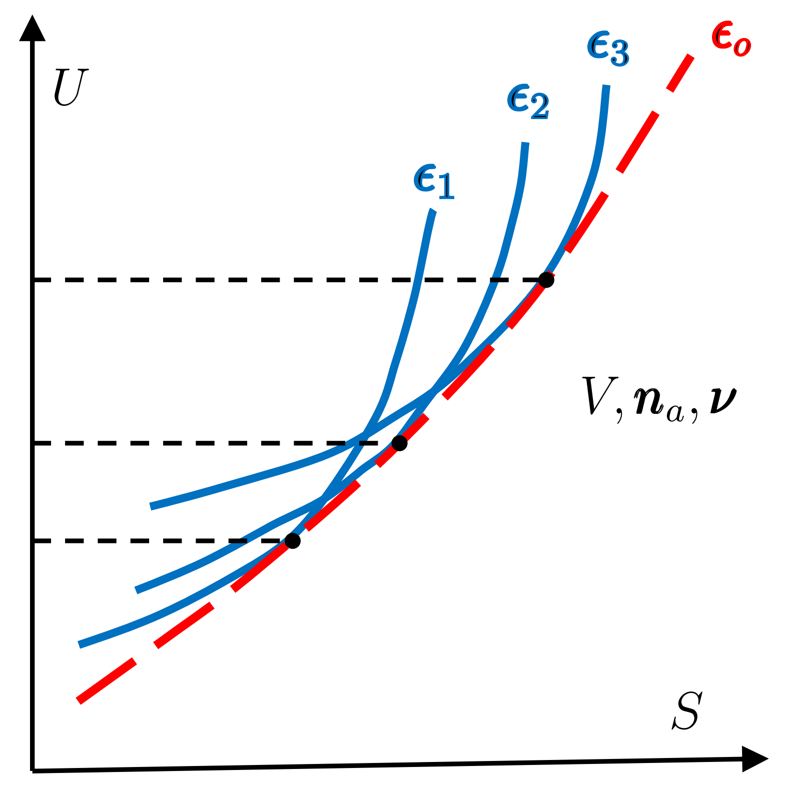
$$S_{\boldsymbol{\epsilon}}^{\text{on}} = S_{\text{off}}(U, V, \boldsymbol{n}(\boldsymbol{n}_a, \boldsymbol{\nu}, \boldsymbol{\epsilon})) \quad \text{with} \quad \boldsymbol{n}(\boldsymbol{n}_a, \boldsymbol{\nu}, \boldsymbol{\epsilon}) = \boldsymbol{n}_a + \boldsymbol{\nu} \cdot \boldsymbol{\epsilon}$$

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

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

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



Fundamental relation for CSES (CSES: chemical stable equilibrium states)

Simple system (frozen equilibrium) model for non-CSES:

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

Definition of affinities:

$$Y_j = \left(\frac{\partial S_{\text{off}}}{\partial \epsilon_j}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_j}$$

Maxwell relations:

$$\left(\frac{\partial Y_j}{\partial \epsilon_k}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_k} = \left(\frac{\partial^2 S_{\text{off}}}{\partial \epsilon_j \partial \epsilon_k}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_{jk}} = \left(\frac{\partial Y_k}{\partial \epsilon_j}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_j}$$

At chemical equilibrium:

$$Y_j(U,V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}_o) = 0 \ \forall j \qquad \Rightarrow \qquad \boldsymbol{\epsilon}_o = \boldsymbol{\epsilon}_o(U,V,\boldsymbol{n}_a,\boldsymbol{\nu})$$

Fundamental CSES relation:

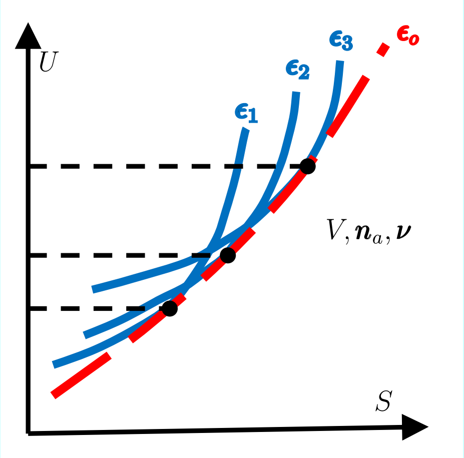
$$S^{\text{on}}_{\boldsymbol{\epsilon}_o} = S_{\text{off}}(U,V,\boldsymbol{n}_a+\boldsymbol{\nu}\cdot\boldsymbol{\epsilon}_o(U,V,\boldsymbol{n}_a,\boldsymbol{\nu})) = S^{\text{on}}(U,V,\boldsymbol{n}_a,\boldsymbol{\nu})$$

From the definition of temperature, at CSES:

$$\frac{1}{T^{\text{on}}} = \left(\frac{\partial S^{\text{on}}_{\boldsymbol{\epsilon}_o}}{\partial U}\right)_{V,\boldsymbol{n}_a,\boldsymbol{\nu}} = \underbrace{\left(\frac{\partial S_{\text{off}}}{\partial U}\right)_{V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}}}_{=1/T_{\text{off}}} + \sum_{j=1}^{z} \underbrace{\left(\frac{\partial S_{\text{off}}}{\partial \epsilon_j}\right)_{V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_j}}_{=Y_j=0\text{ at CSES}} \left(\frac{\partial \epsilon_{jo}}{\partial U}\right)_{V,\boldsymbol{n}_a,\boldsymbol{\nu}} = \frac{1}{T_{\text{off}}}$$

$$\frac{p^{\text{on}}}{T^{\text{on}}} = \left(\frac{\partial S^{\text{on}}_{\boldsymbol{\epsilon}_o}}{\partial V}\right)_{U,\boldsymbol{n}_a,\boldsymbol{\nu}} = \underbrace{\left(\frac{\partial S_{\text{off}}}{\partial V}\right)_{U,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}}}_{=p_{\text{off}}/T_{\text{off}}} + \sum_{j=1}^{z} \underbrace{\left(\frac{\partial S_{\text{off}}}{\partial \epsilon_j}\right)_{U,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_j}}_{=Y_j=0\text{ at CSES}} \left(\frac{\partial \epsilon_{jo}}{\partial V}\right)_{U,\boldsymbol{n}_a,\boldsymbol{\nu}} = \frac{p_{\text{off}}}{T_{\text{off}}}$$

$$-\frac{\mu_i^{\text{on}}}{T^{\text{on}}} = \left(\frac{\partial S^{\text{on}}_{\boldsymbol{\epsilon}_o}}{\partial n_i}\right)_{V,\boldsymbol{n}_a,\boldsymbol{\nu}} = \underbrace{\left(\frac{\partial S_{\text{off}}}{\partial n_i}\right)_{V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}}}_{=-\mu_i^{\text{off}}/T_{\text{off}}} + \sum_{j=1}^{z} \underbrace{\left(\frac{\partial S_{\text{off}}}{\partial \epsilon_j}\right)_{V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_j}}_{=Y_j=0\text{ at CSES}} \left(\frac{\partial \epsilon_{jo}}{\partial n_{ia}}\right)_{V,\boldsymbol{n}_a,\boldsymbol{\nu}} = -\frac{\mu_i^{\text{off}}}{T_{\text{off}}}$$



Systems with chemical reactions

Necessary condition of chemical equilibrium (from the maximum entropy principle)

Equilibrium and non-equilibrium forms of the law of mass action

Complete chemical equilibrium

Non-equilibrium law of mass action for ideal GD gas mixture

Assume $S^{\rm on}_{\boldsymbol{\epsilon}} = S_{\rm off}(U,V,\boldsymbol{n}(\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}))$ with $\boldsymbol{n}(\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}) = \boldsymbol{n}_a + \boldsymbol{\nu}\cdot\boldsymbol{\epsilon}$

recall that $\partial S_{\rm off}(U,V,\boldsymbol{n})/\partial n_i = -\mu_i^{\rm off}/T_{\rm off}$ and note that $\partial n_i/\partial \epsilon_j = \nu_i^{(j)}$

$$Y_j = \left(\frac{\partial S_{\rm off}}{\partial \epsilon_j}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_j} = -\frac{1}{T_{\rm off}}\sum_i \nu_i^{(j)}\mu_i^{\rm off}$$

Assume ideal mixture of ideal gases $\mu_i^{\rm off} = \mu_{ii}(T,p_o) + RT\ln\dfrac{p}{p_o} + RT\ln y_i$

$$\text{Recall}\quad \Delta g_j^o(T) = \sum_i \nu_i^{(j)}\mu_{ii}(T,p_o) \qquad \nu^{(j)} = \sum_i \nu_i^{(j)}$$

$$\sum_i \nu_i^{(j)} \ln y_i = \ln\prod_i (y_i)^{\nu_i^{(j)}} \qquad [N_i] = \frac{p}{RT}y_i$$

We obtain the **non-equilibrium law of mass action**

$$\prod_i (y_i)^{\nu_i^{(j)}} = K_j(T,p)\exp\left[-\frac{Y_j}{R}\right] \qquad K_j(T,p) = \left[\frac{p_o}{p}\right]^{\nu^{(j)}} \overbrace{\exp\left[-\frac{\Delta g_j^o(T)}{RT}\right]}^{K_j(T)}$$

$$\prod_i [N_i]^{\nu_i^{(j)}} = K_j^c(T)\exp\left[-\frac{Y_j}{R}\right] \qquad K_j^c(T) = \left[\frac{p_o}{RT}\right]^{\nu^{(j)}} \exp\left[-\frac{\Delta g_j^o(T)}{RT}\right]$$

Non-equilibrium law of mass action for ideal solutions

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

recall that $\partial S_{\text{off}}(U, V, \boldsymbol{n})/\partial n_i = -\mu_i^{\text{off}}/T_{\text{off}}$ and note that $\partial n_i/\partial \epsilon_j = \nu_i^{(j)}$

$$Y_j = \left(\frac{\partial S_{\text{off}}}{\partial \epsilon_j}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_j} = -\frac{1}{T_{\text{off}}} \sum_i \nu_i^{(j)} \mu_i^{\text{off}}$$

Assume ideal liquid solution $\mu_i^{\text{off}} = \mu_{ii}(T, p_o) + (p - p_o)\, v_{ii}^o(T) + RT \ln y_i$

Recall: $\Delta g_j^o(T) = \sum_i \nu_i^{(j)} \mu_{ii}(T, p_o)$ $\quad \Delta v_j^o(T) = \sum_i \nu_i^{(j)} v_{ii}(T, p_o)$ $\quad \nu^{(j)} = \sum_i \nu_i^{(j)}$

$$\sum_i \nu_i^{(j)} \ln y_i = \ln \prod_i (y_i)^{\nu_i^{(j)}} \qquad [N_i] = \frac{n}{V} y_i = [N]\, y_i$$

We obtain the **non-equilibrium law of mass action**

$$\prod_i (y_i)^{\nu_i^{(j)}} = K_j(T, p) \exp\left[-\frac{Y_j}{R}\right] \qquad K_j(T, p) = \exp\left[-\frac{\Delta g_j^o(T) + (p - p_o)\, \Delta v_j^o(T)}{RT}\right]$$

$$\prod_i [N_i]^{\nu_i^{(j)}} = K_j^c(T) \exp\left[-\frac{Y_j}{R}\right] \quad K_j^c(T) = [N]^{\nu^{(j)}} \exp\left[-\frac{\Delta g_j^o(T) + (p - p_o)\, \Delta v_j^o(T)}{RT}\right]$$

Equilibrium law of mass action in terms of activities

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

$$Y_j = \left(\frac{\partial S_{\rm off}}{\partial \epsilon_j}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu},\boldsymbol{\epsilon}'_j} = -\frac{1}{T_{\rm off}}\sum_i \nu_i^{(j)}\mu_i^{\rm off}$$

Assume non-ideal solution and reference states ^{o} such that the pure solvent has $a_{ss} = 1$, $\mu_s^o = \mu_{ss}$, and for dilute solutions $a_s = y_s$. Define activities and Gibbs free energies of reaction as

$$\mu_i^{\rm off} = \mu_i^o(T) + RT\ln a_i \qquad \Delta g_j^o(T) = \sum_i \nu_i^{(j)}\mu_i^o(T)$$

From $Y_j^{\rm off} = 0$ we obtain the **equilibrium law of mass action**

$$\prod_i (a_i)^{\nu_i^{(j)}} = K_j(T) \qquad K_j(T) = \exp\left[-\frac{\Delta g_j^o(T)}{RT}\right]$$

Defining activity coefficients $\gamma_i = a_i/[N_i]$ we may rewrite as

$$\prod_i [N_i]^{\nu_i^{(j)}} = K_j^c(T) \qquad K_j^c(T) = \frac{K_j(T)}{\prod_i \gamma_i^{\nu_i^{(j)}}}$$

Temperature dependence of the equilibrium constants

Recall we proved

$$-\frac{\mathrm{d}}{\mathrm{d}T}\frac{\Delta g^o(T)}{RT} = \frac{\Delta h^o(T)}{RT^2}$$

or

$$\frac{\mathrm{d}[\Delta g^o(T)/RT]}{\mathrm{d}(1/T)} = \frac{\Delta h^o(T)}{R}$$

$$K(T) = \exp\left[-\frac{\Delta g^o(T)}{RT}\right]$$

or

$$\ln K(T) = -\frac{\Delta g^o(T)}{RT}$$

$$\frac{\mathrm{d}\ln K(T)}{\mathrm{d}(1/T)} = -\frac{\Delta h^o(T)}{R}$$

or

$$\frac{\mathrm{d}\log_{10} K(T)}{\mathrm{d}(1/T)} = -\frac{\Delta h^o(T)}{\ln(10)R}$$

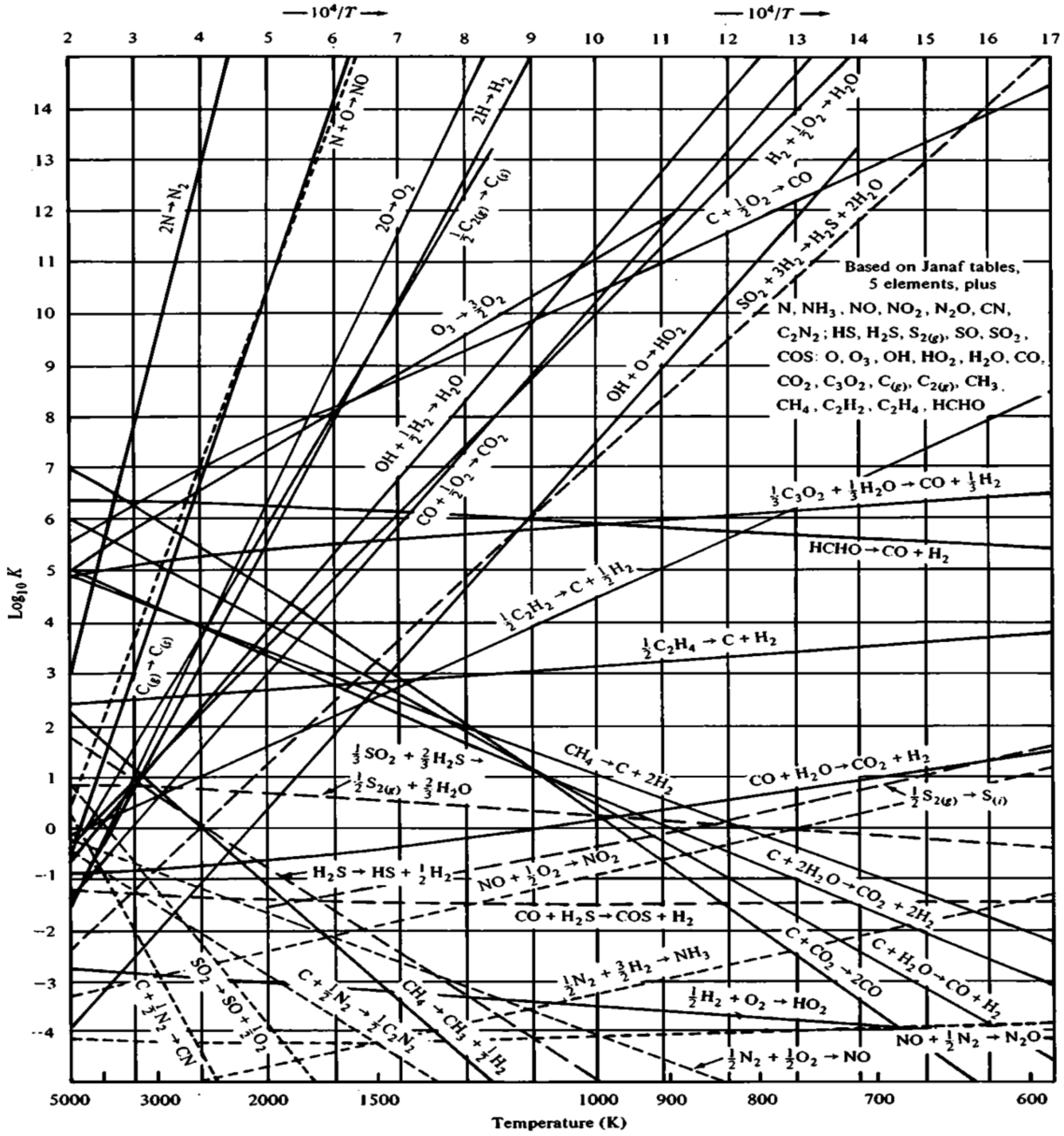


Figure 30.1 Graph of $\log_{10} K(T)$, the logarithm to the base 10 of the equilibrium constant $K(T)$, of various chemical reaction mechanisms versus temperature T on a $1/T$ scale (from M. Modell and R.C. Reid, *Thermodynamics and its Applications*, Prentice-Hall, 1974).

Fig.30.1 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Equilibrium constants from properties of formation at STP

Recall the Hess relation

$$\Delta g^o(T) = \textstyle\sum_i \nu_i \, \Delta g^o_\mathrm{f}(T)|_i$$

$$K(T) = \exp\left[-\frac{\Delta g^o(T)}{RT}\right]$$

$$RT \ln K(T) = -\Delta g^o(T) = -\textstyle\sum_i \nu_i \, \Delta g^o_\mathrm{f}(T)|_i$$

hence, $K(T) = \prod_i [K_\mathrm{f}(T)]_i^{\nu_i}$

Integrate $\dfrac{\mathrm{d} \ln K(T)}{\mathrm{d}(1/T)} = -\dfrac{\Delta h^o(T)}{R} \approx -\dfrac{\Delta h^o}{R}$

$$\ln K(T) \approx \ln K(T_o) - \frac{\Delta h^o}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

Using $\ln K(T_o) = -\dfrac{\Delta g^o}{RT_o}$ and

$\Delta g^o = \Delta h^o - T_o \Delta s^o$ finally yields

$$\ln K(T) \approx \frac{\Delta s^o}{R} - \frac{\Delta h^o}{RT}$$

$$K(T) \approx \exp\left(\frac{\Delta s^o}{R} - \frac{\Delta h^o}{RT}\right)$$

$$K(T) \approx \exp\left(\frac{\sum_i \nu_i \, \Delta s^o_\mathrm{f}|_i}{R} - \frac{\sum_i \nu_i \, \Delta h^o_\mathrm{f}|_i}{RT}\right)$$

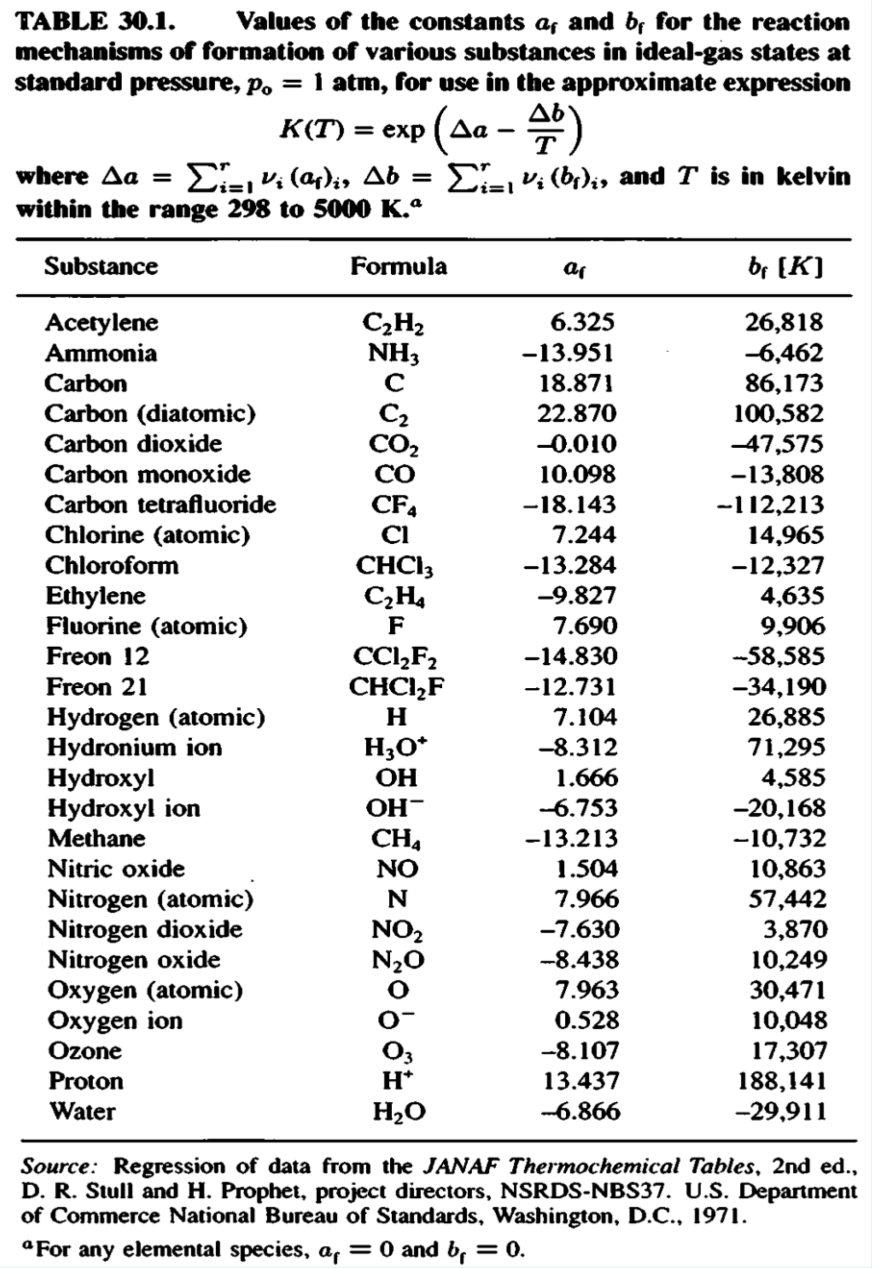


TABLE 30.1. Values of the constants a_f and b_f for the reaction mechanisms of formation of various substances in ideal-gas states at standard pressure, $p_o = 1$ atm, for use in the approximate expression

$$K(T) = \exp\left(\Delta a - \frac{\Delta b}{T}\right)$$

where $\Delta a = \sum_{i=1}^{r} \nu_i (a_\mathrm{f})_i$, $\Delta b = \sum_{i=1}^{r} \nu_i (b_\mathrm{f})_i$, and T is in kelvin within the range 298 to 5000 K.[a]

Substance	Formula	a_f	b_f [K]
Acetylene	C_2H_2	6.325	26,818
Ammonia	NH_3	–13.951	–6,462
Carbon	C	18.871	86,173
Carbon (diatomic)	C_2	22.870	100,582
Carbon dioxide	CO_2	–0.010	–47,575
Carbon monoxide	CO	10.098	–13,808
Carbon tetrafluoride	CF_4	–18.143	–112,213
Chlorine (atomic)	Cl	7.244	14,965
Chloroform	$CHCl_3$	–13.284	–12,327
Ethylene	C_2H_4	–9.827	4,635
Fluorine (atomic)	F	7.690	9,906
Freon 12	CCl_2F_2	–14.830	–58,585
Freon 21	$CHCl_2F$	–12.731	–34,190
Hydrogen (atomic)	H	7.104	26,885
Hydronium ion	H_3O^+	–8.312	71,295
Hydroxyl	OH	1.666	4,585
Hydroxyl ion	OH^-	–6.753	–20,168
Methane	CH_4	–13.213	–10,732
Nitric oxide	NO	1.504	10,863
Nitrogen (atomic)	N	7.966	57,442
Nitrogen dioxide	NO_2	–7.630	3,870
Nitrogen oxide	N_2O	–8.438	10,249
Oxygen (atomic)	O	7.963	30,471
Oxygen ion	O^-	0.528	10,048
Ozone	O_3	–8.107	17,307
Proton	H^+	13.437	188,141
Water	H_2O	–6.866	–29,911

Source: Regression of data from the *JANAF Thermochemical Tables*, 2nd ed., D. R. Stull and H. Prophet, project directors, NSRDS-NBS37. U.S. Department of Commerce National Bureau of Standards, Washington, D.C., 1971.

[a] For any elemental species, $a_\mathrm{f} = 0$ and $b_\mathrm{f} = 0$.

Table 30.1 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Non-equilibrium law of mass action for ideal GD gas mixture

Example: CO_2 dissociation at $T = 3200\,\mathrm{K}$ and $p = p_o = 1\,\mathrm{atm}$.

$$\mathrm{CO_2} = \mathrm{CO} + \frac{1}{2}\mathrm{O_2} \qquad -\mathrm{CO_2} + \mathrm{CO} + \frac{1}{2}\mathrm{O_2} = 0$$

$$\prod_i (y_i)^{\nu_i} = K(T,p)$$

$$= \left[\frac{p_o}{p}\right]^{\nu} K(T)$$

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

$$y_i = \frac{n_i}{n} = \frac{n_{ia} + \nu_i \epsilon}{n_a + \nu \epsilon}$$

$$= \frac{y_{ia} + \nu_i \xi}{1 + \nu \xi}$$

i	A_i	ν_i	$\dot{n}_{ia}$	y_{ia}	$\dot{n}_{ib}$	y_{ib}
1	CO_2	–1.0	1	1	$1-\xi$	$(1-\xi)/(1+0.5\,\xi)$
2	CO	1.0	0	0	ξ	$\xi/(1+0.5\,\xi)$
3	O_2	0.5	0	0	$0.5\,\xi$	$0.5\,\xi/(1+0.5\,\xi)$
$\sum_{i=1}^{3}$		0.5	1	1	$1+0.5\,\xi$	1

The composition of the outlet stream is found from the balance between the inlet and outlet flow rates, which can be expressed in terms of the degree of reaction ξ as $CO_2 = (1-\xi)CO_2 + \xi\,CO + (\xi/2)O_2$. For $T = 3200$ K, the equilibrium constant of the dissociation reaction mechanism, $CO_2 = CO + \frac{1}{2}O_2$, $K(3200\text{ K}) = 0.641$ (Example 30.4). Assuming that the outlet stream behaves as an ideal-gas mixture, the chemical equilibrium equation becomes ($p = p_o$)

$$\prod_i \left(\frac{y_{ia} + \nu_i \xi}{1 + \nu \xi}\right)^{\nu_i} = K(T) \;\Rightarrow\; \left(\frac{1+\xi/2}{1-\xi}\right)\left(\frac{\xi}{1+\xi/2}\right)\left(\frac{\xi/2}{1+\xi/2}\right)^{1/2} = 0.641$$

and yields $\xi = 0.58$. Hence $\dot{n}_b = 1.29$ kmol/s per kilomole of CO_2 per second, $y_{1b} = 0.33$, $y_{2b} = 0.45$, $y_{3b} = 0.22$.

Adapted from Example 30.5 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Dissociation and NOx formation in combustion in IC engines

Complete oxidation of isooctane premixed with dry air and initially at 700 K and 10 atm according to

$$C_8H_{18} + 12.5\,O_2 = 8\,CO_2 + 9\,H_2O$$

assuming chemical equilibrium of

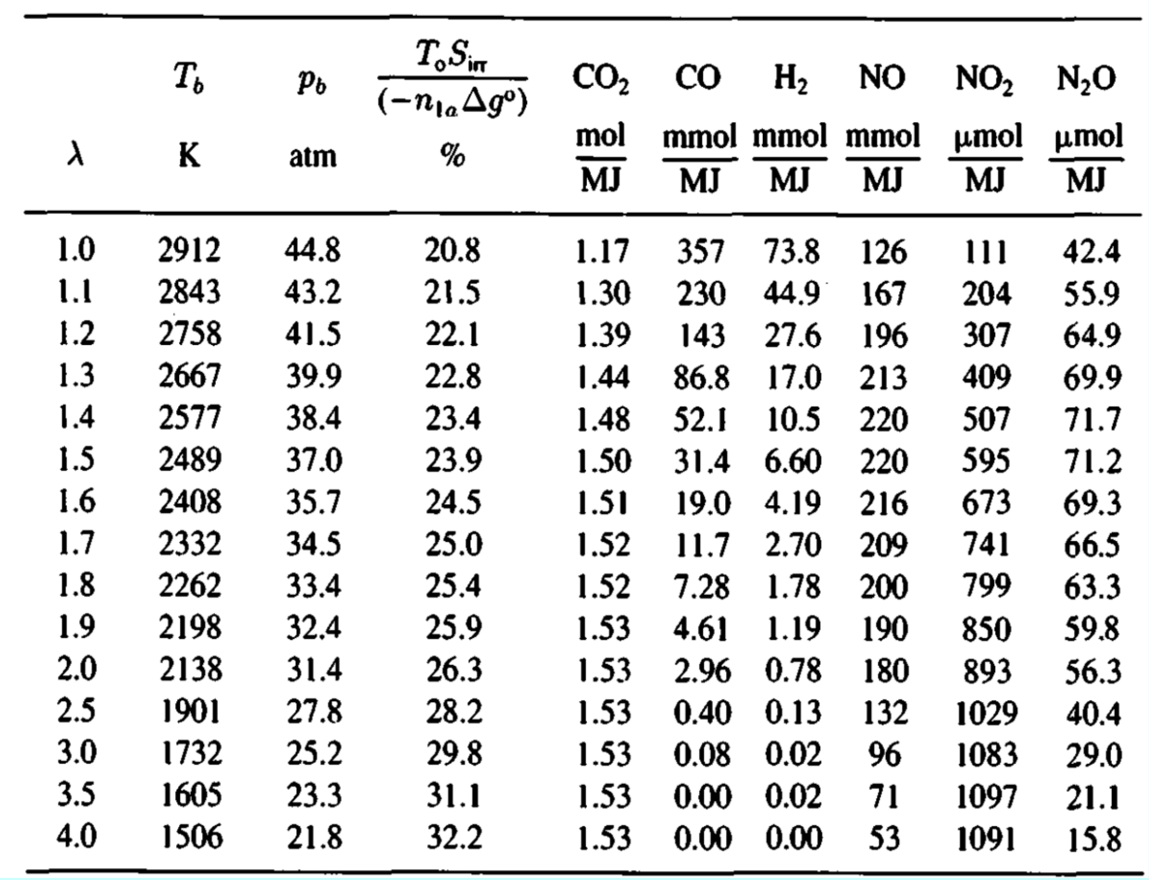
$$CO_2 = CO + \tfrac{1}{2}O_2$$

$$H_2O = H_2 + \tfrac{1}{2}O_2$$

$$N_2 + O_2 = 2\,NO$$

$$\tfrac{1}{2}N_2 + O_2 = NO_2$$

$$N_2 + \tfrac{1}{2}O_2 = N_2O$$



λ	T_b K	p_b atm	$\dfrac{T_o S_{irr}}{(-n_{1a}\Delta g^o)}$ %	CO_2 $\frac{\text{mol}}{\text{MJ}}$	CO $\frac{\text{mmol}}{\text{MJ}}$	H_2 $\frac{\text{mmol}}{\text{MJ}}$	NO $\frac{\text{mmol}}{\text{MJ}}$	NO_2 $\frac{\mu\text{mol}}{\text{MJ}}$	N_2O $\frac{\mu\text{mol}}{\text{MJ}}$
1.0	2912	44.8	20.8	1.17	357	73.8	126	111	42.4
1.1	2843	43.2	21.5	1.30	230	44.9	167	204	55.9
1.2	2758	41.5	22.1	1.39	143	27.6	196	307	64.9
1.3	2667	39.9	22.8	1.44	86.8	17.0	213	409	69.9
1.4	2577	38.4	23.4	1.48	52.1	10.5	220	507	71.7
1.5	2489	37.0	23.9	1.50	31.4	6.60	220	595	71.2
1.6	2408	35.7	24.5	1.51	19.0	4.19	216	673	69.3
1.7	2332	34.5	25.0	1.52	11.7	2.70	209	741	66.5
1.8	2262	33.4	25.4	1.52	7.28	1.78	200	799	63.3
1.9	2198	32.4	25.9	1.53	4.61	1.19	190	850	59.8
2.0	2138	31.4	26.3	1.53	2.96	0.78	180	893	56.3
2.5	1901	27.8	28.2	1.53	0.40	0.13	132	1029	40.4
3.0	1732	25.2	29.8	1.53	0.08	0.02	96	1083	29.0
3.5	1605	23.3	31.1	1.53	0.00	0.02	71	1097	21.1
4.0	1506	21.8	32.2	1.53	0.00	0.00	53	1091	15.8

From Table 31.10 of Gyftopoulos, Beretta, Thermodynamics. Foundations and applications, Dover, 2005

Detailed kinetic mechanism for the oxidation of hydrocarbons

Hydrogen: K=8 species, I=24 reactions

	Reactions	*A*	*b*	*E*
1	O+O+M=O2+M	1.20E+17	-1	0
2	O+H+M=OH+M	5.00E+17	-1	0
3	H+H+M=H2+M	1.00E+18	-1	0
4	H+H+H2=H2+H2	9.00E+16	-0.6	0
5	H+H+H2O=H2+H2O	6.00E+19	-1.3	0
6	H+OH+M=H2O+M	2.20E+22	-2	0
7	H+O2+M=HO2+M	2.80E+18	-0.9	0
8	H+O2+O2=HO2+O2	2.08E+19	-1.2	0
9	H+O2+H2O=HO2+H2O	1.13E+19	-0.8	0
10	OH+OH+M=H2O2+M	7.40E+13	-0.4	0
11	O+H2=H+OH	3.87E+04	2.7	6260
12	O+HO2=OH+O2	2.00E+13	0	0
13	O+H2O2=OH+HO2	9.63E+06	2	4000
14	H+O2=O+OH	2.65E+16	-0.7	17041
15	H+HO2=O+H2O	3.97E+12	0	671
16	H+HO2=O2+H2	4.48E+13	0	1068
17	H+HO2=OH+OH	8.40E+13	0	635
18	H+H2O2=HO2+H2	1.21E+07	2	5200
19	H+H2O2=OH+H2O	1.00E+13	0	3600
20	OH+H2=H+H2O	2.16E+08	1.5	3430
21	OH+OH=O+H2O	3.57E+04	2.4	-2110
22	OH+HO2=O2+H2O	1.45E+13	0	-500
23	OH+H2O2=HO2+H2O	2.00E+12	0	427
24	HO2+HO2=O2+H2O2	1.30E+11	0	-1630

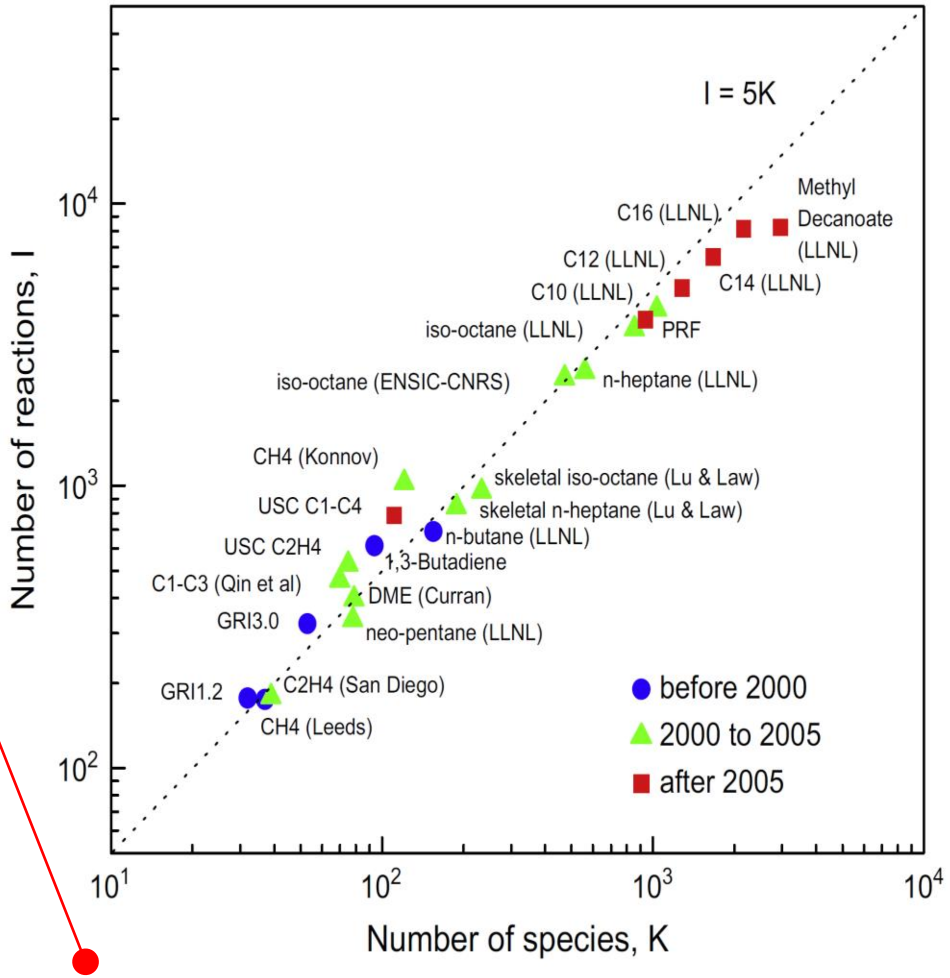


Fig. 10. Size of selected detailed and skeletal mechanisms for hydrocarbon fuels, together with the approximate years when the mechanisms were compiled.

Fig.10 in T. Lu and C.K. Law, Progress in Energy and Combustion Science 35, 192 (2009).

Alternative derivation of the **chemical equilibrium conditions**
using the method of Lagrange multipliers

maximize $S_{\text{off}}(U,V,\boldsymbol{n})\big|_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu}}$ subject to the constraints $n_i = n_{ia} + \sum_j \nu_i^{(j)} \epsilon_j$

introduce a Lagrange multiplier λ_i for each constraint and

define $L(U,V,\boldsymbol{n},\boldsymbol{n}_a,\boldsymbol{\epsilon},\boldsymbol{\lambda}) = S_{\text{off}}(U,V,\boldsymbol{n}) - \sum_i \lambda_i \left(n_i - n_{ia} - \sum_j \nu_i^{(j)} \epsilon_j\right)$

maximize $L(U,V,\boldsymbol{n},\boldsymbol{n}_a,\boldsymbol{\epsilon},\boldsymbol{\lambda})|_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu}}$ i.e., impose $\dfrac{\partial L}{\partial n_i} = 0$ and $\dfrac{\partial L}{\partial \epsilon_j} = 0$

$$\frac{\partial L}{\partial n_i} = \frac{\partial S_{\text{off}}}{\partial n_i} - \lambda_i = -\frac{\mu_i^{\text{off}}}{T_{\text{off}}} - \lambda_i = 0 \Rightarrow \lambda_i = -\frac{\mu_i^{\text{off}}}{T_{\text{off}}}$$

$$\frac{\partial L}{\partial \epsilon_j} = \sum_i \lambda_i \, \nu_i^{(j)} = -\frac{1}{T_{\text{off}}} \sum_i \mu_i^{\text{off}} \, \nu_i^{(j)} = Y_j = 0$$

Complete chemical equilibrium

maximize $S_{\text{off}}(U,V,\boldsymbol{n})\big|_{U,V,\boldsymbol{n}_a,\boldsymbol{\nu}}$ subject to the constraints $c_k = \sum_i n_{ia} a_{ik} = \sum_i n_i a_{ik}$

introduce a Lagrange multiplier λ_k for each constraint and

define $L(U,V,\boldsymbol{n},\boldsymbol{n}_a,\boldsymbol{\lambda}) = S_{\text{off}}(U,V,\boldsymbol{n}) - \sum_k \lambda_k \sum_i (n_i - n_{ia})\, a_{ik}$

maximize $L(U,V,\boldsymbol{n},\boldsymbol{n}_a,,\boldsymbol{\lambda})|_{U,V,\boldsymbol{n}_a}$ i.e., impose $\dfrac{\partial L}{\partial n_i} = 0$

$$\frac{\partial L}{\partial n_i} = \frac{\partial S_{\text{off}}}{\partial n_i} - \sum_k \lambda_k a_{ik} = -\frac{\mu_i^{\text{off}}}{T_{\text{off}}} - \sum_k \lambda_k a_{ik} = 0$$

assuming ideal behavior $\mu_i^{\text{off}} = \mu_{ii}(T,p) + RT \ln y_i$ yields

$$y_i = \exp\left(-\frac{\mu_{ii}(T,p)}{RT} - \frac{1}{R}\sum_k \lambda_k a_{ik}\right)$$

substitute this back into the constraints

$$c_\ell = \sum_i n_i a_{i\ell} = n \sum_i y_i a_{i\ell}$$

$$= n \sum_i \exp\left(-\frac{\mu_{ii}(T,p)}{RT} - \frac{1}{R}\sum_k \lambda_k a_{ik}\right) a_{i\ell}$$

since the initial numbers of nuclei are known, solving this system of equations, yields the Lagrange multipliers, i.e., $\lambda_k = \lambda_k(\boldsymbol{c})$

Coefficients a_{ik} = number nuclei of type k in species i

i	k	C	H	O	N
CH_4		1	4	0	0
O_2		0	0	2	0
N_2		0	0	0	2
H_2O		0	2	0	1
CO_2		1	0	2	0
CO		1	0	1	0
NO		0	0	1	1
NO_2		0	0	2	1
N_2O		0	0	1	2
$\vdots$		$\vdots$	$\vdots$	$\vdots$	$\vdots$

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Slides 17–20:

Figure 30.1, tables and text excerpt from the book *Thermodynamics: Foundations and Applications* courtesy of Elias P. Gyftopoulos and Gian Paolo Beretta.

Slide 21:

Image showing size of selected detailed and skeletal mechanisms for hydrocarbon fuels, together with the approximate years when the mechanisms were compiled, courtesy Elsevier, Inc., https://www.sciencedirect.com. Used with permission.

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