Aerospace Combustion

Lecture 5:

Combustion: Basic Definitions and Equations Part 2

Content

- Standard Entropy and Enthalpy
- Chemical Potential and Chemical Equilibrium
- Propellant Mixtures
- Standard Enthalpy and Entropy and Changes
- Gibbs and Helmholtz Energies
- Fugacity

Chemical Reactions

Standard Entropy

- Standard means at standard pressure (1 atm) and temperature (298 K)
- Values can be found in the literature for almost any substance
- Entropy is an extensive property (function of the number of moles)
- The more complex the molecule, the higher the standard entropy value
- Literature provides data for almost any substance

Element	$S°_{298}$	Compound	$S°_{298}$
$H_2(g)$	131	$H_2O(l)$	70
$O_2(g)$	205	$H_2O(g)$	189
$N_2(g)$	193	$H_2O_2(g)$	110
$Cl_2(g)$	223	$N_2O_4(g)$	304
He(g)	126	$NH_3(g)$	192
Ne(g)	146	NaCl(s)	72
C(s, diamond)	2.4	NaCl(aq)	116
C(s, graphite)	5.7	$CH_4(g)$	186
S(s)	32	$CO_2(g)$	213

Some Standard Molar Entropy Values at 298.15 K*

Compound or Element	Entropy, $S°$(J/K·mol)	Compound or Element	Entropy, $S°$(J/K·mol)	Compound or Element	Entropy, $S°$(J/K·mol)
C(graphite)	5.740	Ar(g)	154.7	$Cl_2(g)$	223.036
C(g)	158.096	$H_2(g)$	130.684	$Br_2(\ell)$	152.2
$CH_4(g)$	186.64	$O_2(g)$	205.138	$I_2(s)$	116.135
$C_2H_6(g)$	229.60	$N_2(g)$	191.61	NaCl(s)	72.8
$C_3H_8(g)$	269.9	$H_2O(g)$	188.825	NaF(s)	51.5
$CH_3OH(\ell)$	126.8	$H_2O(\ell)$	69.91	MgO(s)	26.94
CO(g)	197.674	$NH_3(g)$	192.45	$MgCO_3(s)$	65.854
$CO_2(g)$	213.74	HCl(g)	186.908		
Ca(s)	41.42	$F_2(g)$	202.78		

Taken from "The NBS Tables of Chemical Thermodynamic Properties," 1982.

Chemical Reactions

Entropy Change in a Reaction

Using standard molar entropies you are able to predict the entropy change of reactions

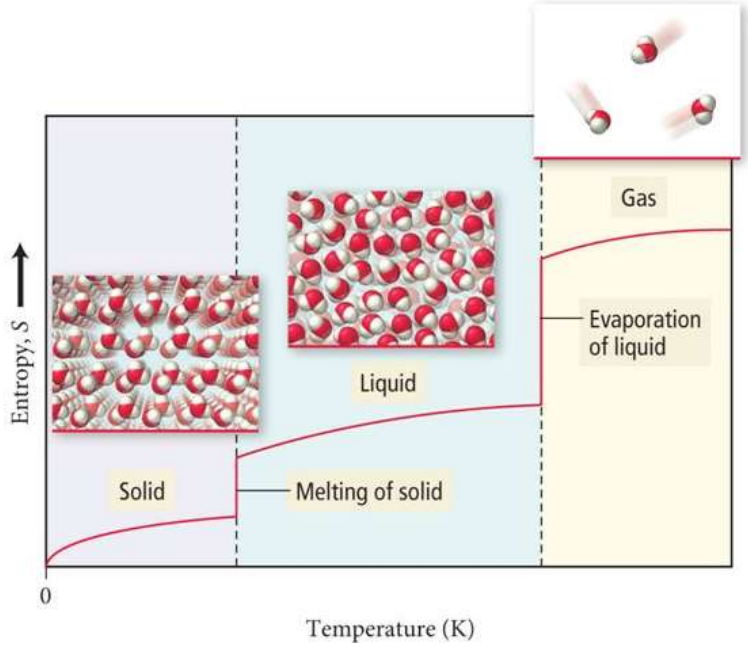
$$\Delta S = \sum n_p S^0_{products} - \sum n_r S^0_{reactants}$$

Phase changes lead to entropy changes which is important since propellants generally enter in liquid state and the products are gaseous.

Example:

$n_1A + n_2B \rightarrow n_3H + n_4E + n_5F$

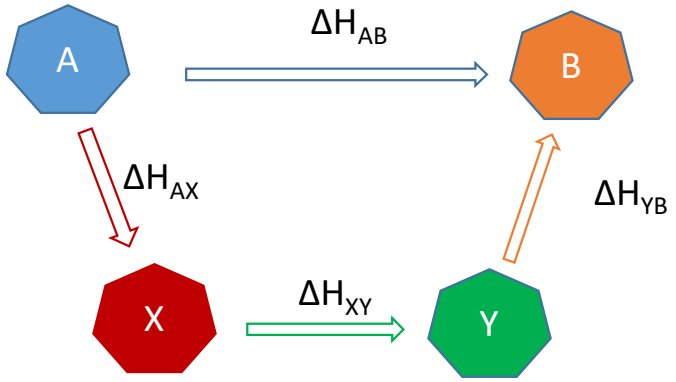
$$\Delta S = [n_3 S^0_H + n_4 S^0_E + n_5 S^0_F] - [n_1 S^0_A + n_2 S^0_B]$$



Chemical Reactions

Enthalpy of Formation

Law of Hess: "The *sum* of the enthalpy changes for a number of individual reaction steps equals the enthalpy change of the overall reaction.



$$\Delta H_{AB} = \Delta H_{AX} + \Delta H_{XY} + \Delta H_{YB}$$

This holds even for larger and more complex systems

A + B → C + D
K + C → G + H
D + G → E + F

A + B → H + E + F

Step 1: elements → reactants provides $AH_{reactants}$
Step 2: elements → products provides $AH_{products}$
Step 3: $AH_{reaction} = AH_{reactants} + AH_{products}$

Combustion of methane $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$C + 2H_2$	$\rightarrow CH_4$	- 74.80 kJ
O_2	$\rightarrow O_2$	0
$C + O_2$	$\rightarrow CO_2$	-393.50 kJ
$H_2 + 1/2O_2$	$\rightarrow H_2O$	-285.83 kJ
$CH_4 + C$	$\rightarrow C + 2H_2$	+74.80 kJ

- Formation of an element from an element is **Zero.**
- The reactants have to appear on the left side of the equation.

Chemical Reactions

Example

Let's predict the standard entropy of the formation reaction of ammonia from the elements at standard conditions

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$

$$\Delta S^0 = 2S^0(NH_3) - \left[S^0(N_2) + 3S^0(H_2)\right]$$

$$= (2\,mol)\left(192.3\frac{J}{K\cdot mol}\right) - \left[(1\,mol)\left(191.5\frac{J}{K\cdot mol}\right) + (3\,mol)\left(130.6\frac{J}{K\cdot mol}\right)\right]$$

$$= -198.7\frac{\mathrm{J}}{\mathrm{K}}$$

The formation entropy is negative since the reaction reduces the number of moles from four to two .

Chemical Reactions

Literature provides Data for $\Delta G°$, $\Delta H°$, $S°$, *and* $c_p°$

@ 1 bar, 298K	M/ (g/mol)	$\Delta_f \bar{H}^o$ /$(kJmol^{-1})$	$\Delta_f \bar{G}^o$ /$(kJmol^{-1})$	$\bar{S}^o$ /$(Jmol^{-1}K^{-1})$	$\bar{C}_p^o$ /$(Jmol^{-1}K^{-1})$
H_2 (g)	2.016	0	0	130.684	28.824
H (g)	1.008	217.97	203.25	114.71	20.784
H^+ (aq)	1.008	0	0	0	0
H^+ (g)	1.008	1536.20			
H_2O (s)	18.015			37.99	
H_2O (l)	18.015	-285.83	-237.13	69.91	75.291
H_2O (g)	18.015	-241.82	-228.57	188.83	33.58
H_2O_2 (l)	34.015	-187.78	-120.35	109.6	89.1
O_2 (g)	31.999	0	0	205.138	29.355
O (g)	15.999	249.17	231.73	161.06	21.912
O_3 (g)	47.998	142.7	163.2	238.93	39.20
HO^- (aq)	17.007	-229.99	-157.24	-10.75	-148.5

Chemical Reactions

Chemical Equilibrium

Chemical equilibrium accounts for impact of pressure and temperature on the formation of reaction products

- Does not hold for slow chemical reactions, typically low temperatures where in the residence time of the propellants in the control volume won't reach equilibrium
- Such cases finite rate kinetic mechanisms
- Chemical equilibrium represents exact thermodynamic limit

Chemical Potential

Chemical potential is equivalent to the partial molar free Gibbs energy

Chemical Reactions

Equilibrium Constants

Several ways to predict equilibrium constants

Use chemical potentials and apply

- Enthalpies of formation
- Entropies of formation
- Specific heats

Use an approximation approach by neglecting temperature dependency of specific heat

Chemical Reactions

Chemical Equilibrium, Chemical Potential

Partial molar entropy of chemical species in an ideal gas mixture

$$s_{i,m} = s^0{}_{i,m} - R \ln\left(\frac{p_i}{p_0}\right); i = 1,2,...k$$

with p_0 = 1 atm
and

$$s^0{}_{i,m} = s^0{}_{i,m,ref} + \int_{T_{ref}}^{T} \frac{c_{p_{i,m}}}{T} dT; i = 1,2,...k$$

and which depends only on temperature. Values for these are listed in tables.

The constant pressure heat capacity is a function of the temperature only and is usually represented by a power series in *T*.

$$c_p = a_0 + a_1 T + a_2 T^2 - a_3 T^3 + ...$$

Chemical Reactions

Chemical Equilibrium, Chemical Potential

Free Gibbs energy for mixtures

$$G = \sum_{i=1}^{n} n_i g_{i,m};$$

Equilibrium is reached when Gibbs free energy is minimum, i.e. *dG = 0*

$$dG = Vdp - sdT + \sum_{i=1}^{N} \mu_i dn_i;$$

from total differential $$dG = \left.\frac{\partial G}{\partial p}\right|_{T,\{n_i\}} dp + \left.\frac{\partial G}{\partial T}\right|_{p,\{n_i\}} dT + \sum_{i=1}^{N} \left.\frac{\partial G}{\partial p}\right|_{T,p,\{n_{j,i\neq j}\}} dn_i;$$

follows $$\left.\frac{\partial G}{\partial p}\right|_{T,p,\{n_{j,i\neq j}\}} = \mu_i$$ and since $$G = \sum_{i=1}^{n} n_i g_{i,m};$$

→ $$\mu_i = g_{i,m}$$

Chemical potential is equivalent to the partial molar free Gibbs energy

Chemical Reactions

Prediction of Equilibrium Constant

Generally an equilibrium constant can be predicted using the stiochiometric coefficients and the chemical potential of the species in question and the latter depends on their enthalpies and entropies of formation and their specific heats

$$K_p(T) = \exp\left(\sum_{i=1}^{n} \frac{\nu_i \mu_i^0}{RT}\right)$$

with

$$\frac{\mu_i^0}{RT} = \frac{h_{i,m_{ref}}}{RT} - \frac{s_{ref}}{R} + \frac{1}{RT}\int c_{p_i} dT + \int \frac{c_p}{RT} dT$$

Chemical Reactions

Approximation of Equilibrium Constants

For constant specific heats c_{p_i}

the approximate solution

$$K_p(T) = \exp\left(\frac{-\sum_{i=1}^{n}\nu_i h_{i,m,ref}}{RT}\right) \underbrace{\exp\left(\sum_{i=1}^{n}\nu_i s_{ref}/R\right)}_{\text{constant}} \underbrace{\exp\left(\sum_{i=1}^{n}\nu_i c_{p_i}\frac{T-T_{ref}}{RT}\right)}_{\approx\text{constant}} \underbrace{\exp\left(\sum_{i=1}^{n}\nu_i \frac{c_{p_i}}{R}\ln\left(\frac{T}{T_{ref}}\right)\right)}_{\approx\exp(n\ln T)}$$

finally reads:

$$K_p(T) = \exp\left(\frac{-\Delta h_{m,ref}}{RT}\right)\exp\left(\sum_{i=1}^{n}\nu_i\pi_{i,A}\right)\exp\left(\sum_{i=1}^{n}\nu_i\pi_{i,B}\ln(T)\right)$$

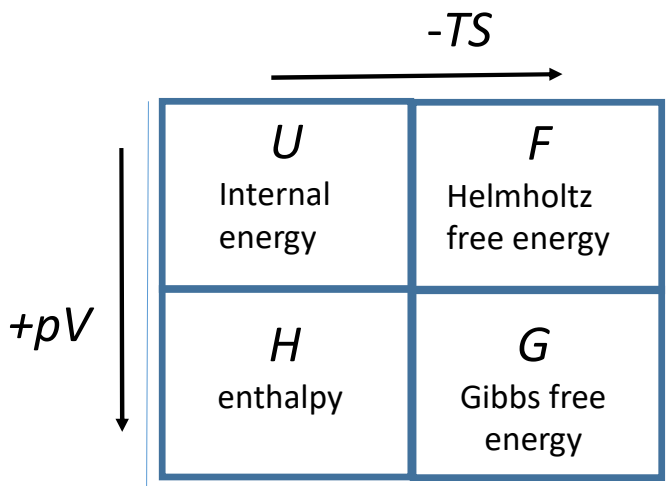
* Values for $\pi_{i,A}$ and $\pi_{i,B}$ for some species can be found in the annex

Chemical Reactions

Gibbs free Energy

$$\Delta G^0 = \Delta H^0 - TdS^0$$

- Allows to calculate maximum non-expansive, reversible work that can be performed by a thermodynamic system at constant (p,T)
- For a system is at equilibrium at (p,T constant) the free Gibb's energy is a its minimum



Not to be mixed with Helmholtz free Energy

$$F = U - TS$$

- Allows to calculate the useful work obtainable from a closed system at constant temperature and volume
- ***F*** is quite often used in explosives research where pressure changes come naturally.

The four thermodynamic potentials *U, F, H,* and *G* are related by offsets of the energy from the environment term *TS* and the expansion work term *pV*.

Chemical Reactions

Equilibrium Constant

Let's look at the reaction

A + B → C + D

and formulate this in terms of free Gibbs energy

with *ΔG = 0*

$$G_A = G_A^0 + aRT\ln(p_A)$$
$$G_B = G_B^0 + bRT\ln(p_B)$$
$$G_C = G_C^0 + cRT\ln(p_C)$$
$$G_D = G_D^0 + dRT\ln(p_D)$$

$$\Delta G = G_{prod} - G_{react}$$
$$= \Delta G^0 + RT\ln\left(\frac{p_C^c p_D^d}{p_A^a p_B^b}\right)$$

$$\Delta G^0 = -RT\ln\left(\frac{p_C^c p_D^d}{p_A^a p_B^b}\right) = RT\ln K_p$$

Large negative values of ΔG^0 are meanly due to large equilibrium constant K_p which means that the reaction is faster. In case the free energy of reactants and products are the same, there will be no progress of the reaction and *ΔG = 0.*

A general reaction of the form $\sum_{i=1}^{N} \nu'_i M_i \Leftrightarrow \sum_{i=1}^{N} \nu''_i M_i$ yields such an equilibrium constant $K_p = \prod_{i=1}^{N} \left(p_{i,e}\right)^{\left(\nu''_{i,s} - \nu'_{i,s}\right)}$

Chemical Reactions

Various Equilibrium Constant Formulations

$$K_p = \prod_{i=1}^{N} \left(p_{i,e}\right)^{\left(\nu''_{i,s} - \nu'_{i,s}\right)}$$

$$K_n = \prod_{i=1}^{N} \left(n_{i,e}\right)^{\left(\nu''_{i,s} - \nu''_{i,s}\right)}$$

$$K_c = \prod_{i=1}^{N} \left(c_{i,e}\right)^{\left(\nu''_{i,s} - \nu'_{i,s}\right)}$$

$$K_X = \prod_{i=1}^{N} \left(X_{i,e}\right)^{\left(\nu''_{i,s} - \nu'_{i,s}\right)}$$

$$K_Y = \prod_{i=1}^{N} \left(Y_{i,e}\right)^{\left(\nu''_{i,s} - \nu'_{i,s}\right)}$$

$$c_i = \frac{p_i}{RT}$$

Concentration of species i

$$n_i = \frac{p_i V}{RT} = \frac{p_i}{p} n_T$$

actual number of moles of species i

$$X_i = \frac{p_i}{p} = \frac{n_i}{n_T}$$

mole fraction of species i

$$Y_i = \frac{W_i p_i}{\rho RT} = \frac{W_i c_i}{\rho} = \frac{\rho_i}{\rho}$$

Mass fraction of species i

$$n_T = \sum_{i=1}^{N} n_i$$

Total number of moles in mixture

$$p = \sum_{i=1}^{N} p_i$$

Total mixture pressure

ρ

Mixture density

Chemical Reactions

Interrelation of Various Formulations

$$K_p = K_c (RT)^{\Delta n} =$$

$$= K_n \left(\frac{p}{n_T} \right)^{\Delta n} =$$

$$= K_X (p)^{\Delta n} =$$

$$= K_Y (RT\rho)^{\Delta n} \prod_{i=1}^{N} (W_i)^{(\nu'_{i,s} - \nu''_{i,s})}$$

for cases where

$$\Delta n = \sum_{i=1}^{N} \nu''_i - \sum_{i=1}^{N} \nu'_i \neq 0$$

then K_p is a function of temperature only,

all others are functions of pressure and temperature

Chemical Reactions

Example 1:

Let's consider the reaction of methane with oxygen to form carbon-monoxide and water

$$CH_4 + 1.5O_2 = CO + 2H_2O$$

Quite often at high temperatures the chemical equilibrium may look like

$$(1-\eta)CO + (2-\eta)H_2O + \eta CO_2 + \eta H_2$$

due to a reaction called water-gas reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Question: Write the necessary mathematical relationships required to solve the equilibrium composition

Chemical Reactions

Example 1:

K_p for the water-gas reaction reads

$$K_p = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} \qquad n_T = \sum_{i=1}^{N} n_i = (1-\eta)+(2-\eta)+\eta+\eta = 3$$

$$\rightarrow \quad X_{CO} = \frac{1-\eta}{3}; X_{H_2O} = \frac{2-\eta}{3}; X_{CO_2} = \frac{\eta}{3} = X_{H_2};$$

$$\rightarrow \quad p_{CO} = \frac{1-\eta}{3} p; p_{H_2O} = \frac{2-\eta}{3} p; p_{CO_2} = \frac{\eta}{3} p = p_{H_2};$$

$$\rightarrow \quad K_p = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} = \frac{\left(\frac{\eta}{3}\right)^2 p^2}{\left(\frac{1-\eta}{3}\right) p \left(\frac{2-\eta}{3}\right) p} = \frac{\eta^2}{(1-\eta)(2-\eta)}$$

Chemical Reactions

Example 2:

Let's heat 1 mole of nitrogen and 0.5 mole of oxygen to 4000 K at 1 bar and consider an equilibrium composition of N_2, O_2 and NO only.

$$N_2 + 0.5O_2 = aN_2 + bO_2 + cNO$$

Question: What is the final equilibrium composition?

Conservation of atoms yields:

$$N: 2 = 2a + c$$
$$O: 1 = 2b + c$$
$$a = 1 - \frac{c}{2}; b = \frac{1}{2} - \frac{c}{2}$$

From tables we know that $K_p \sim 0.3$:

$$K_p = \frac{p_{NO}}{p_{N_2} p_{O_2}} = \frac{x}{(1 - x/2)^{1/2} (1/2 - x/2)^{1/2}} \left(\frac{p}{\sum n} \right)^{1-1/2-1/2} \Rightarrow 0.09 = \frac{x^2}{(1 - x/2)(1/2 - x/2)} \Rightarrow x = 0.1825$$

Final mixture composition is then: $0.90875N_2 + 0.40875O_2 + 0.1825NO$

Chemical Reactions

Fugacity (f)

Fugacity is a quantity which represents the actual behavior of real gases

For ideal gases at constant temperature

$$dG = nRTd\left(\ln p\right)$$

for non-ideal gases

$$dG = nRTd\left(\ln f\right)$$

Fugacity may be considered a correction to the partial pressure

The proportionality constant Γ is a function of many parameters such as temperature and pressure

$$f_i = p_i \Gamma\left(p, T, \ldots\right)$$

For an ideal gas

$$\frac{f_i}{p_i} = 1$$

Chemical Reactions

Fugacity (f)

For decreasing pressure real gases approach ideal gas behavior

$$\lim_{p \to 0} \left(\frac{f}{p} \right) = 1$$

Assuming an isothermal process at temperature ***T,*** the fugacity ***f*** can be determined from the compressibility factor ***Z*** and the pressure ***p*** by

$$Z \; d\left(\ln \; p\right)_\tau = d\left(\ln \; f\right)_\tau$$

Integration at constant ***T*** from ***p = 0*** to a certain finite pressure ***p*** yields

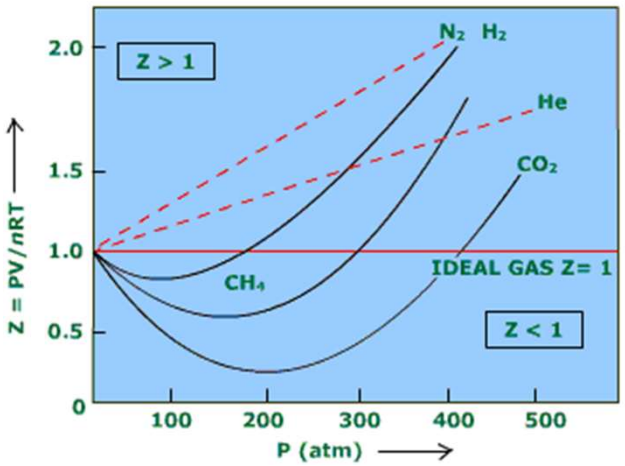
$$\ln \frac{f}{p} = \int_0^{p_r} (Z - 1) \, d\left(\ln \; p_r\right)_T$$

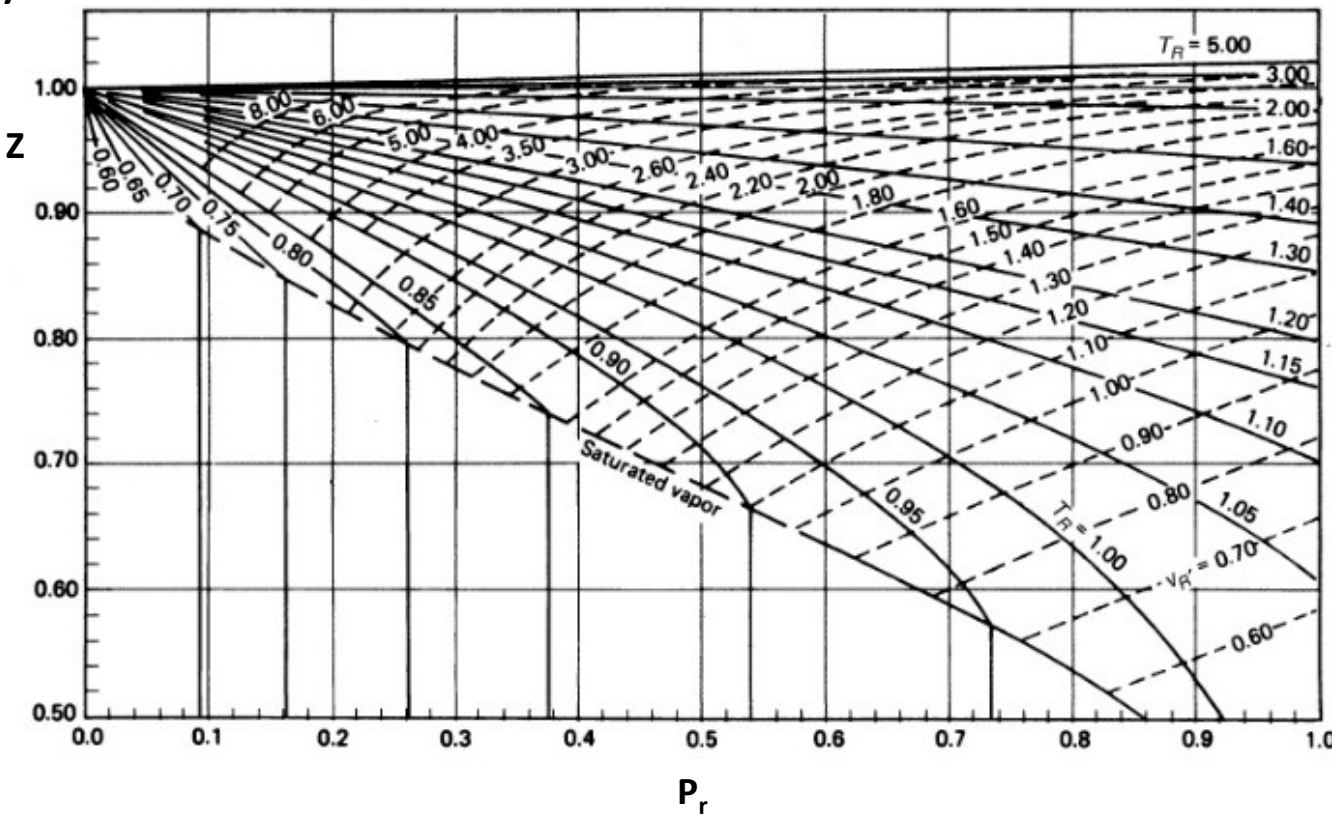
The right hand side is accessible from compressibility charts, see next page

Chemical Reactions

Generalized Compressibility Chart

Such charts are available for almost any common species





Type of Chemical Reactions

Order of Sample Reactions

A) 1st order reactions

$$A_2 \xrightarrow{k_f} 2A \qquad \frac{dc_A}{dt} = 2k_f c_{A_2} = -2\frac{dc_{A2}}{dt} \Rightarrow \quad \text{after integration} \quad \ln\left(\frac{c_{A_2,0}}{c_{A_2,t}}\right) = k_f t$$

$$A + C \xrightarrow{k_f} D \quad \text{with} \quad c_A << c_C \qquad \frac{dc_A}{dt} = \frac{dc_D}{dt} = -k_f c_A c_D = k' c_A \quad k' \text{ new rate constant since } c_C \approx const.$$

$$AB \xrightarrow{k_f} A + B \qquad \frac{dc_{AB}}{dt} = -k_f c_{AB}$$

While the decomposition of A2 is a uni-molecular reaction which obeys first order kinetics, the formation of D out of A+B is a bi-molecular reaction which again obeys first order kinetics.

→ Uni-molecular reactions are always first order but not all first order reactions are mono-molecular.

Type of Chemical Reactions

Order of Sample Reactions

B. 2nd order reactions

$$A + B \xrightarrow{k_f} AB \qquad \frac{dc_A}{dt} = -k_f c_A c_B; \quad \frac{dc_B}{dt} = -k_f c_A c_B; \quad \frac{dc_{AB}}{dt} = k_f c_A c_B$$

$$2A \xrightarrow{k_f} C + D \qquad \frac{dc_A}{dt} = -2k_f c_A^2; \quad \frac{dc_C}{dt} = k_f c_A^2; \quad \frac{dc_D}{dt} = k_f c_A^2$$

C. 3rd order reactions

$$2AB + B_2 \xrightarrow{k_f} 2AB_2 \qquad \frac{dc_{AB_2}}{dt} = k_f c_{AB}^2 c_{B_2}; \quad \frac{dc_{AB}}{dt} = -k_f c_{AB}^2 c_{B_2}$$

$$M + 2A \xrightarrow{k_f} A_2 + M^* \qquad \frac{dc_{A2}}{dt} = k_f c_M c_A^2; \quad \frac{dc_A}{dt} = -2k_f c_M c_A^2$$

Type of Chemical Reactions

Order of Sample Reactions

D. Consecutive reactions $A + B \xrightarrow{k_{f_1}} AB \xrightarrow{k_{f_2}} C + D$

1st reaction $$\frac{dc_{AB}}{dt} = k_1 c_A c_B; \quad \frac{dc_A}{dt} = \frac{dc_B}{dt} = -k_1 c_A c_B;$$

2nd reaction $$\frac{dc_{AB}}{dt} = k_2 c_{AB}; \quad \frac{dc_C}{dt} = \frac{dc_D}{dt} = -k_2 c_{AB};$$

net reaction $$\left(\frac{dc_{AB}}{dt}\right)_{net} = k_1 c_A c_B - k_2 c_{AB};$$

Type of Chemical Reactions

Order of Sample Reactions

E. Competing reactions $A + B \xrightarrow{k_{f_1}} AB$ 1st reaction $\frac{dc_A}{dt} = -k_1 c_A c_B; \quad \frac{dc_B}{dt} = -k_1 c_A c_B;$

$A + B \xrightarrow{k_{f_2}} C + D$ 2nd reaction $\frac{dc_A}{dt} = -k_2 c_A c_B; \quad \frac{dc_B}{dt} = -k_2 c_A c_B;$

net rate of disappearance of species *A* $\frac{dc_A}{dt} = -(k_1 + k_2) c_A c_B;$

Quite often competing reaction may have different rates depending on temperature.

F. Opposing reactions (1st order / 1st order) $A \underset{k_b}{\overset{k_f}{\leftrightarrow}} B$

Note c_X is the portion of *A* converted to *B* by the forward reaction with $c_{A,0}$ the initial concentration

$c_A = c_{A,0} - c_X; \qquad \frac{dc_X}{dt} = k_f (c_{A,0} - c_X) - k_b c_X;$

$c_B = c_X; \;\; c_{B,0} = 0$

Type of Chemical Reactions

Order of Sample Reactions

G. Opposing reactions (1st order / 2nd order)

$$A \underset{k_b}{\overset{k_f}{\leftrightarrow}} B + C \qquad \frac{dc_X}{dt} = -k_f\left(c_{A,0} - c_X\right) - k_b c_X^2;$$

H. Opposing reaction (2nd order / 2nd order)

$$A + B \underset{k_b}{\overset{k_f}{\leftrightarrow}} C + D \qquad \frac{dc_X}{dt} = -k_f\left(c_{A,0} - c_X\right)^2 - k_b c_X^2;$$

I. Chain reaction (formation of radical)

$$A + B \underset{k_b}{\overset{k_f}{\leftrightarrow}} A^* + A; \quad \frac{\text{(fast)}}{\text{(fast)}}$$

$$A^* \overset{k'_f}{\rightarrow} products \quad \text{(slow)}$$

According to Lindemann only a small portion of molecules will become energized by collisions *A** and as long as their conversion rate into products is small the following relations hold.

$$\frac{dc_A}{dt} = k_f c_A^2 + k_b c_{A^*} c_A$$

$$\frac{dc_{A^*}}{dt} = k_f c_A^2 - k_b c_{A^*} c_A - k'_f c_{A^*};$$

Type of Chemical Reactions

Order of Sample Reactions

J. Chain branching reactions

General formulation of a chain-branching reaction

$$A \xrightarrow{k_1} R^*$$

$$R^* + M \xrightarrow{k_2} \alpha' R^* + M^*$$

$$R^* + M^* \xrightarrow{k_3} P$$

$$R^* \xrightarrow{k_4} M\,(\text{wall})$$

$$R^* \xrightarrow{k_5} \text{nonreactive species}$$

Assuming steady-state condition

$$\frac{dc_{R^*}}{dt} = 0 = k_1 c_M + (\alpha' - 1) k_2 c_{R^*} c_M - k_3 c_{R^*} c_{M^*} - k_4 c_{R^*} - k_5 c_{R^*}$$

$$\frac{dc_P}{dt} = k_3 c_{R^*} c_{M^*}$$

$$\alpha'_{crit} = 1 + \frac{k_3 c_{R^*} c_{M^*} + k_4 + k_5}{k_2 c_{M^*}}$$

if

$\alpha' \geq \alpha'_{crit} \Rightarrow$ chain-branching explosion

$\alpha' \leq \alpha'_{crit} \Rightarrow$ no explosion

Type of Chemical Reactions

Order of Sample Reactions

J. Chain branching reactions

In a hydrogen oxygen mixture and in presence of an OH radical the following reaction cycle is plausible

$$\left.\begin{aligned} H^* + O_2 &\rightarrow OH^* + O^* \\ O^* + H_2 &\rightarrow OH^* + H^* \end{aligned}\right\}$$ chain-branching

$$OH^* + H_2 \rightarrow H_2O + H^*$$ chain-carrying

Let's consider that the chain-carrying reaction is dominating and we have a volume of *1 cm^3* which contains roughly *10^{19}* molecules and 1 radical. At a collision rate of *10^8 1/s* it would take around 30000 years for all molecules to react.

Now let's assume that 1 radical is able to generate 2 radicals (*$\alpha'=2$*) then all molecules will react within about 1 *μs*.

If we assume that only 1% of the reactions are chain-branching (*$\alpha'=1.01$*) this time increase to about 40 *μs*.

Basics

What you should not forget

- Mole fraction, mass fraction, molar density,
- Mixture fraction, stoichiometric value, equivalence ratio
- Why a cubic equation of state combustion is often necessary
- Difference between global and elementary reactions
- Reaction rate
- Enthalpy, entropy at standard conditions and for formation
- Gibbs and Helmholtz energy
- Order of reactions
- Fugacity
- Chain reactions
- Explosions

Annex

Content

- Properties of common species in combustion
- Enthalpies and entropies of formation of common species
- Relations to predict fluid properties

Annex

Properties of Gases

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$s_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
1	H	1,008	217,986	114,470	-1,2261	1,9977
2	HNO	31,016	99,579	220,438	-1,0110	4,3160
3	OH	17,008	39,463	183,367	3,3965	2,9596
4	HO_2	33,008	20,920	227,358	-,1510	4,3160
5	H_2	2,016	0,000	130,423	-2,4889	2,8856
6	H_2O	18,016	-241,826	188,493	-1,6437	3,8228
7	H_2O_2	34,016	-136,105	233,178	-8,4782	5,7218
8	N	14,008	472,645	153,054	5,8661	1,9977
9	NO	30,008	90,290	210,442	5,3476	3,1569
10	NO_2	46,008	33,095	239,785	-1,1988	4,7106
11	N_2	28,016	0,000	191,300	3,6670	3,0582
12	N_2O	44,016	82,048	219,777	-5,3523	4,9819

Annex

Properties of Gases

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$s_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
13	O	16,000	249,194	160,728	6,85561	1,9977
14	O_2	32,000	0,000	204,848	4,1730	3,2309
15	O_3	48,000	142,674	238,216	-3,3620	5,0313
16	NH	15,016	331,372	180,949	3,0865	2,9596
17	NH_2	16,024	168,615	188,522	-1,9835	3,8721
18	NH_3	17,032	-46,191	192,137	-8,2828	4,8833
19	N_2H_2	30,032	212,965	218,362	-8,9795	5,4752
20	N_2H_3	31,040	153,971	228,513	-17,5062	6,9796
21	N_2H_4	32,048	95,186	236,651	-25,3185	8,3608
22	C	12,011	715,003	157,853	6,4461	1,9977
23	CH	13,019	594,128	182,723	2,4421	3,,0829
24	HCN	27,027	130,540	201,631	-5,3642	4,6367

Annex

Properties of Gases

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$s_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
25	HCNO	43,027	-116,733	238,048	-10,1563	6,0671
26	HCO	29,019	-12,133	224,421	-,2313	4,2667
27	CH_2	14,027	385,220	180,882	-5,6013	4,2667
28	CH_2O	30,027	-115,896	218,496	-8,5350	5,4012
29	CH_3	15,035	145,686	193,899	-10,7155	5,3026
30	CH_2OH	31,035	-58,576	227,426	-15,3630	6,6590
31	CH_4	16,043	-74,873	185,987	-17,6257	6,1658
32	CH_3OH	32,043	-200,581	240,212	-18,7088	7,3989
33	CO	28,011	-110,529	197,343	4,0573	3,1075
34	CO_2	44,011	-393,522	213,317	-5,2380	4,8586
35	CN	26,019	456,056	202,334	4,6673	3,1075
36	C_2	24,022	832,616	198,978	1,9146	3,5268

Annex

Properties of Gases

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$s_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
37	C_2H	25,030	476,976	207,238	-4,6242	4,6367
38	C_2H_2	26,038	226,731	200,849	-15,3457	6,1658
39	C_2H_3	27,046	279,910	227,861	-17,0316	6,9056
40	CH_3CO	43,046	-25,104	259,165	-24,2225	8,5334
41	C_2H_4	28,054	52,283	219.,468	-26,1999	8,1141
42	CH_3COH	44,054	-165,979	264.061	-30,7962	9,6679
43	C_2H_5	29,062	110,299	228,183	-32,6833	9,2980
44	C_2H_6	30,070	-84,667	228,781	-40,4718	10,4571
45	C_3H_8	44,097	-103,847	269,529	-63,8077	14,7978
46	C_4H_2	50,060	465,679	250,437	-34,0792	10,0379
47	C_4H_3	51,068	455,847	273,424	-36,6848	10,8271
48	C_4H_8	56,108	16,903	295,298	-72,9970	16,7215

Annex

Properties of Gases

		M_i [kg/kmol]	$h_{i,m,ref}$ [kJ/mol]	$s_{i,m,ref}$ [kJ/mol K]	$\pi_{A,i}$	$\pi_{B,i}$
49	C_4H_{10}	58,124	-134,516	304,850	-86,8641	19,0399
50	C_5H_{10}	70,135	-35,941	325,281	-96,9383	20,9882
51	C_5H_{12}	72,151	-160,247	332,858	-110,2702	23,3312
52	C_6H_{12}	84,152	-59,622	350,087	-123,2381	25,5016
53	C_6H_{14}	86,178	-185,560	380,497	-137,3228	28,2638
54	C_7H_{14}	98,189	-72,132	389,217	-147,4583	29,6956
55	C_7H_{16}	100,205	-197,652	404,773	-162,6188	32,6045
56	C_8H_{16}	112,216	-135,821	418,705	-173,7077	34,5776
57	C_8H_{18}	114,232	-223,676	430,826	-191,8158	37,6111
58	C_2H_4O	44,054	-51,003	243,044	-34,3705	
59	HNO_3	63,016	-134,306	266,425	-19,5553	
60	He	4,003	0,000	125,800		

Annex

Enthalpies of Alkanes

Alkane	$\Delta H°_{exp}$	$\Delta H°_{calcd}$	$\lvert\Delta\rvert$	Alkane	$\Delta H°_{exp}$	$\Delta H°_{calcd}$	$\lvert\Delta\rvert$
n-Pentane	−41.36	−41.41	0.05	2-Methylheptane	−60.98	−60.96	0.02
n-Hexane	−47.52	−47.51	0.01	3-Methylheptane	−60.34	−60.34	0.00
n-Heptane	−53.63	−53.62	0.01	4-Methylheptane	−60.17	−60.17	0.00
n-Octane	−59.74	−59.73	0.01	3-Ethylhexane	−59.88	−59.88	0.00
n-Nonane	−65.84	−65.84	0.00	5-Methylnonane	−74.28	−74.28	0.00
n-Decane	−71.95	−71.94	0.01	2-Methylnonane	−74.74	−74.74	0.00
n-Undecane	−78.06	−78.05	0.01	2,2-Dimethylbutane	−51.00	−51.01	0.01
n-Dodecane	−84.16	−84.16	0.00	2,3-Dimethylbutane	−49.48	−49.55	0.07
n-Tridecane	−90.27	−90.27	0.00	2,2-Dimethylpentane	−57.05	−57.06	0.01
n-Tetradecane	−96.38	−96.37	0.01	2,3-Dimethylpentane	−55.81	−55.81	0.00
n-Pentadecane	−102.49	−102.48	0.01	2,4-Dimethylpentane	−56.17	−56.17	0.00
n-Cetane	-108.58	−108.59	0.01	3,3-Dimethylpentane	−56.07	−56.05	0.02
n-Heptadecane	−114.69	−114.70	0.01	2,2-Dimethylhexane	−62.63	−62.63	0.00
n-Octadecane	−120.80	−120.80	0.00	2,3-Dimethylhexane	−60.40	−60.42	0.02
n-Nonadecane	−126.90	−126.91	0.01	2,4-Dimethylhexane	−61.47	−61.44	0.03
n-Eicosane	−133.01	−133.02	0.01	2,5-Dimethylhexane	−62.26	−62.21	0.05
2-Methylbutane	−42.85	−42.82	0.03	3,3-Dimethylhexane	−61.58	−61.56	0.02
2-Methylpentane	−48.82	−48.87	0.05	3,4-Dimethylhexane	−60.23	−60.23	0.00
3-Methylpentane	−48.28	−48.30	0.02	2-Methyl-3-ethylpentane	−59.69	−59.68	0.01
2-Methylhexane	−54.93	−54.92	0.01	3-Methl-3-ethylpentane	−60.46	−60.48	0.02
3-Methylhexane	−54.35	−54.34	0.01	3,3-Diethylpentane	−65.84	−65.84	0.00
3-Ethylpentane	−53.77	−53.77	0.00				

Annex

Rx of Formation	Standard Enthalpy of Formation Table $\Delta H_{formation}$	
	Substance	kJ/mol
$Al(s) \rightarrow Al(s)$		0
$Al(s) + 3/2\ O_2(g) \rightarrow Al_2O_3(s)$		-1670
$C(s, graphite) \rightarrow C(s, graphite)$		0
$C(s) + ½\ O_2(g) \rightarrow CO\ (g)$		-111
$C(s) + O_2(g) \rightarrow CO_2\ (g)$		-394
$C(s) + 2H_2(g) \rightarrow CH_4\ (g)$		-75
$C(s) + 2H_2(g) + 1/2\ O_2(g) \rightarrow CH_3OH\ (l)$		-239
$2C(s) + H_2(g) \rightarrow C_2H_2\ (g)$		227
$2C(s) + 2H_2\ g) \rightarrow C_2H_4\ (g)$		52
$2C(s) + 3H_2(g) \rightarrow C_2H_6\ (g)$		-85
$2C(s) + 3H_2(g) + ½\ O_2(g) \rightarrow C_2H_5OH\ (l)$		-278
$Ca(s) + ½\ O_2(g) \rightarrow CaO\ (s)$		-636
$Ca(s) + O_2(g) + H_2(g) \rightarrow Ca(OH)_2\ (s)$		-987
$Ca(s) + S(s) + 2O_2(g) \rightarrow CaSO_4(s)$		-1433
$Cl_2(g) \rightarrow Cl_2\ (g)$		0
$2Fe(s) + 3/2\ O_2(g) \rightarrow Fe_2O_3(s)$		-822
$H_2(g) \rightarrow H_2\ (g)$		0
$½\ H_2(g) + ½\ Cl_2(g) \rightarrow HCl(g)$		-92
$H_2(g) + ½\ O_2(g) \rightarrow H_2O\ (g)$		-242
$H_2(g) + ½\ O_2(g) \rightarrow H_2O\ (l)$		-286
$H_2(g) + O_2(g) \rightarrow H_2O_2\ (l)$		-188
$½\ H_2(g) + S(s) \rightarrow H_2S\ (g)$		-20.
$H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4\ (l)$		-811
$Hg(l) \rightarrow Hg\ (l)$		0
$Hg(l) \rightarrow Hg\ (g)$		61
$Mg(s) + ½O_2(g) \rightarrow MgO(s)$		-602
$N_2\ (g) \rightarrow N_2\ (g)$		0
$½N_2(g) + 3/2H_2(g) \rightarrow NH_3\ (g)$		-46
$½N_2(g) + 2H_2(g)\ ½Cl_2(g) \rightarrow NH_4Cl(s)$		-315
$N_2(g) + ½O_2(g) \rightarrow N_2O\ (g)$		82
$N_2(g) + 2O_2(g) \rightarrow N_2O_4\ (g)$		10
$Na(s) + ½Cl_2(g) \rightarrow NaCl\ (s)$		-411
$Na(s) + ½O_2(g) + ½H_2(g) \rightarrow NaOH\ (s)$		-427
$O_2\ (g) \rightarrow O_2\ (g)$		0
$4P(s) + 5O_2\ (g) \rightarrow P_4O_{10}(s)$		-2980
$S(s) \rightarrow S(s)$		0
$S(s) + O_2\ (g) \rightarrow SO_2\ (g)$		-297
$S(s) + 3/2O_2\ (g) \rightarrow SO_3\ (g)$		-395

ΔH_f° (kJ/mol) (concentration of aqueous solutions is 1*M*)

Substance	ΔH_f°	Substance	ΔH_f°	Substance	ΔH_f°	Substance	ΔH_f°
Ag(s)	0	CsCl(s)	−443.04	H_3PO_4(aq)	−1279.0	NaBr(s)	−361.062
AgCl(s)	−127.068	Cs_2SO_4(s)	−1443.02	H_2S(g)	−20.63	NaCl(s)	−411.153
AgCN(s)	146.0	CuI(s)	−67.8	H_2SO_3(aq)	−608.81	$NaHCO_3$(s)	−950.8
Al_2O_3	−1675.7	CuS(s)	−53.1	H_2SO_4(aq)	−814.0	$NaNO_3$(aq)	−447.48
$BaCl_2$(aq)	−871.95	Cu_2S(s)	−79.5	$HgCl_2$(s)	−224. 3	NaOH(s)	−425.609
$BaSO_4$	−1473.2	$CuSO_4$(s)	−771.36	Hg_2Cl_2(s)	−265.22	Na_2CO_3(s)	−1130.7
BeO(s)	−609.6	F_2(g)	0	Hg_2SO_4(s)	−743.12	Na_2S(aq)	−447.3
$BiCl_3$(s)	−379.1	$FeCl_3$(s)	−399.49	I_2(s)	0	Na_2SO_4(s)	−1387.08
Bi_2S_3(s)	−143.1	FeO(s)	−272.0	K(s)	0	NH_4Cl(s)	−314.4
Br_2	0	FeS(s)	−100.0	KBr(s)	−393.798	O_2(g)	0
CCl_4(l)	−128.2	Fe_2O_3(s)	−824.2	$KMnO_4$(s)	−837.2	P_4O_6(s)	−1640.1
CH_4(g)	−74.81	Fe_3O_4(s)	−1118.4	KOH	−424.764	P_4O_{10}(s)	−2984.0
C_2H_2(g)	226.73	H(g)	217.965	LiBr(s)	−351.213	$PbBr_2$(s)	−278.7
C_2H_4(g)	52.26	H_2(g)	0	LiOH(s)	−484.93	$PbCl_2$(s)	−359.41
C_2H_6(g)	−84.68	HBr(g)	−36.40	Mn(s)	0	SF_6(g)	−1220.5
CO(g)	−110.525	HCl(g)	−92.307	$MnCl_2$(aq)	−555.05	SO_2(g)	−296.830
CO_2(g)	−393.509	HCl(aq)	−167.159	$Mn(NO_3)_2$(aq)	−635.5	SO_3(g)	−454.51
CS_2(l)	89.70	HCN(aq)	108.9	MnO_2(s)	−520.03	SrO(s)	−592.0
Ca(s)	0	HCHO	−108.57	MnS(s)	−214.2	TiO_3(s)	−939.7
$CaCO_3$(s)	−1206.9	HCOOH(l)	−424.72	N_2(g)	0	TlI(s)	−123.5
CaO(s)	−635.1	HF(g)	−271.1	NH_3(g)	−46.11	UCl_4(s)	−1019.2
$Ca(OH)_2$(s)	−986.09	HI(g)	26.48	NH_4Br(s)	−270.83	UCl_5(s)	−1059
Cl_2(g)	0	H_2O(l)	−285.830	NO(g)	90.25	Zn(s)	0
Co_3O_4(s)	−891	H_2O(g)	−241.818	NO_2(g)	33.18	$ZnCl_2$(aq)	−488.19
CoO(s)	−237.94	H_2O_2(l)	−187.8	N_2O(g)	82.05	ZnO(s)	−348.28
Cr_2O_3(s)	−1139.7	H_3PO_4(l)	−595.4	Na(s)	0	$ZnSO_4$(aq)	−1063.15

$\Delta_f H°_{298}$/kJ mol^{-1}					
H_2O(l)	− 286	NO_2(g)	+ 33	CH_4(g)	− 75
H_2O(g)	− 242	N_2O_4(g)	+ 9	C_2H_6(g)	− 85
CO(g)	− 111	CaO(s)	− 635	C_2H_4(g)	+ 52
CO_2(g)	− 394	$CaCO_3$(s)	− 1207	C_2H_2(g)	+ 227
HCl(g)	− 92	Fe_2O_3(s)	− 824	C_2H_5OH(l)	− 278
NH_3(g)	− 46	NaCl(s)	− 411	C_6H_6(l)	+ 49
NO(g)	+ 90	$BaSO_4$(s)	− 1473	CH_2O(g)	− 109

Basic Thermodynamics

Transport Coefficients

Momentum

$$\eta_{ij} = 266.93 \cdot 10^{-8} \left(\frac{\sqrt{2 M_i M_j T / (M_i + M_j)}}{\sigma_{ij}^2 \Omega_{ij}^{(2,2)*}(T_{ij}^*)} \right);$$

Heat

$$\lambda_{ij} = 8.3 \cdot 10^{-4} \left(\frac{\sqrt{T (M_i + M_j) / 2 M_i M_j}}{\sigma_{ij}^2 \Omega_{ij}^{(2,2)*}(T_{ij}^*)} \right);$$

Mass

$$D_{ij} = 26.28 \cdot 10^{-8} \left(\frac{\sqrt{T^3 (M_i + M_j) / 2 M_i M_j}}{p \sigma_{ij}^2 \Omega_{ij}^{(1,1)*}(T_{ij}^*)} \right)$$

Already rather complex but this is for binary mixtures only, for multi-component mixtures no general analytical solution exists.

Basic Thermodynamics

Transport Coefficients

Collision integrals

$$\Omega^{(l,s)*}(T) = \frac{1}{(s+1)!}\int_0^\infty \exp(-E/T)\left(\frac{E}{T}\right)^{s+1} Q^{(l)^*}(E)\, d\left(\frac{E}{T}\right),$$

$$Q^{(l)*}(E) = \frac{1}{\left(1-\frac{1+(-1)^l}{2(1+l)}\right)}\int_0^\infty \left(1-\cos^l\chi\right) bdb,$$

$$\chi(E,b) = \pi - 2b\int_{r_m}^\infty \frac{dr}{r^2\sqrt{1-\frac{\varphi(r)}{E}-\frac{b^2}{r^2}}}$$

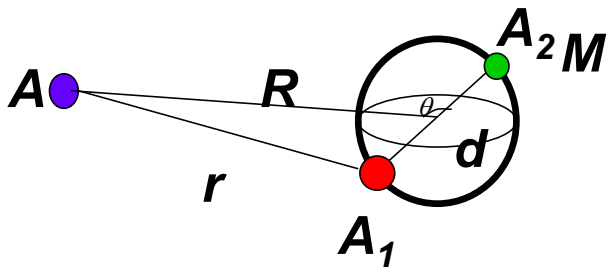
However, the interaction potential $\phi(r)$ is still unknown and therefore approximations (functions) based on experiments with adjustable constants are used.

Basic Thermodynamics

Interaction potential $\varphi_{ij}(r)$

Method of Addition (represent physico-chemical properties of molecule by sum of its structural elements)

$$\varphi(R,\theta)_{A-M} = \sum_i \varphi(r)_{A-A_i^M}$$



Example for two linear molecules:

$$\Phi(r, \overrightarrow{d_1}, \overrightarrow{d_2}) = \sum_i^{n_1} \sum_j^{n_2} \left\langle \varphi_{ij}(R) \right\rangle$$

$$\left\langle \varphi_{ij}(R) \right\rangle = \frac{1}{16\pi^2} \int_0^{\pi} \int_0^{2\pi} \sin\theta_2 d\theta_2 d\phi_2 \int_0^{\pi} \int_0^{2\pi} \varphi_{ij}\left[r_{ij}(R, d_{1i}, d_{2j}, \theta_1, \theta_2, (\phi_1 - \phi_2))\right] \sin\theta_1 d\theta_1 d\phi_1$$