Aalto University

CHEM-E6100 Fundamentals of chemical thermodynamics

Week 1, Fall 2022

Contents

- About thermodynamics
- Various concepts
- Variables of thermodynamics
- Properties of gases
- Equilibrium
- 0^{th} law of thermodynamics

Learning outcomes for Week 1

- **Reflect over relevance of chemical thermodynamics in industrial processes**
- **Understand and distinguish the main concepts and variables in thermodynamics**
- **Be familiar with the main features of an ideal gas and understand the difference compared to real gas**
- **Know the 0^{th} law of thermodynamics**

Thermodynamics – Arnold Sommerfeld

German theoretical physicist (1868-1951)

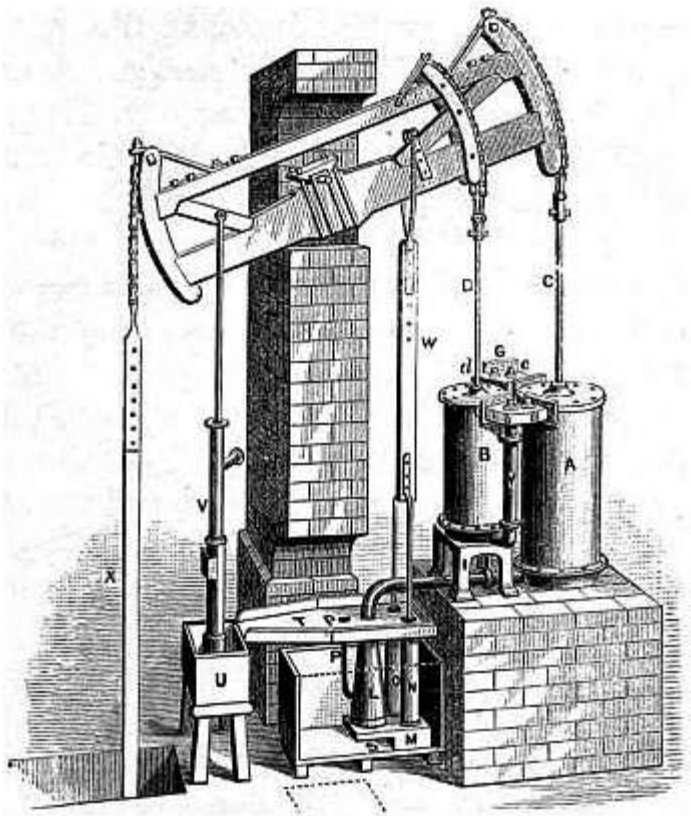
Supervised 7 Nobel prize winners (e.g. Heisenberg, Pauli, Pauling)

“Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all.

The second time you go through it, you think you understand it, except for one or two small points.

The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more.”

What do you associate with ***Thermodynamics***?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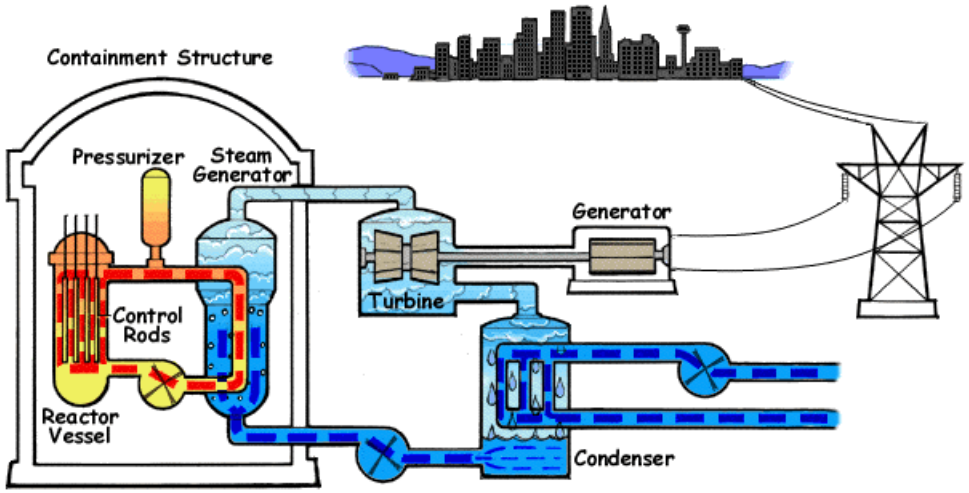
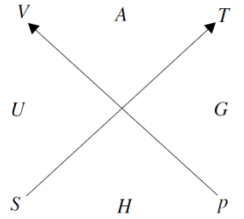

Containment Structure
Pressurizer
Steam Generator
Generator
Turbine
Control Rods
Reactor Vessel
Condenser

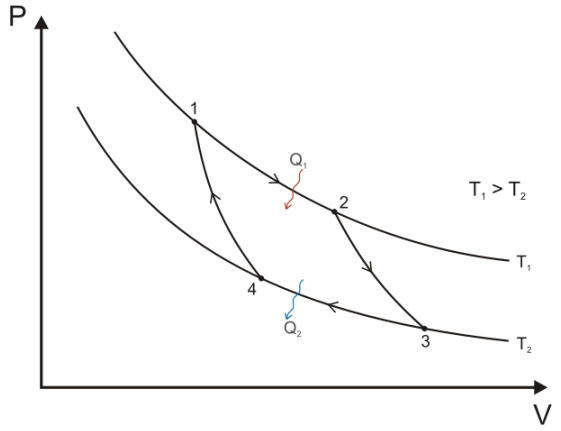
$$G_m = \sum_i x_i G_i^o + RT \sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j \Omega_{ij}$$

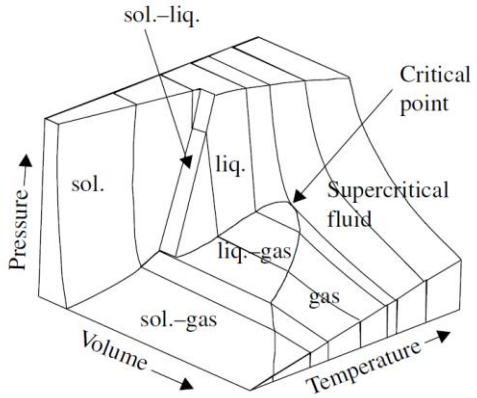
$$\mu_i = \mu_i^o + RT \ln a_i$$

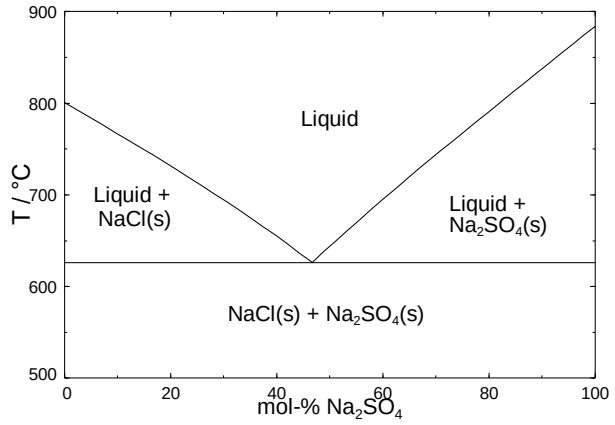
Thermodynamic function	Differential	Equilibrium condition	Maxwell's relations
$U(S, V)$	$dU = TdS - pdV$	$(dU)_{S,V} = 0$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$H(S, p)$	$dH = TdS + Vdp$	$(dH)_{S,p} = 0$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$A(T, V)$	$dA = -SdT - pdV$	$(dA)_{T,V} = 0$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$
$G(T, p)$	$dG = -SdT + Vdp$	$(dG)_{T,p} = 0$	$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

$$\left(\frac{\partial^2 U}{\partial y \partial x}\right) = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\left(\frac{\partial^2 S}{\partial y \partial x}\right) - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - I$$

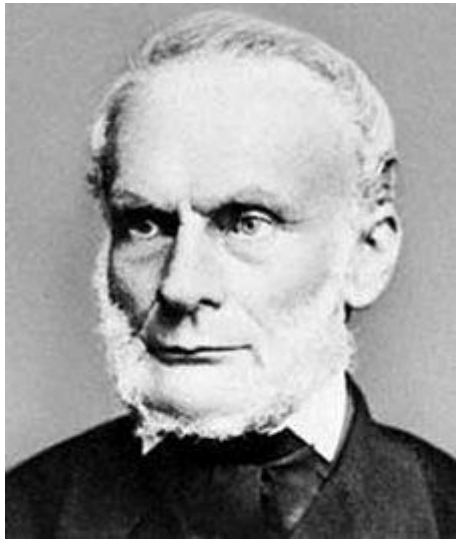




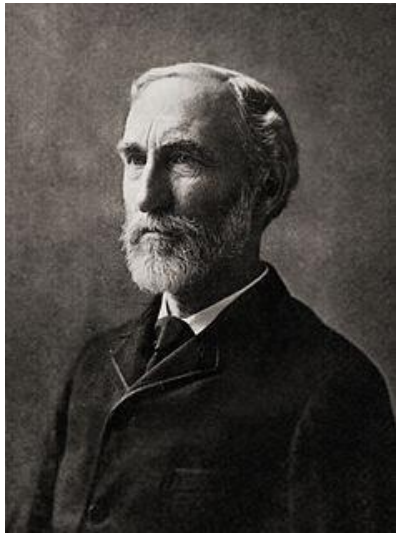




Ludvig Boltzmann

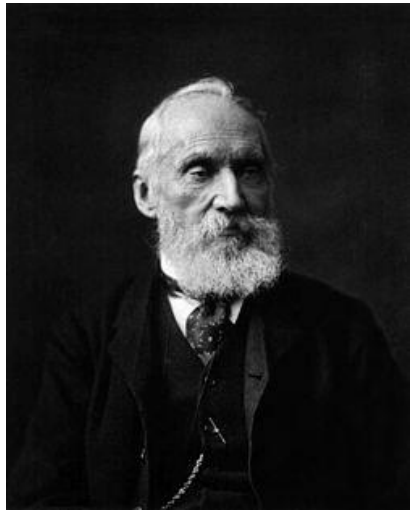


Rudolf Clausius



Josiah Willard Gibbs

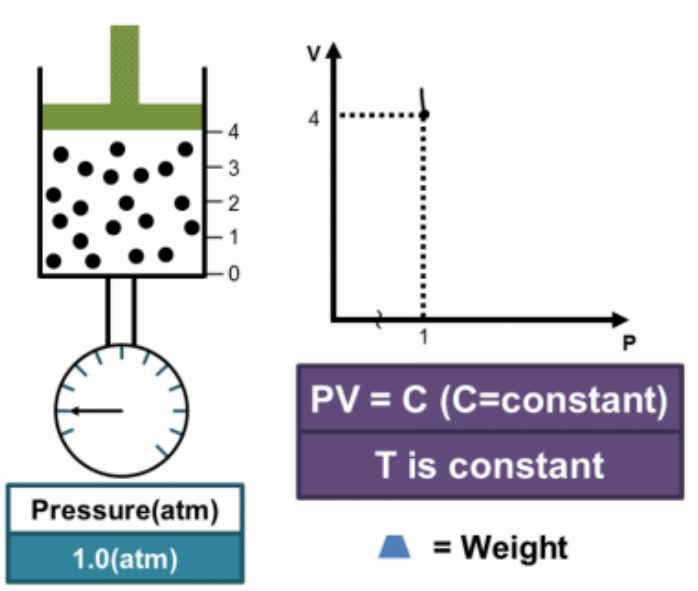
James Joule



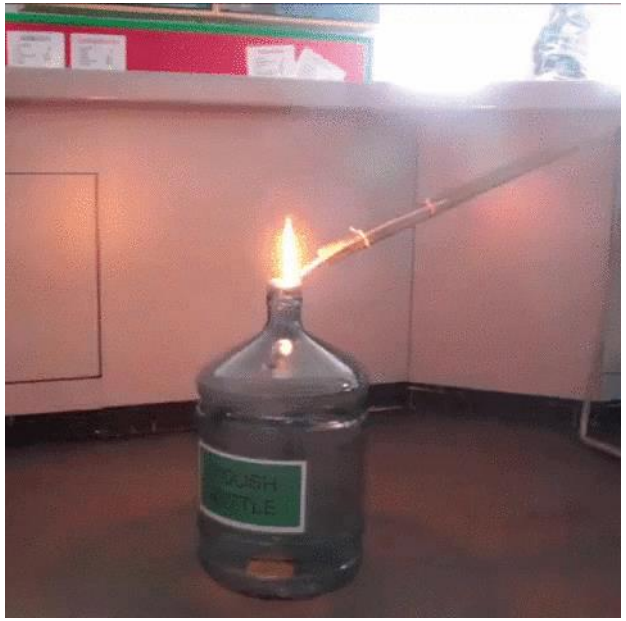
William Thomson,
Lord Kelvin

James Maxwell

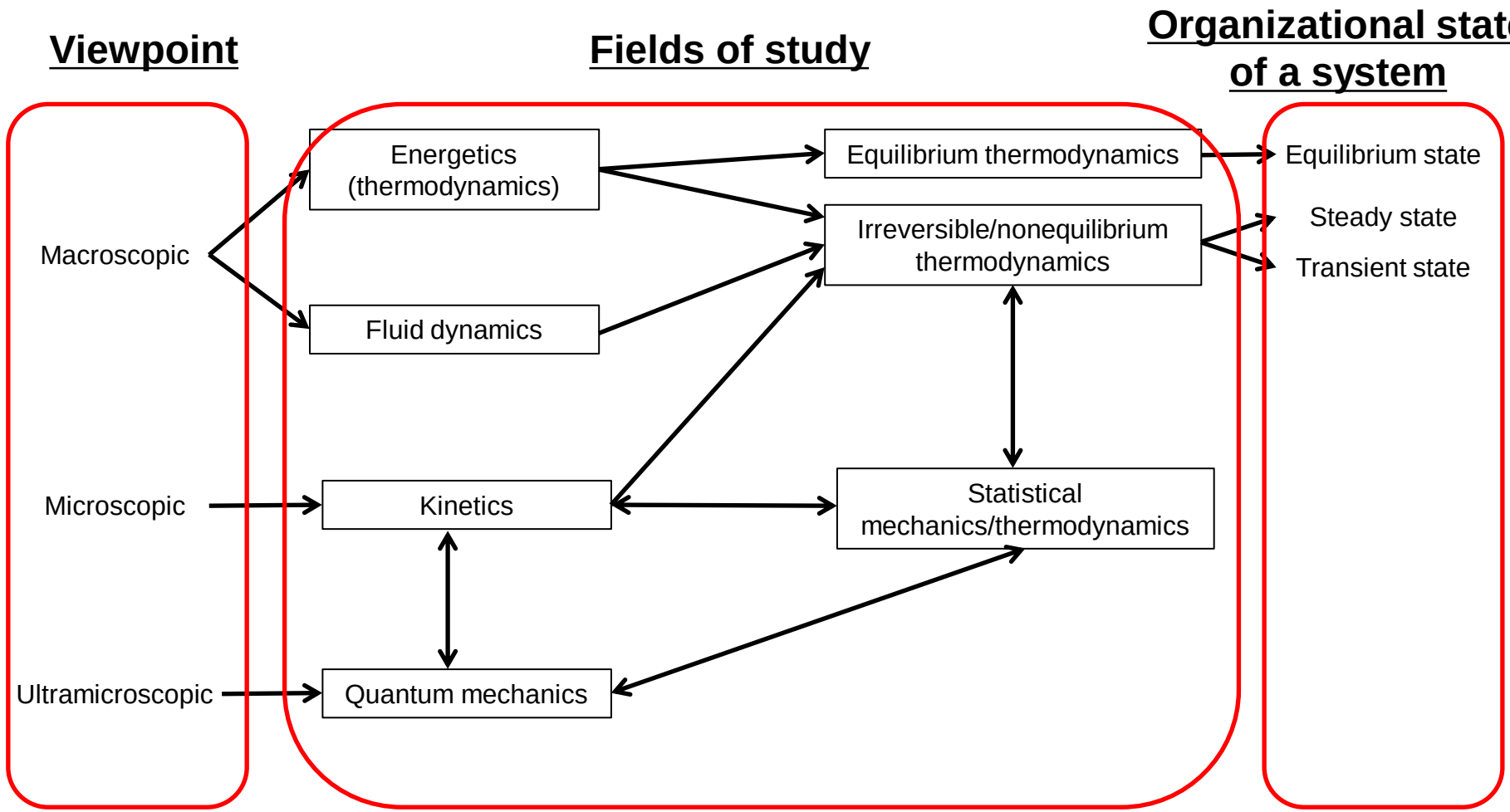
- **Thermodynamics:** Science of the relationship between different types of energy, especially between heat and mechanical energy and of the conversion of either into the other.



- **Chemical thermodynamics:** In thermodynamics, the study of the interrelation of heat and work with chemical reactions or with a physical change of state



Relationships among fields of study



Geochemical thermodynamics, 2nd edition, Darrell Nordstrom & James Munoz

Why is chemical thermodynamics relevant for high-T industrial processes?

- Higher temperature→faster reactions→chemical equilibrium assumption more relevant
- Basis for energy balances in the furnaces/ chemical reactors
- Important tool to predict chemical reactions of complex mixtures of solids, liquids and gas
- Important subtool in process simulations
- Also a component in chemical kinetics

Examples

Gaseous Combustion Equilibria:

Methane combustion as function of lambda (air-to-fuel ratio)

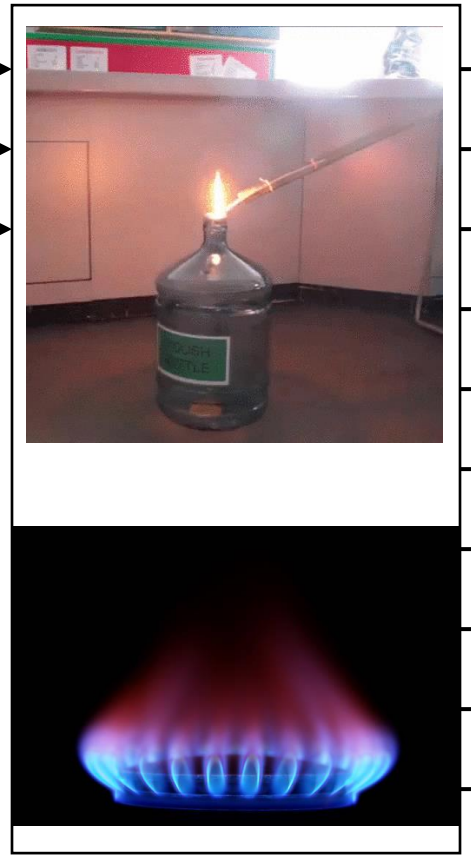
IN (mol)

OUT (mol)

1.000 CH_4

2.400 O_2

9.020 N_2



CH_4

O_2

N_2

CO_2

H_2O

CO

OH

H_2

O

H

T $\Delta_f H^\circ_{298}$

p_{tot} S°_{298}

$c_p(T)$

$f_i(c_i, T, \ldots)$

IN (mol)

1350 °C

OUT (mol)

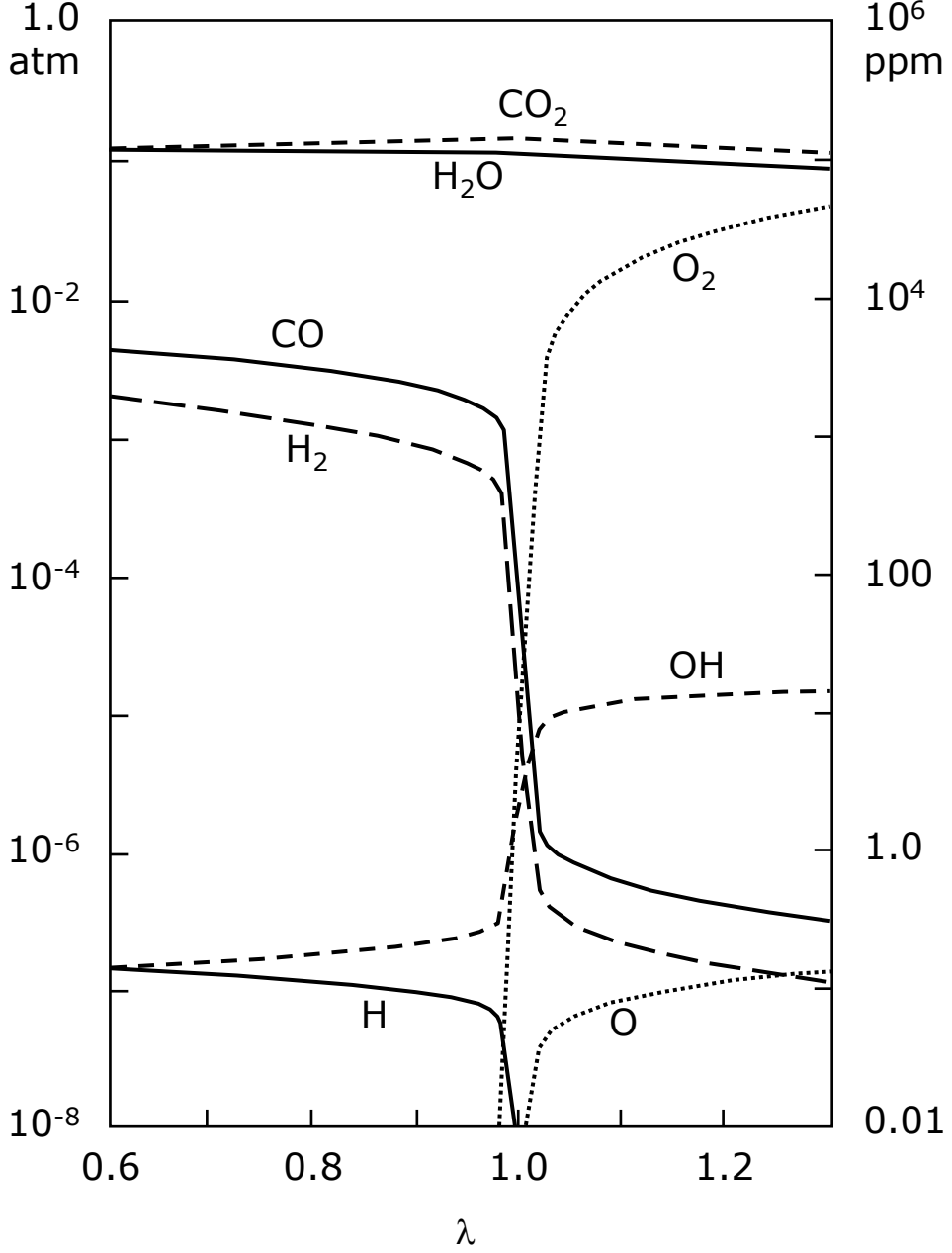
1.000	CH_4		CH_4	$3 \cdot 10^{-15}$
2.400	O_2		O_2	0.400
9.020	N_2		N_2	9.020
			CO_2	0.999
			H_2O	1.999
			CO	$2 \cdot 10^{-4}$
			OH	0.002
			H_2	$1 \cdot 10^{-4}$
			O	$4 \cdot 10^{-5}$
			H	$2 \cdot 10^{-6}$

T $\quad \Delta_f H^\circ_{298}$

$p_{tot} \quad S^\circ_{298}$

$c_p(T)$

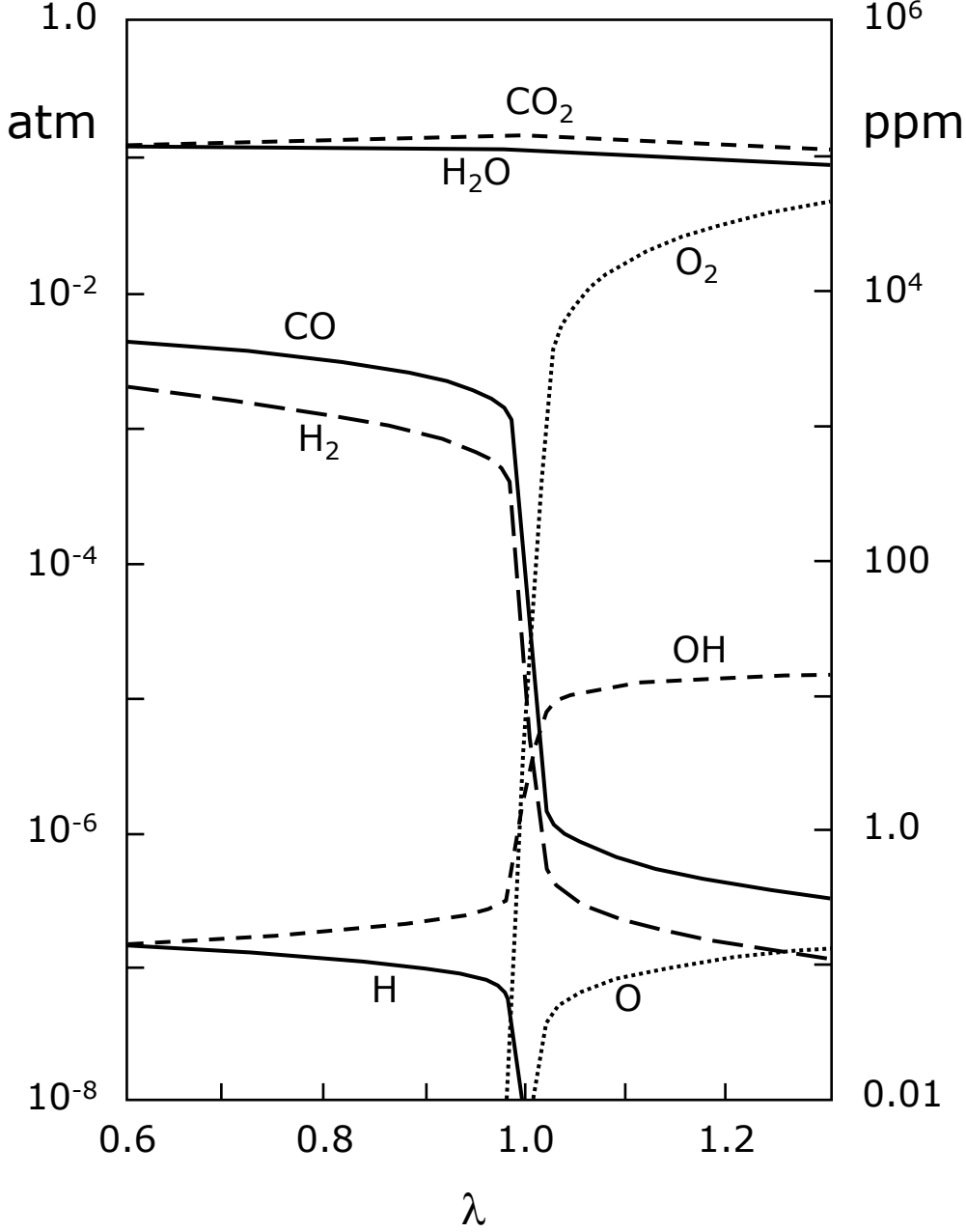
$f_i(c_i, T, \ldots)$



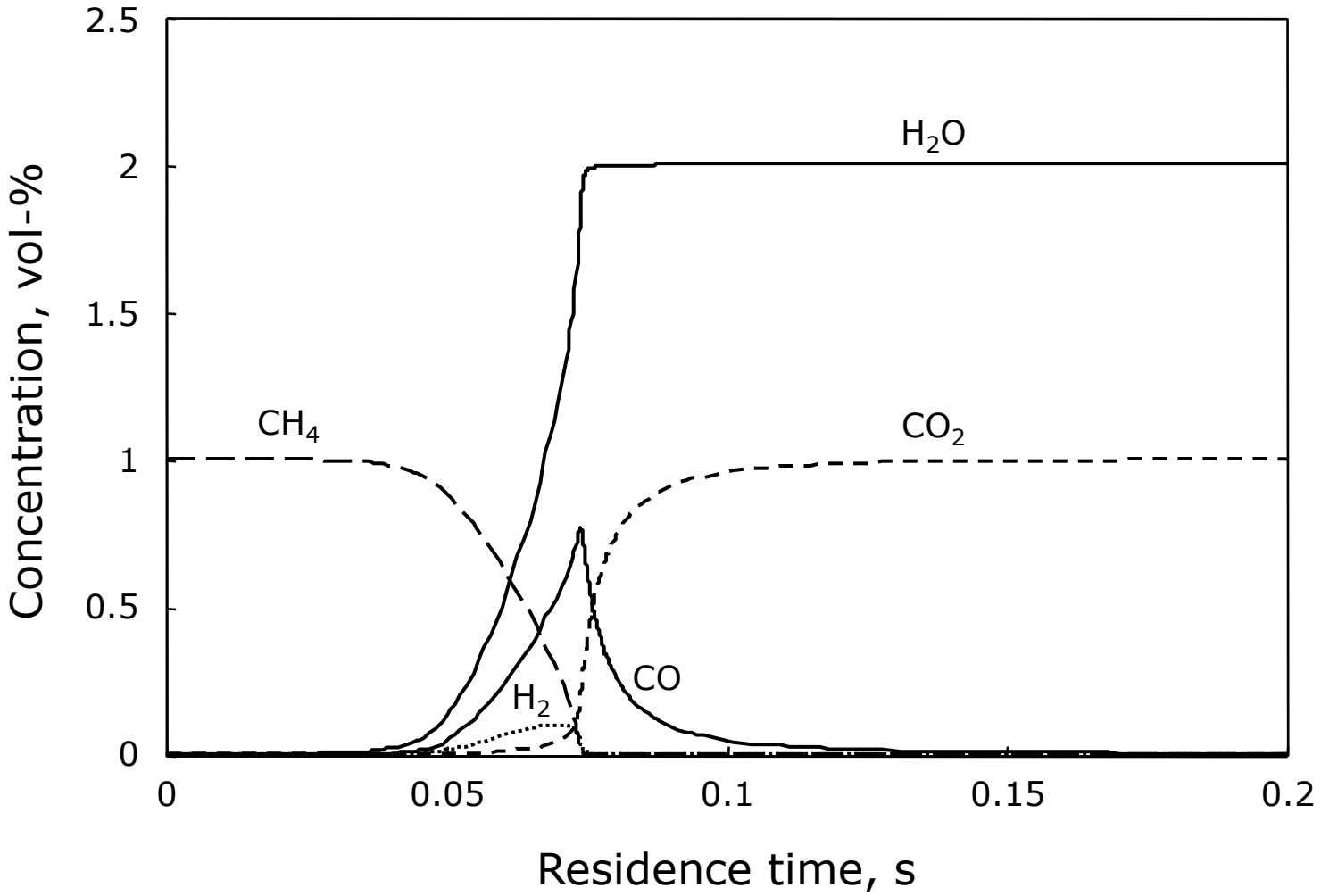
Methane/Air Combustion Equilibrium as Function of Air Factor (at 1100 °C)

Gaseous combustion:

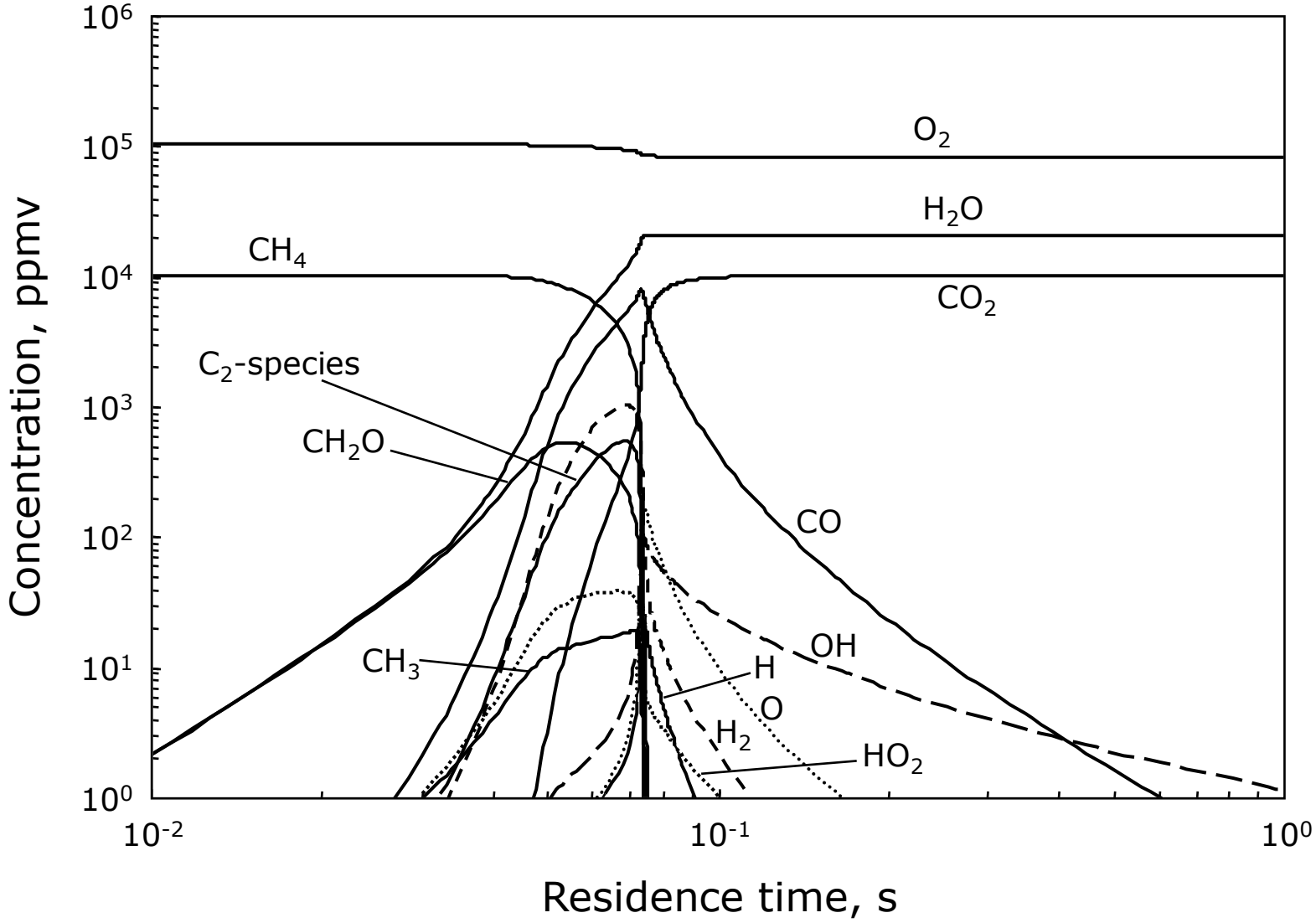
How ”true” is the equilibrium assumption?



Methane/Air Combustion Equilibrium as Function of Air Factor (at 1100 °C)



Combustion of methane (1 vol-%) with air, 850 °C
Kinetic model calculation.



Combustion of methane (1 vol-%) with air, 850 °C

Kinetic model calculation.

Gaseous combustion:

How ”true” is the equilibrium assumption?

Typical time to equilibrium:

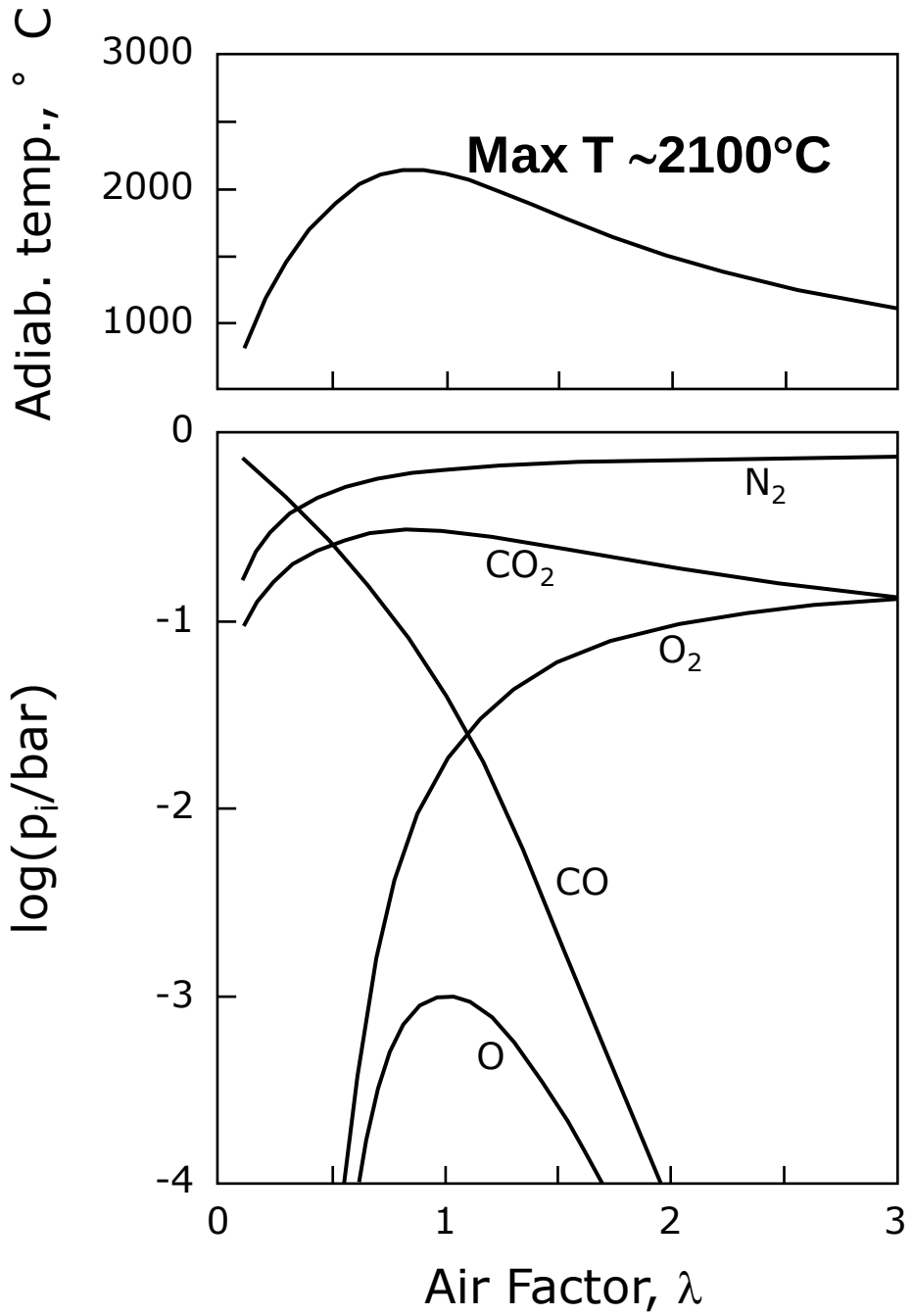
For T = 850 °C, time = 0.1 - 1 s

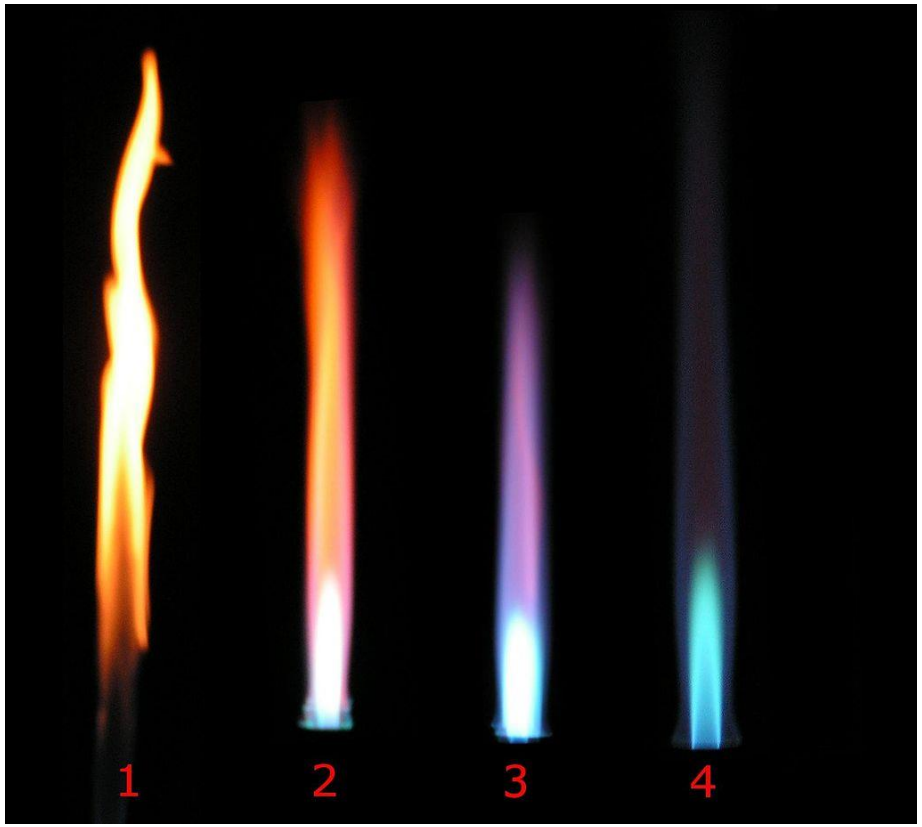
For T=1500 °C, time = 1 – 10 ms

Gaseous Combustion Equilibria:

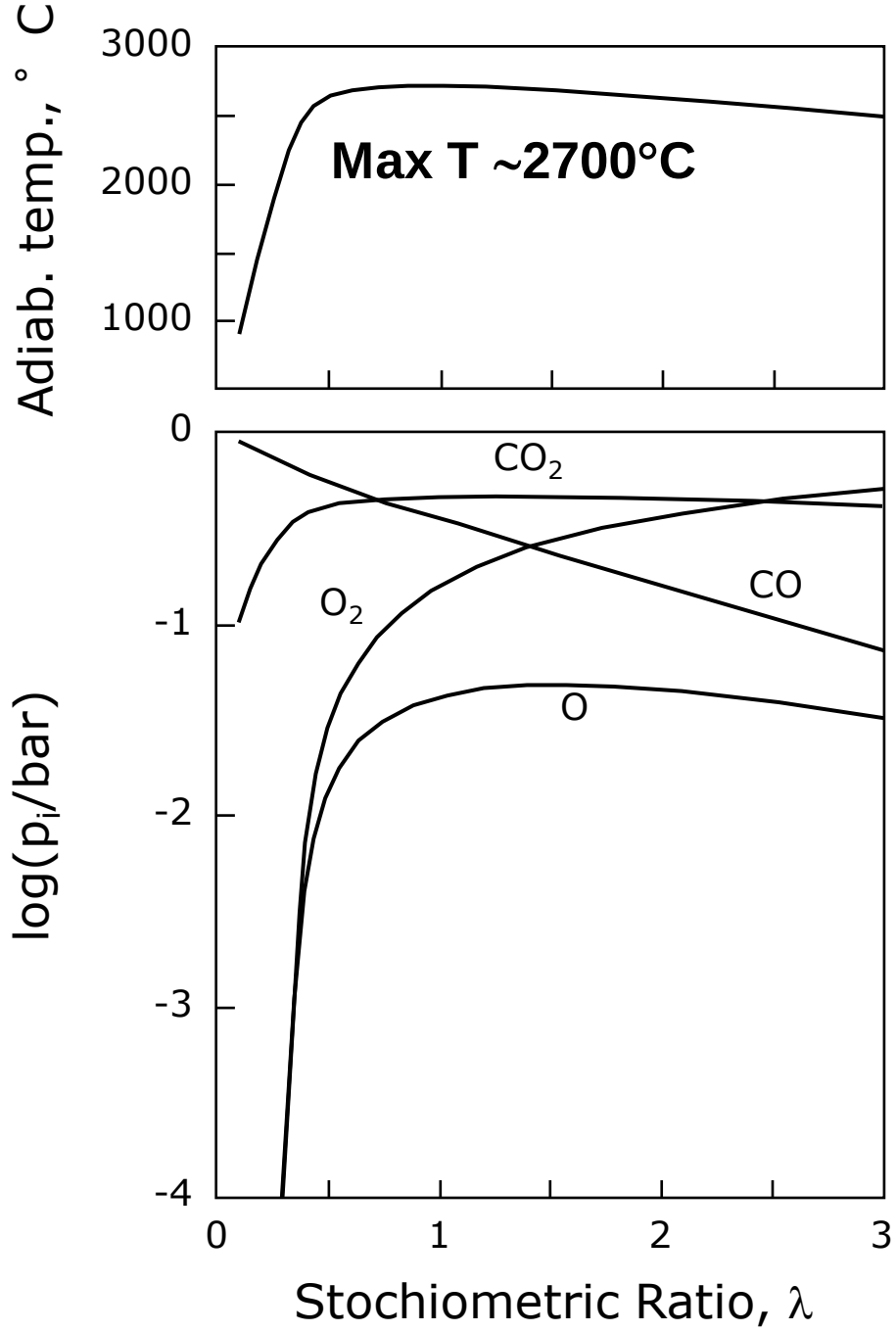
Energy balance and adiabatic combustion temperature

Equilibrium in Combustion of CO with Air – Adiabatic Temperature vs. Air Factor, lambda





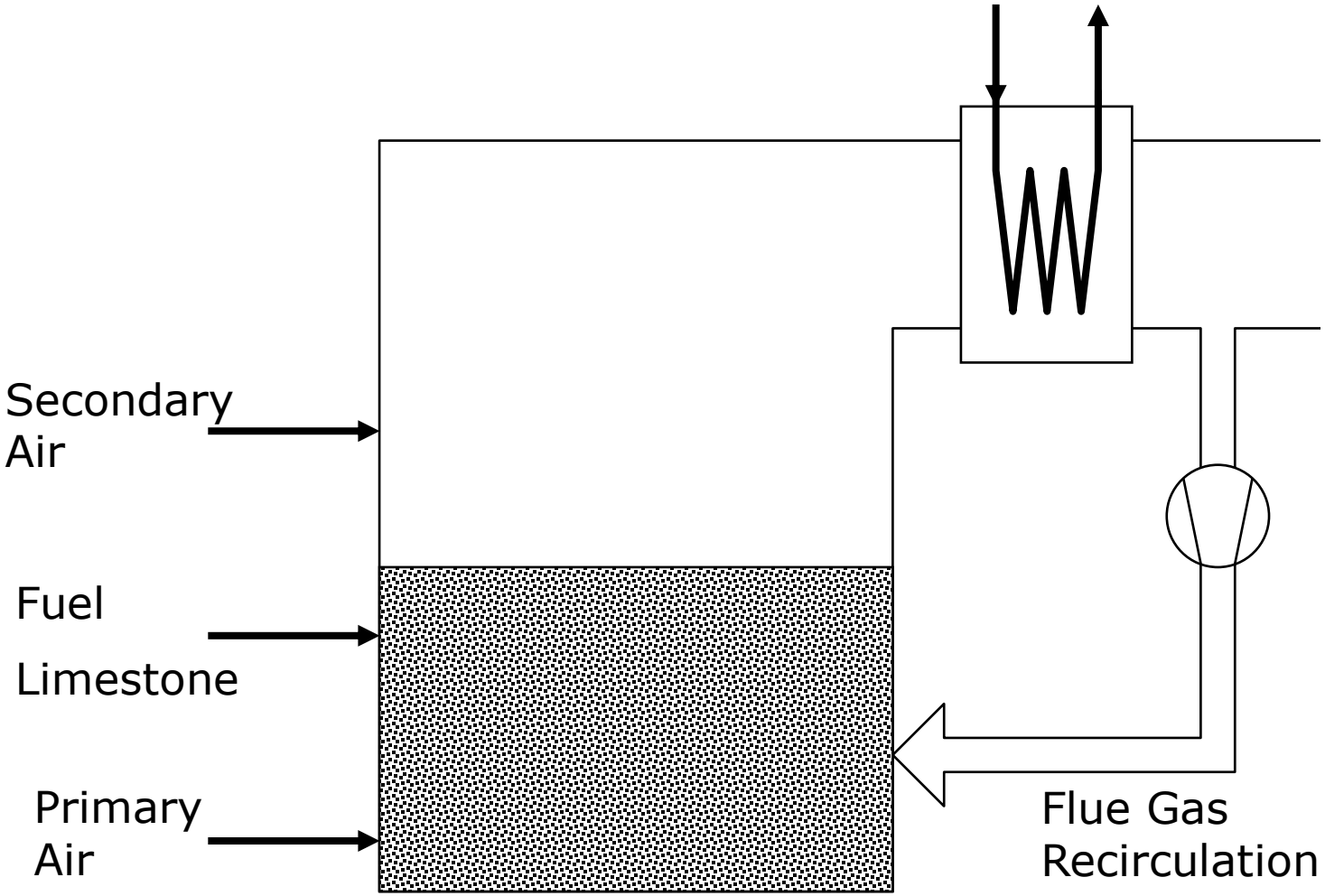
Reducing ↔ Oxidizing



Equilibrium in Combustion of CO with Oxygen – Adiabatic Temperature vs. Air factor, Lambda

Solid-Gas Equilibria:

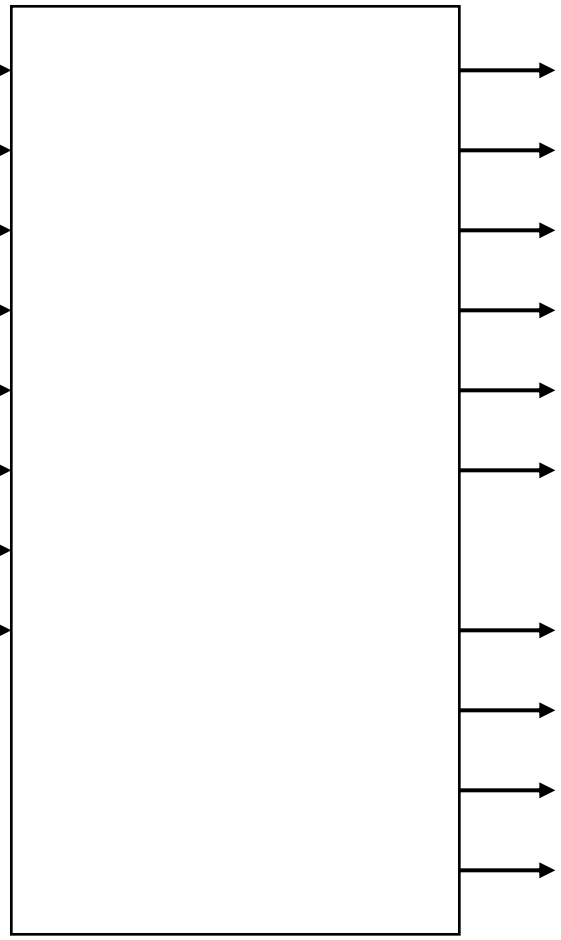
Capture of SO_2, HCl, HF by Limestone



Bubbling Fluidized Bed Combustion with Limestone Addition

IN (mol)

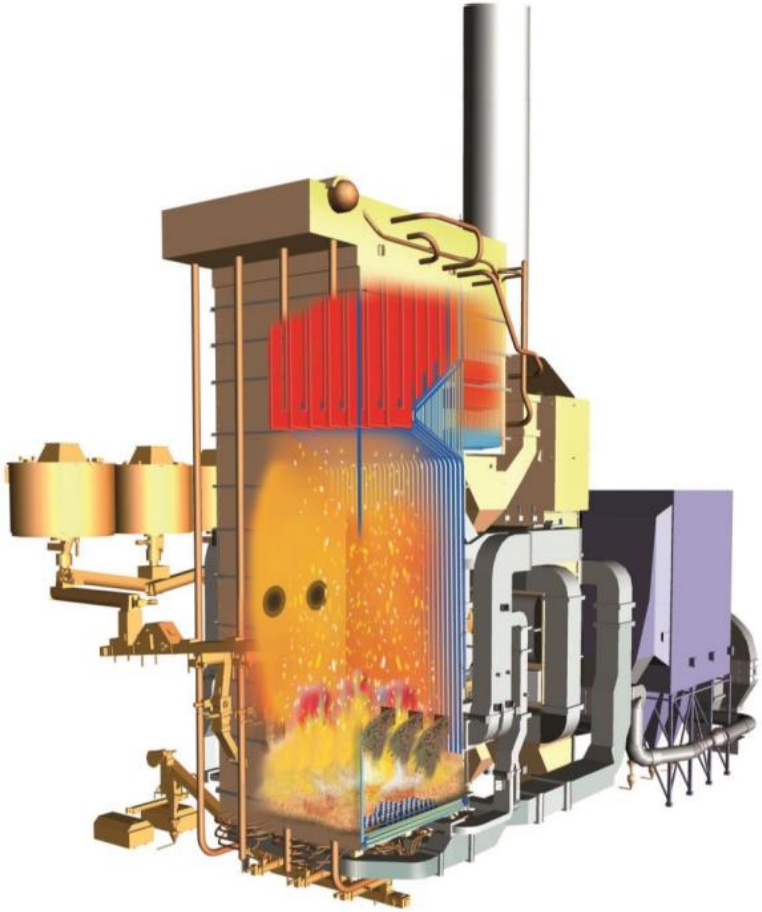
C	14.00
H	36.80
S	0.080
CL	0.035
F	0.006
O	23.36
N	63.60
Ca	0.300



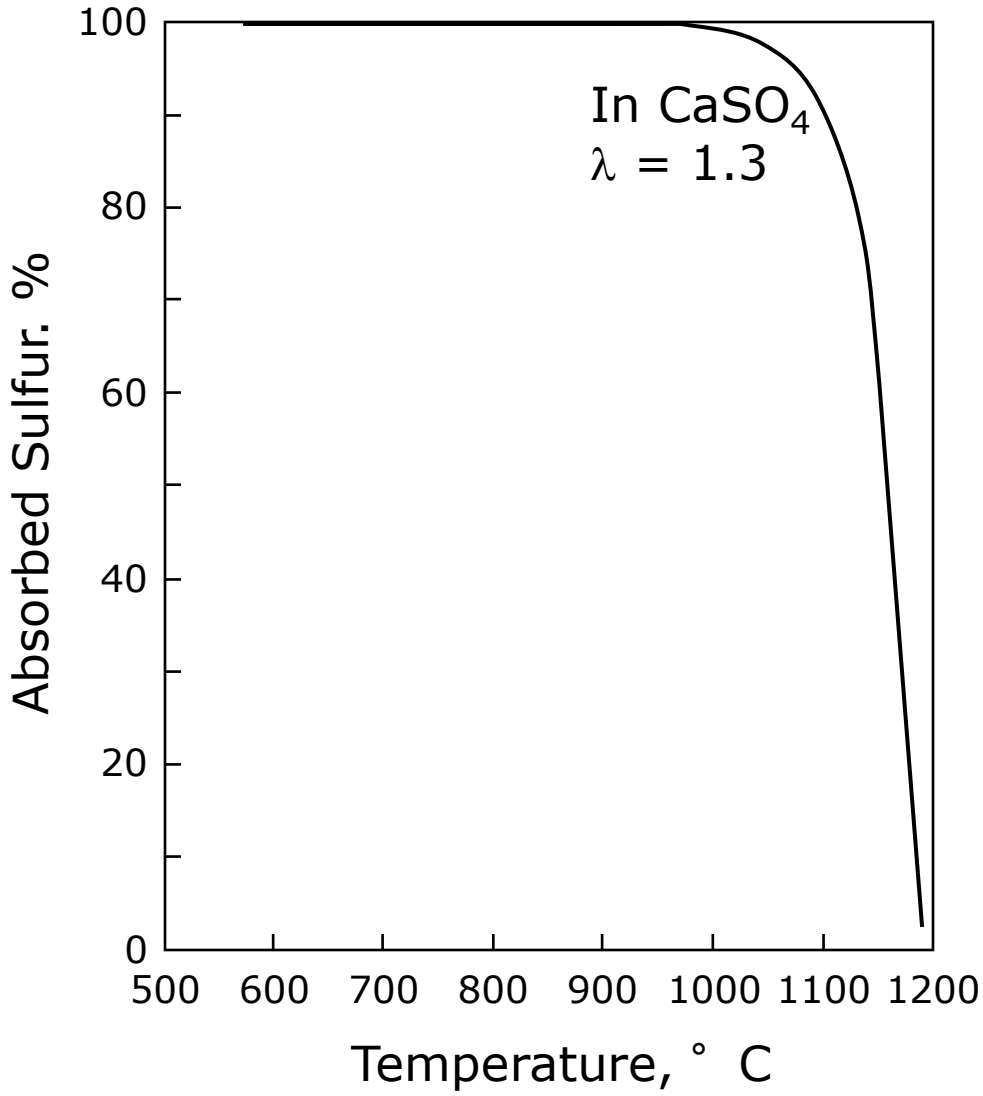
OUT (mol)

CO_2	CO	H_2O
O_2	H_2	OH
H_2S	S_2	SO
SO_2	SO_3	N_2
HCl	HF	Cl_2
F_2		
$CaCO_3$ (s)	CaO (s)	
$CaSO_4$ (s)	$CaSO_3$ (s)	
CaS (s)	$CaCl_2$ (s)	
CaF_2 (s)	$Ca(OH)_2$ (s)	

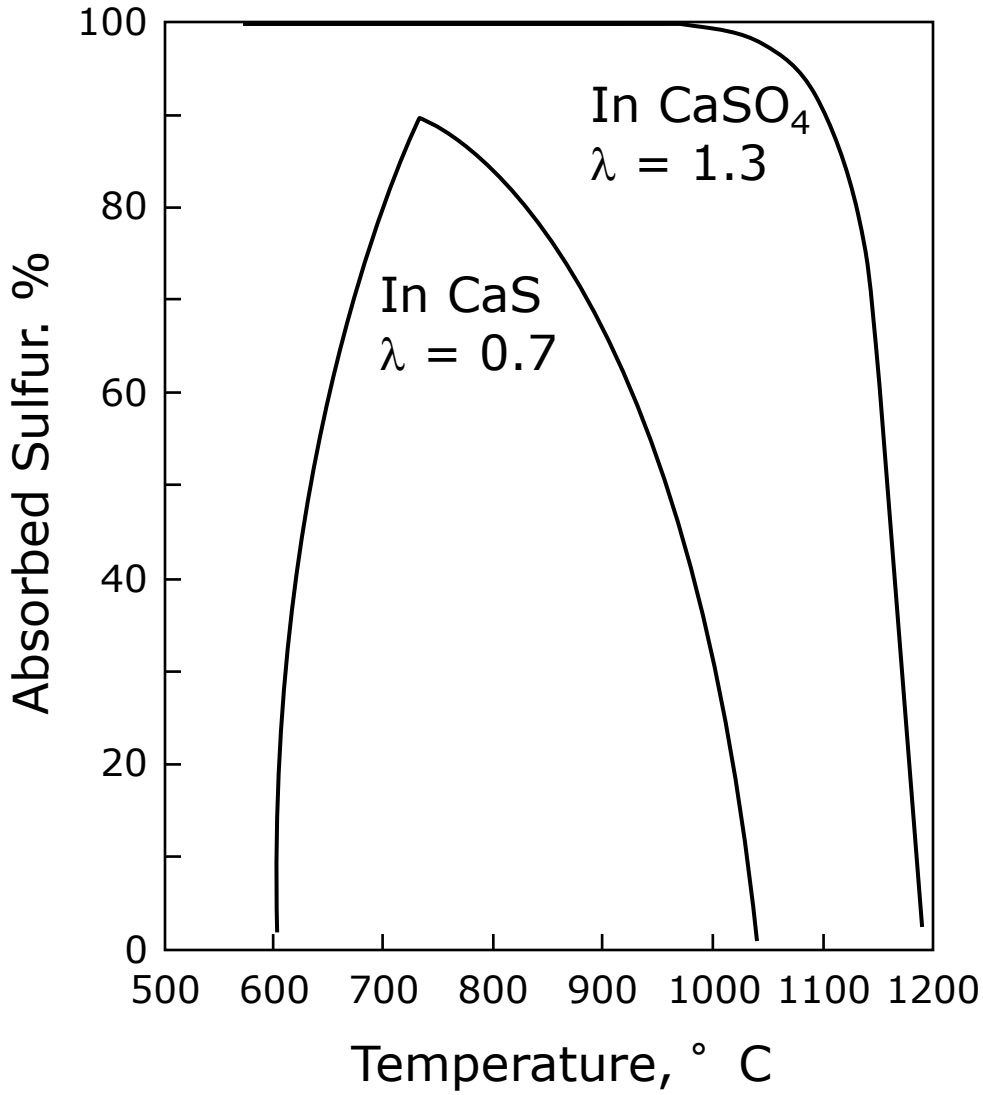
350 . . . 1300 ° C



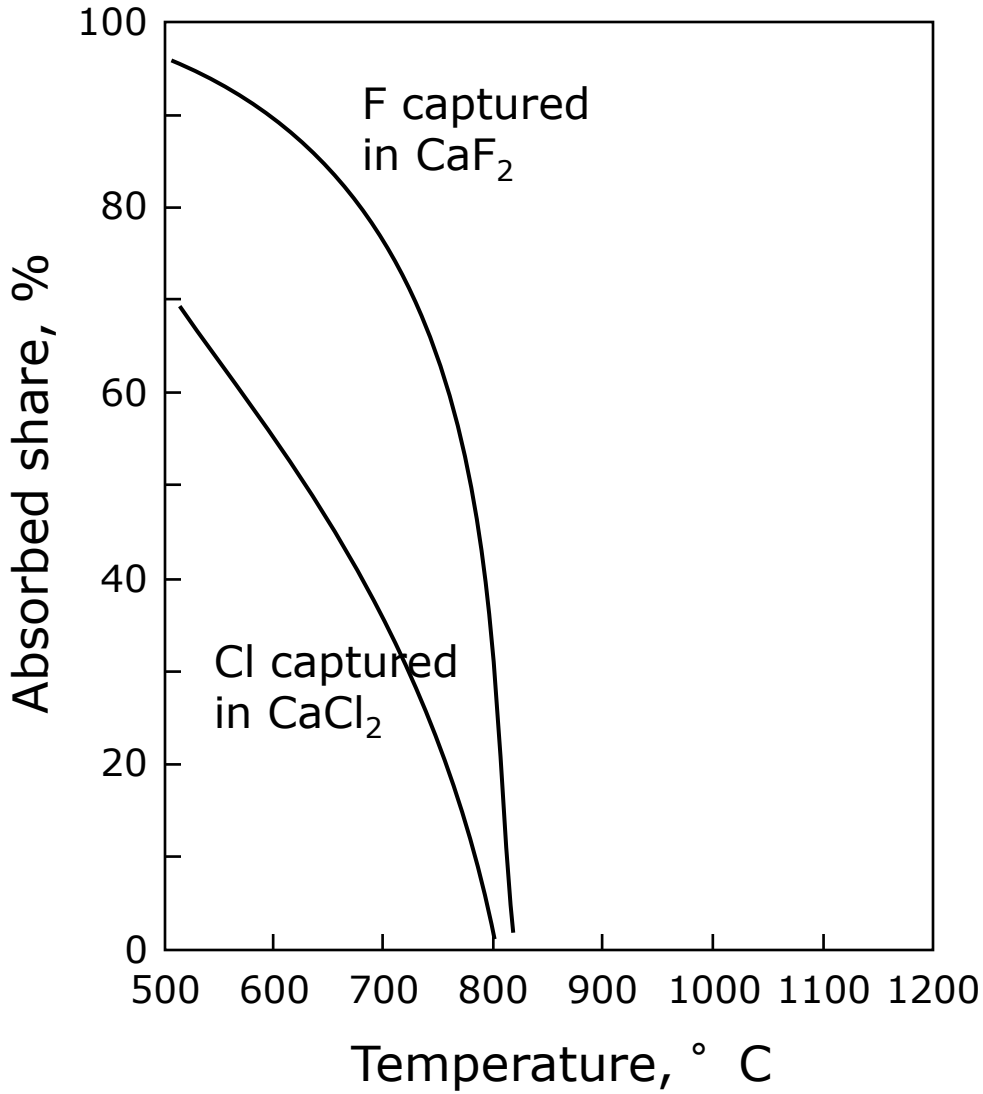
	650 ° C		1050 ° C	
	mol	%-absorption	mol	%-absorption
SO_2 (g) $CaSO_4$ (s)	$6 \cdot 10^{-10}$ 0.080	100.0	0.0017 0.0783	97.9
HCl (g) $CaCl_2$ (s)	0.0346 0.0002	1.2	0.0350 –	0.0
HF (g) CaF_2 (s)	0.0018 0.0021	69.8	0.0060 –	0.0



Sulfur Captured in $CaSO_4$ at λ = 1.3



Sulfur Captured in $CaSO_4$ at λ = 1.3, and in CaS at λ = 0.7



Captured HCl and HF vs. Temperature (λ = 0.7)

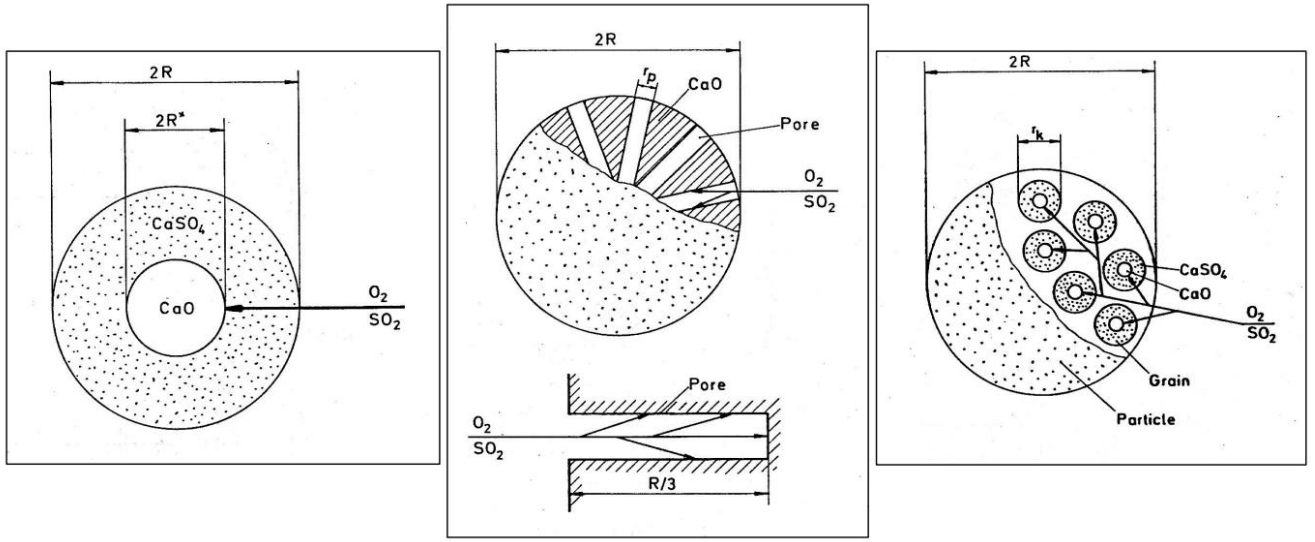
Solid-Gas Equilibria

Equilibrium modelling gives boundary conditions to gas reactions

Equilibrium *percent capture* or *percent solid conversion* case (input) dependent and not generalizable

Kinetic information needed about solid reactivity and conversion rate

Sulphur capture in FBC:
single particle models



SulphOH2-2003 (abo.fi)

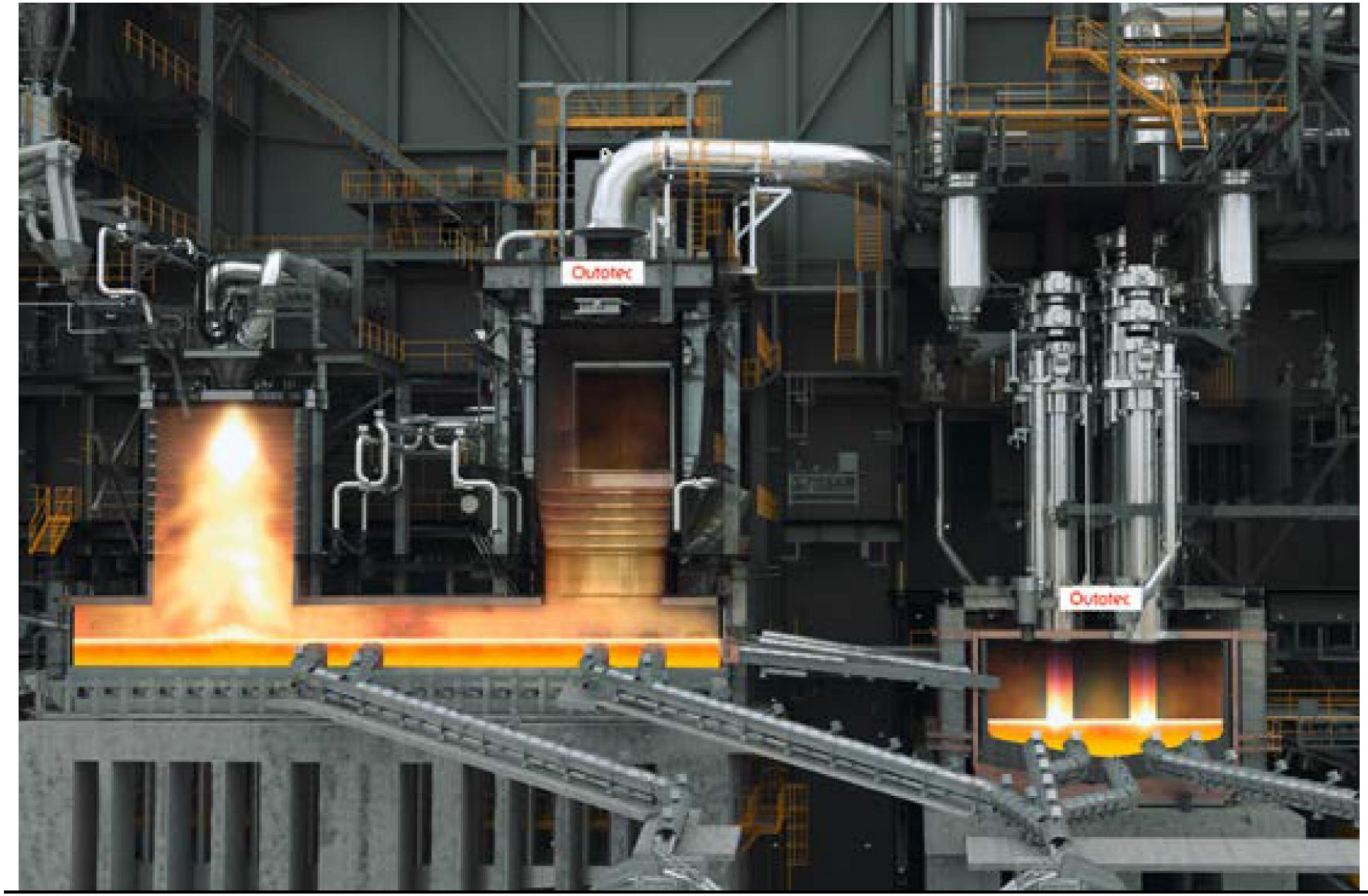
Different industrial furnace processes

- Flash smelters
- Blast furnaces
- Black liquor recovery boiler
- Waste incinerators
- BFB & CFB boilers
- Pulverized fuel boilers
- Aluminum smelters

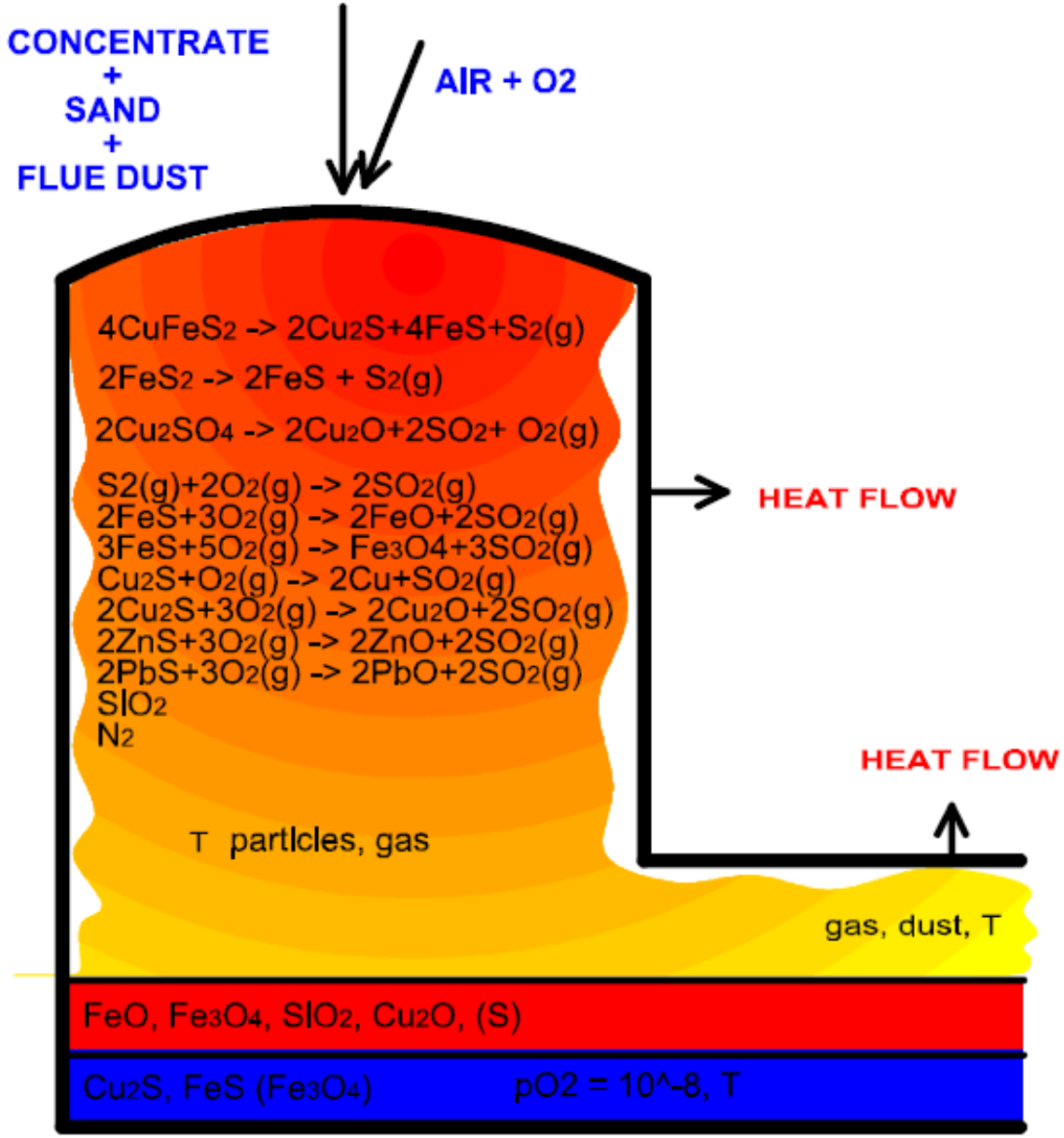
Thermodynamic modeling and metallurgical processes

- Conversion of ore minerals to metals
- Capture of impurities from raw materials
- Slag formation & fluxing
- Chemistry in blast furnaces & smelters
- Refractory wear and corrosion

Flash smelting



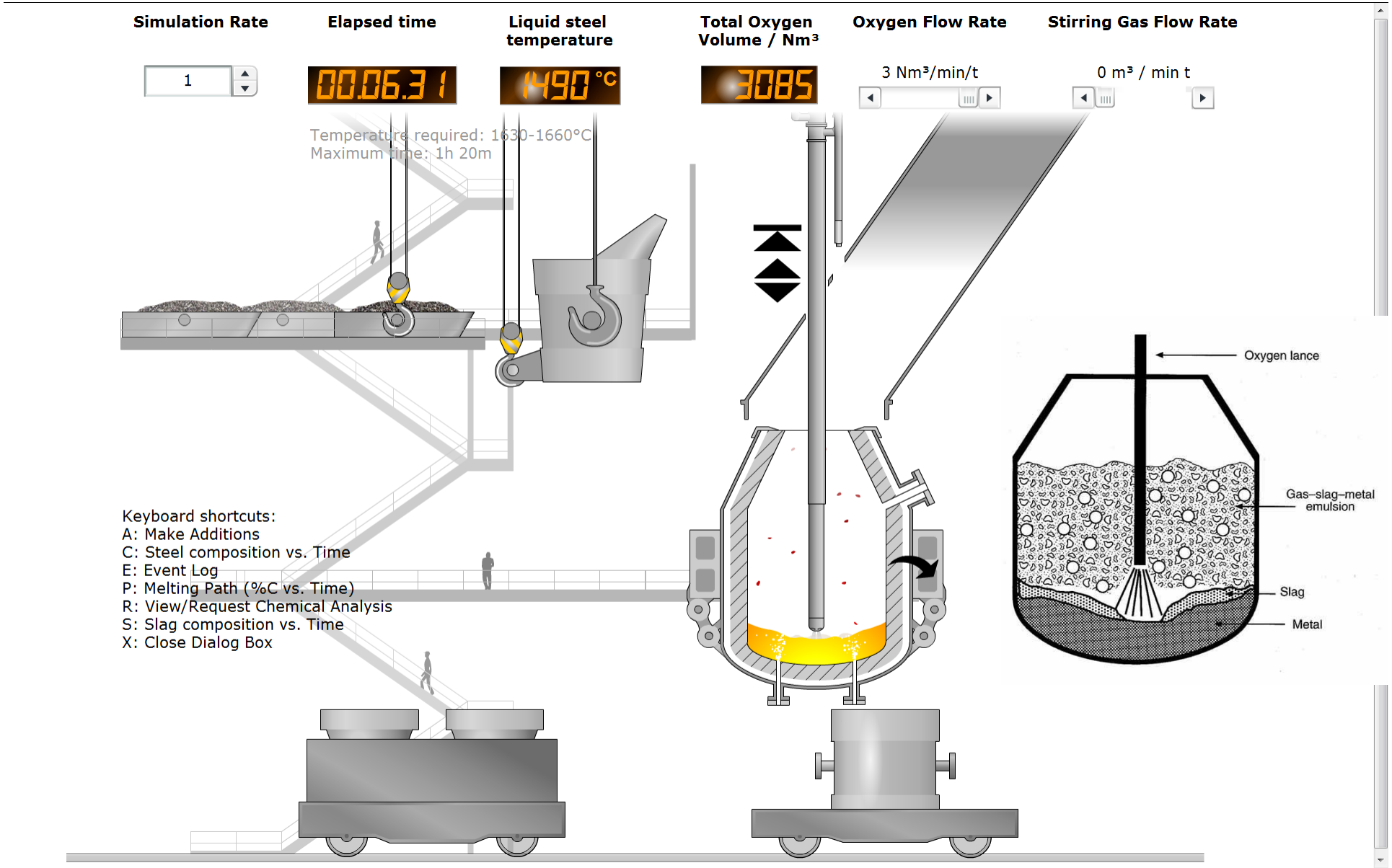
Flash smelting



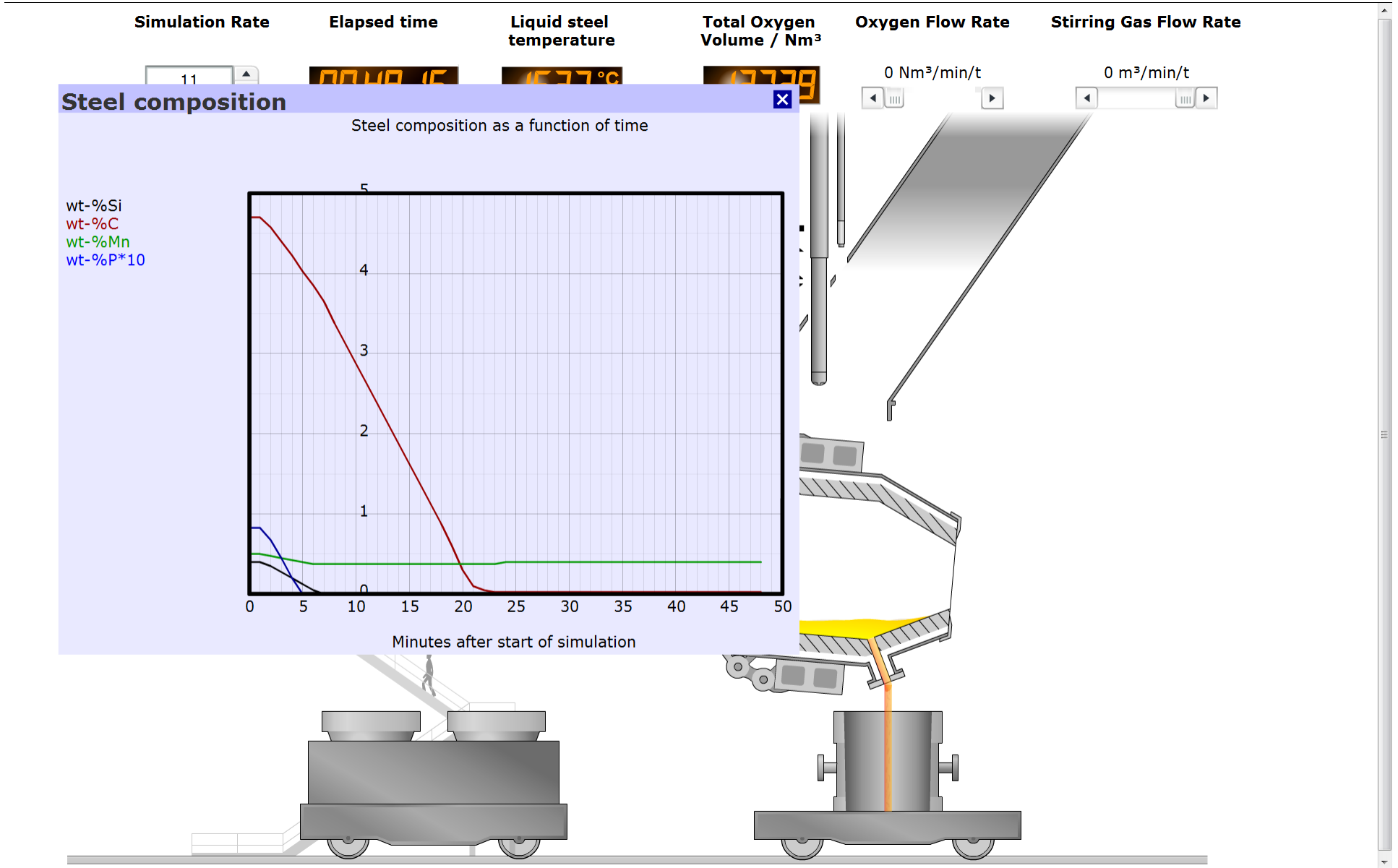
- Particles burn in the reaction shaft but not completely
- Reactions between slag (red) and matte (blue) produce Cu_2S-FeS matte but equilibrium is not reached
- Excess heat is removed by cooling

Steelmaking

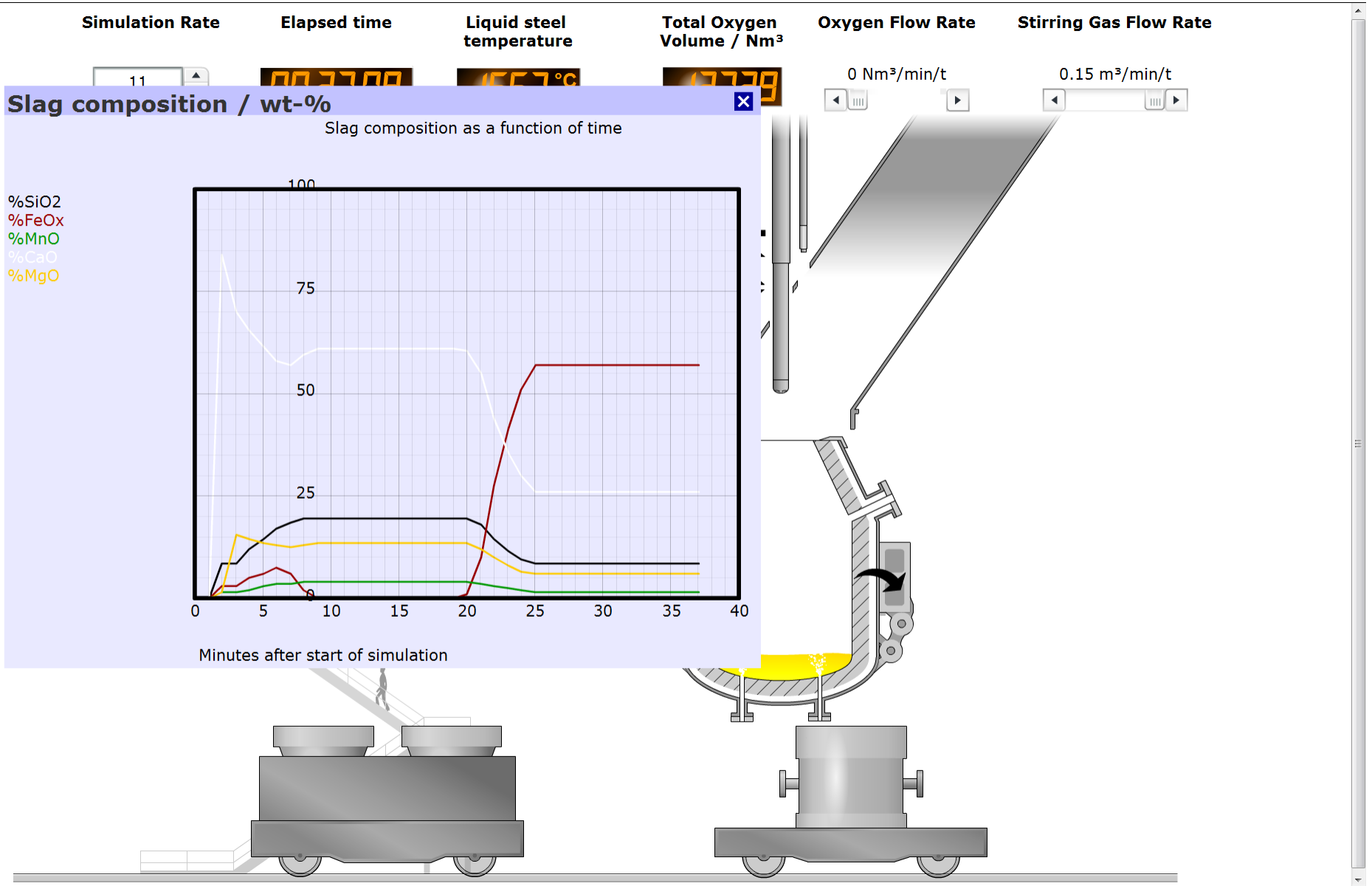
The Basic Oxygen Steelmaking (BOS) Process



Steelmaking



Steelmaking



Thermodynamic modeling & Ash chemistry in combustion

Ash deposition

Bed agglomeration

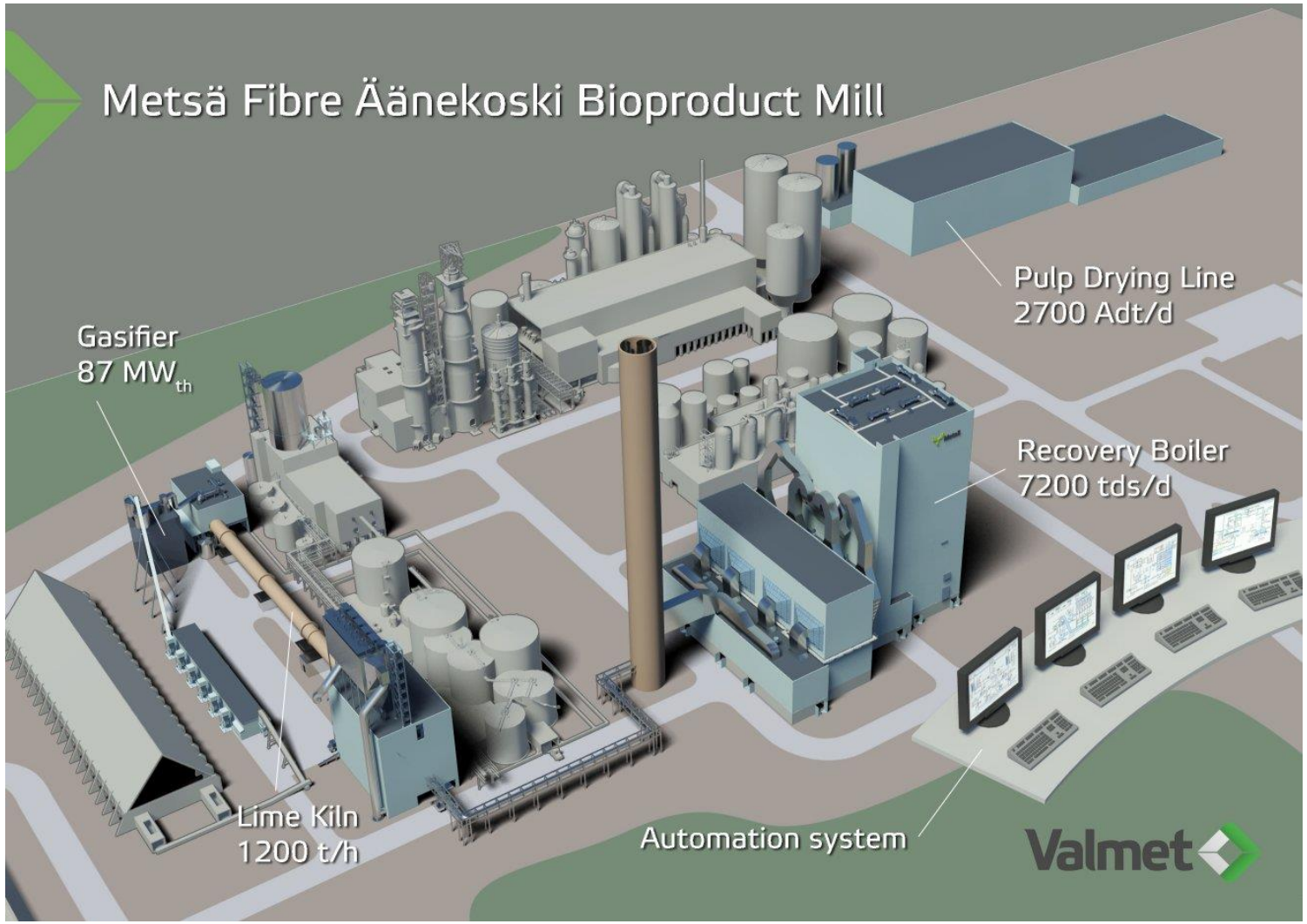
Superheater corrosion

Furnace slagging

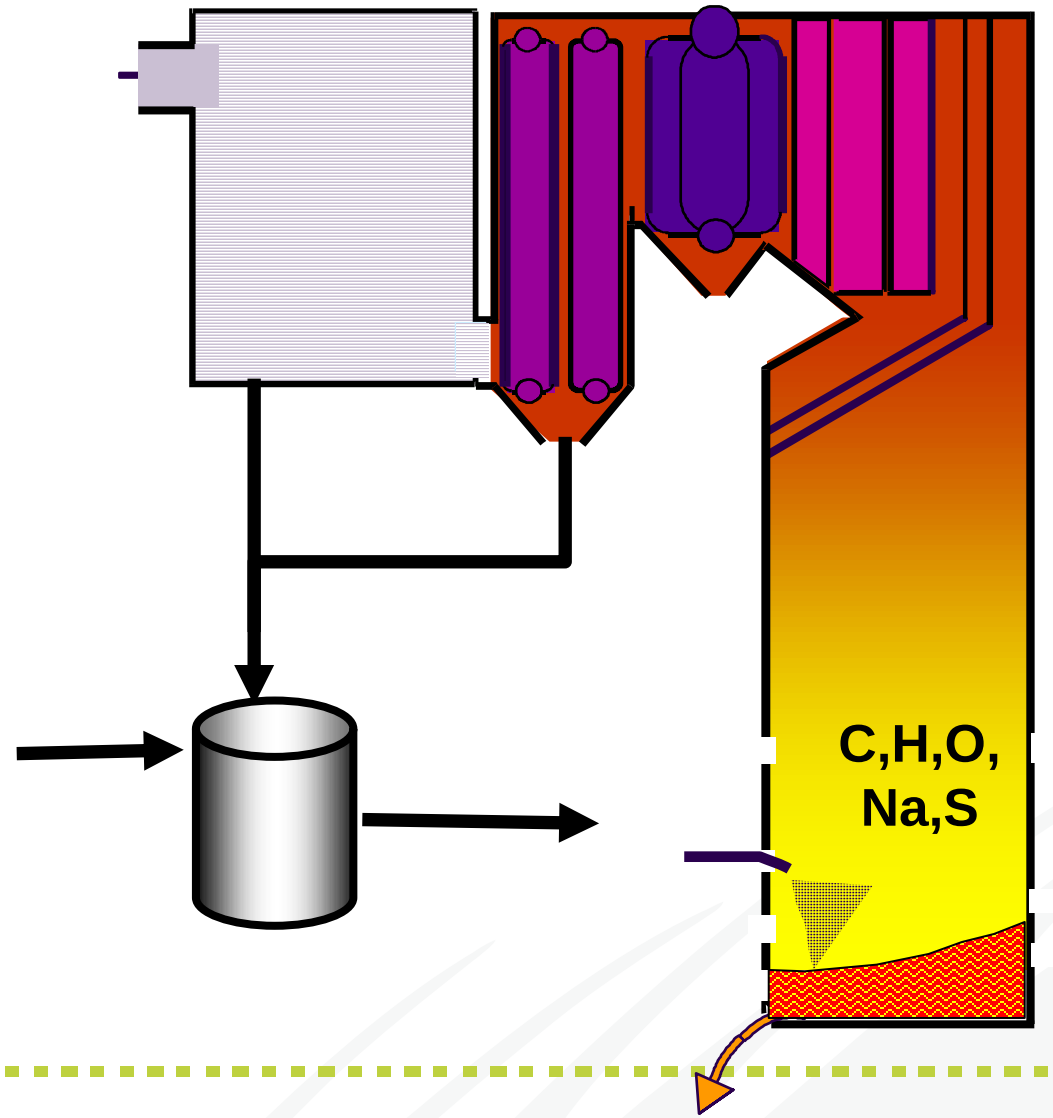
Trace element emissions

Black liquor combustion

Modern forest biorefinery



Molten salts in the recovery boiler



About 200 million tonnes of dry black liquor is burned annually
= 100 million tonnes of smelt is processed

Other materials

Cement	4000 million tonnes
Steel	1500 million tonnes
Aluminum	60 million tonnes
Copper	20 million tonnes

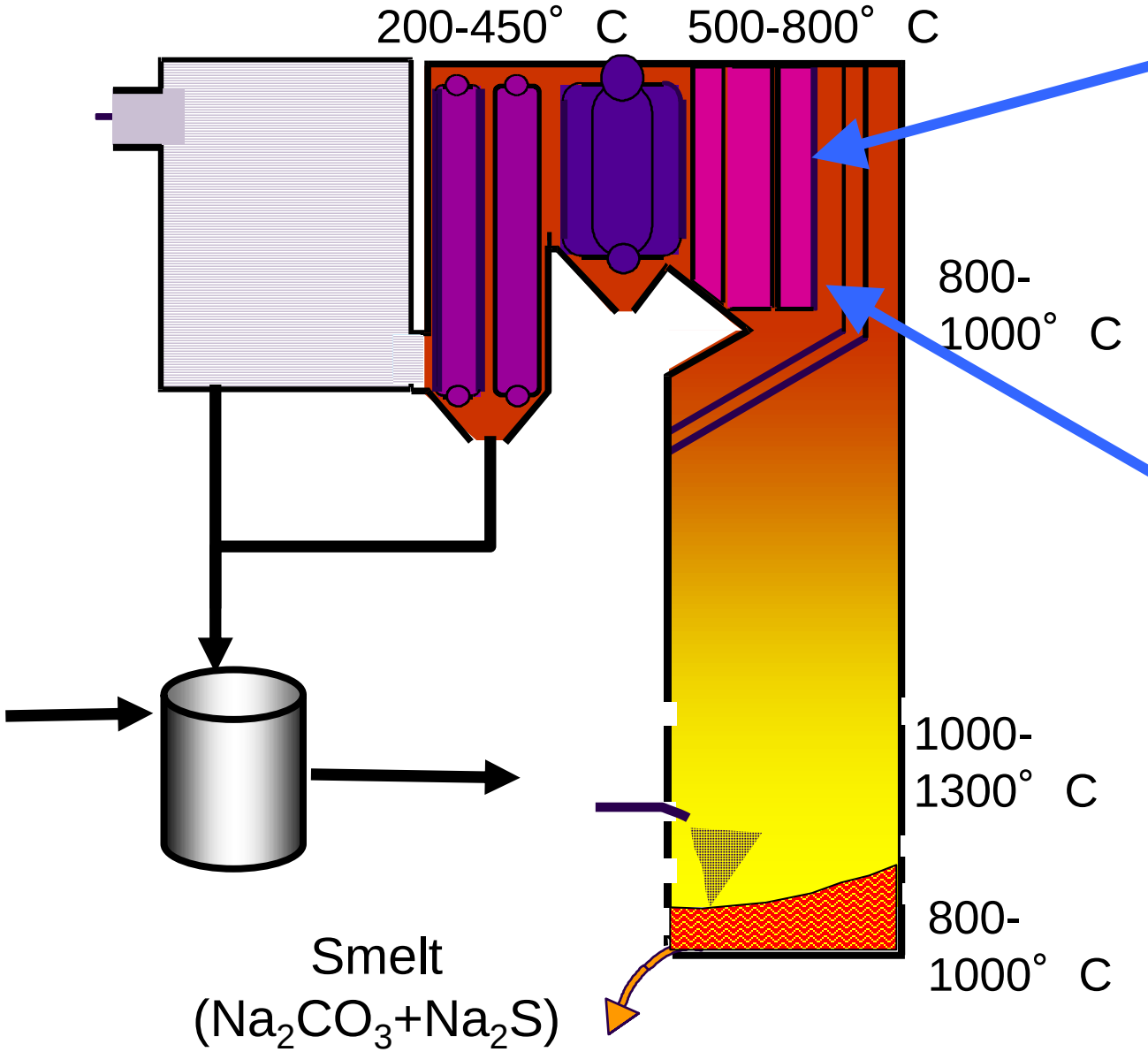
T=800-1000 ° C

$Na_2SO_4+4C \rightarrow Na_2S+4CO$

$Na_2SO_4+2C \rightarrow Na_2S+2CO_2$

Smelt: $Na_2CO_3+Na_2S$

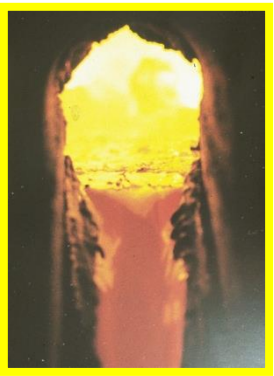
Molten alkali salts in BL recovery boilers



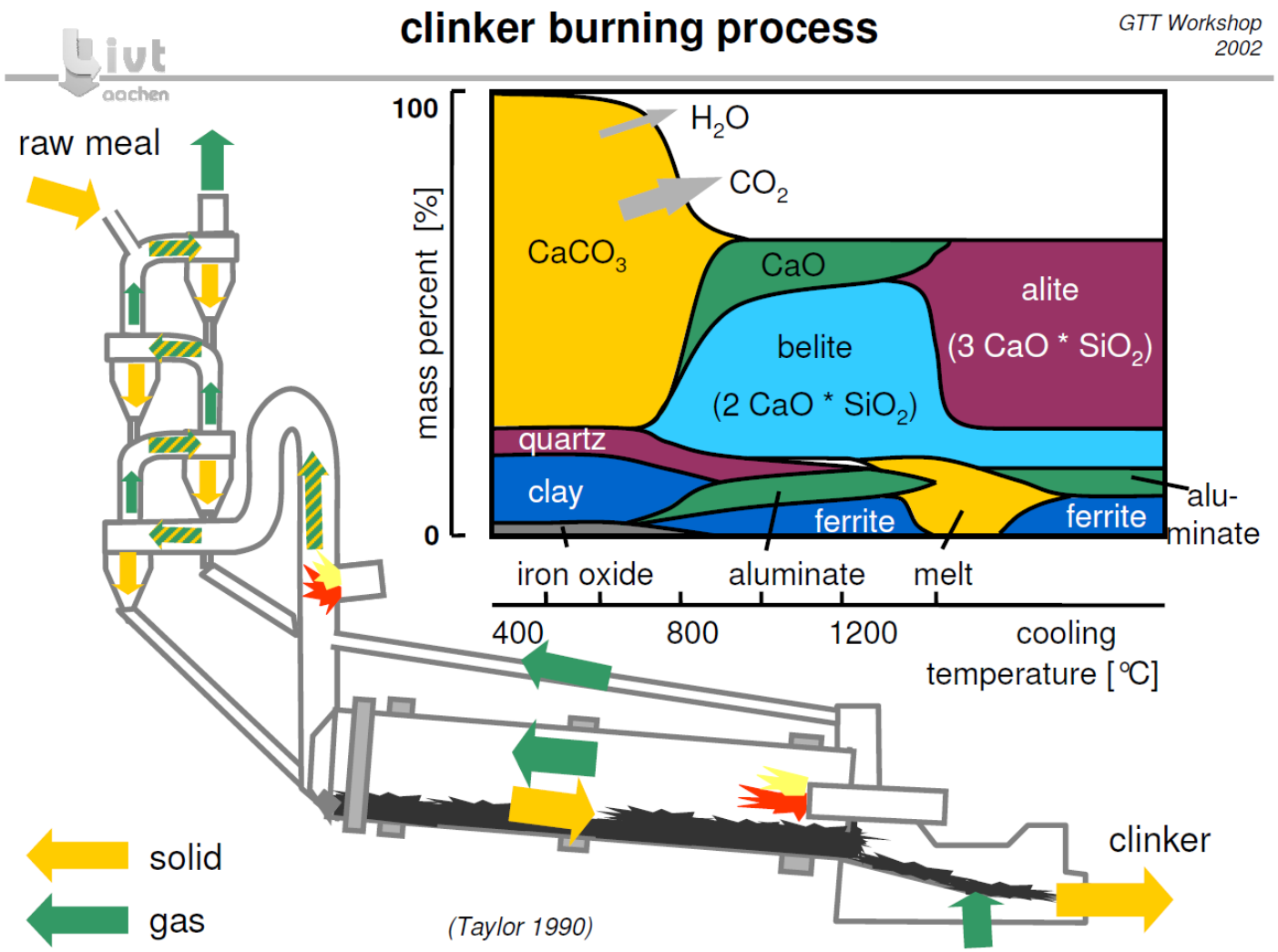
Heat exchanger deposits

Na, K-chlorides, sulfates

Corrosion



Lime & cement kilns



Modigell & Liebig 2002
http://gtt.mch.rwth-aachen.de/gtt-web/Consulting/Workshops/WS2002/Liebig%202002.pdf

About chemical thermodynamics

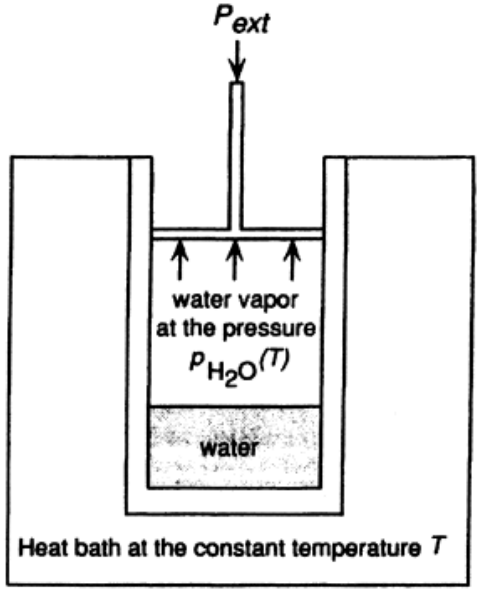
- **Thermodynamics is an experimental science: all properties of substances are known by experiments and not derived from its theory**
- **Thermodynamics studies the properties of equilibrium and systems as well as their behavior, such as**
  - In which directions changes proceed and how far it makes progress in given conditions
  - Which thermal effects are involved in the reactions or processes
- **Many processes in industry and nature are slow and do not reach equilibrium, but the concept of equilibrium is a very good state of reference.**

Concepts and variables

- System
- State
- State function
- Extensive and intensive properties
- Component and species
- Phase
- Process

System

- Thermodynamics is concerned with the behavior of matter, where matter is anything that occupies space
- The matter which is the subject of a thermodynamic analysis is called a system
- The system is a well defined volume or space
- The system is separated from the ‘outer world’ by its boundary or ‘wall’ which often is imaginary

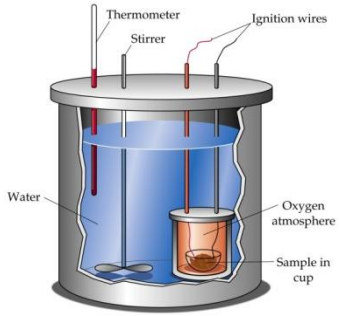


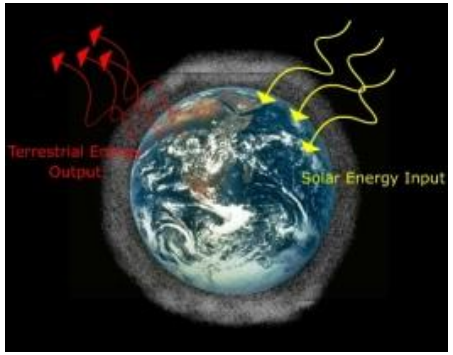
Source: D.R.Gaskell, Introduction to the Thermodynamics of Materials

- **System:** A thermodynamic ***system*** contains everything of thermodynamic interest for a particular chemical process within a ***boundary***. The boundary separates the system from the ***surroundings***

Main type of systems

- isolated (no interaction with surroundings)
- closed (heat and mechanical work exchange, no mass exchanged)
- open (heat, work, mass exchange with surroundings)
- Adiabatic (no heat or mass exchange with surroundings, special case of closed system)





State

- The most important concept of thermodynamics is that of state
- If it were possible to know the masses, velocities, positions, and all modes of motion of all of the constituent particles in a system, this would describe the microscopic state of the system
- This would determine all the properties of the system
- Not possible, because of the large amount of information needed

State

- Thermodynamics begins with a consideration of the properties of the system which define the macroscopic state of the system
- When the values of a small number of properties are fixed then the values of all of the rest are fixed
- When a simple system, such as a given quantity of a substance of fixed composition is being studied, the fixing of two properties fixes the values of all of the rest.
- Usually two independent variable from Pressure-Volume-Temperature

State

- **State is always:**
  - Described by macroscopic and measurable variables, such as pressure, temperature and mass
  - When we know the values of those variables and they are fixed, the entire state of the system is fixed
  - This means that thermodynamics is a science of properties of large quantities [e.g. one mole of a substance that is 6.022×10^{23} atoms or molecules]

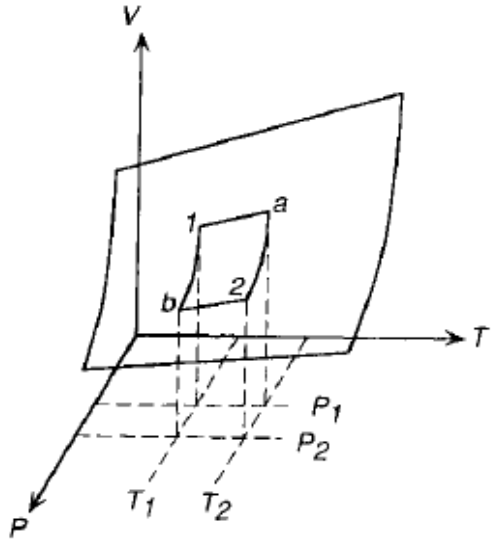
  - Example, accuracy of a lab scale about 0.1 mg
    - *Still dealing with about 10^{15}-10^{20}particles*

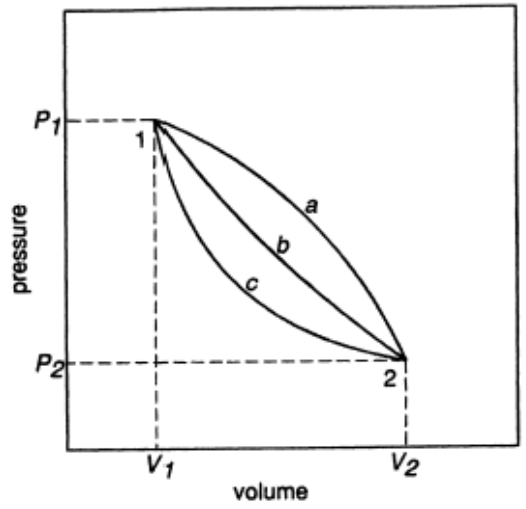
State function

- **A state function describes the property of a substance using two state variables (e.g. P and T) and the amounts (n_i) of the substances:**
  - $f = \Theta(P,T,n_i)$
  - The values of the state function depends only on the values of the state variables, not on its past or history
  - Thus, a process $1 \rightarrow 2$ can be conducted along whatever path, but the difference of the state variable values is always the the same
  - Mathematically for a cyclic process is also valid $\oint f = 0$

State function

- An example: state function V=f(P,T).
- The equilibrium states of existence of a fixed quantity of gas in P-V-T space.
- <u>Above</u> state change 1→2 by point a or b is the same
- <u>Below</u> paths a, b & c result in same change from 1 to 2

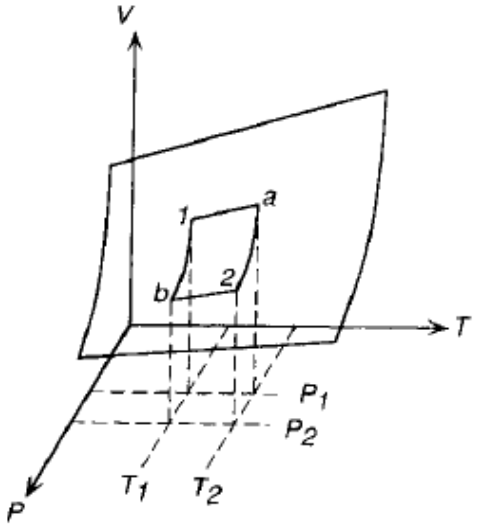




Source: D.R.Gaskell, Introduction to the Thermodynamics of Materials

State function

- **Mathematical expression of a property of a substance is called also its equation of state (EoS).**
- **EoS provides a mathematical relationship between two or more state functions, like pV = nRT.**
- **State functions have their own forms:**
  - change 1→2 is in constant pressure P_1 (1→a)
    $(V_a\text{-}V_1)= {}_{T1}\int^{T2}(\partial V/\partial T)_{p1}\, dT.$
  - and after that at constant temperature T_2 (a→2)
    $(V_2\text{-}V_a)= {}_{P1}\int^{P2}(\partial V/\partial P)_{T2}\, dP.$
  - total molar volume change is sum of the above terms as
    $\Delta V = {}_{T1}\int^{T2}(\partial V/\partial T)_{p1}\, dT + {}_{P1}\int^{P2}(\partial V/\partial P)_{T2}\, dP.$
- **The differential form of above equation is generally called 'complete differential'**
  - $dV = (\partial V/\partial T)_p dT + (\partial V/\partial P)_T dP + \Sigma_k(\partial V/\partial n_k)_{P,T,nj} dn_k.$



State function

- **The properties of substances are either extensive or intensive**
  - the extensive properties depend on the size of the system – e.g. the volume of a system
  - intensive properties do not depend on the size of the system – e.g. temperature or pressure
  - the values of extensive properties, expressed per unit volume or unit mass of the system, have the characteristics of intensive variables
  - molar volume $v \equiv V/n$ where n is system size in moles is an intensive property.

Properties

- The total value of an extensive variable Z in a system of k ‘areas’ or ‘volumes’ is simply their sum

  $Z = \sum_{i=1..k} Z_i$

- Density functions of Z are calculated by dividing the value Z by mass, amount or volume:

  $z = Z/m$ a *specific* function

  $z_m = Z/n$ a *molar* function

  $z_V = Z/V$ an (overall) *density* function.

Properties

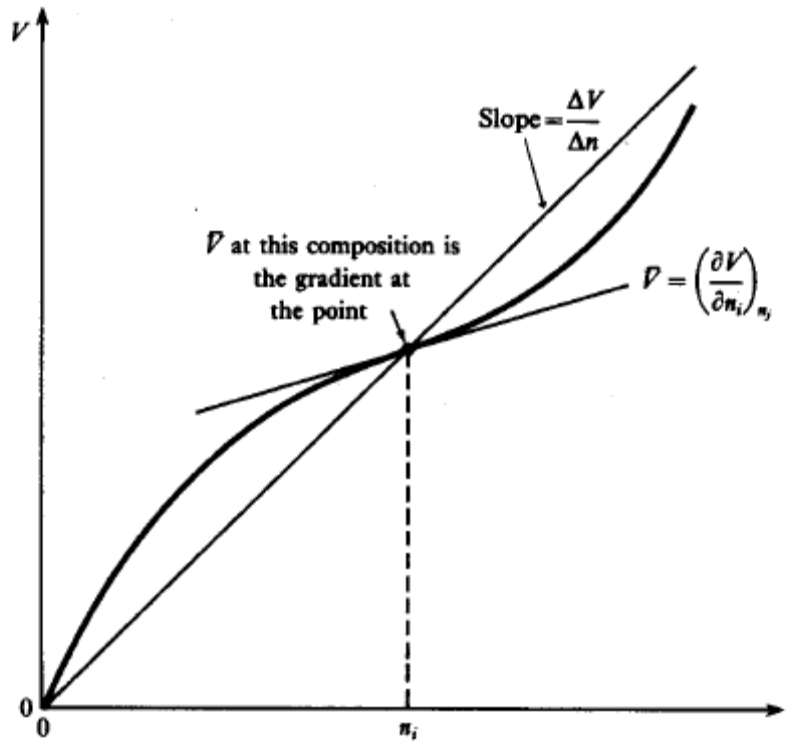
- An important property of a system (phase) is its Z value as a function of each of its component's (k) amount, when T and P as well as the amounts of the other components j are constant.
- This system/phase property or its 'partial molar function' is defined as

$$z_k \equiv (\partial z/\partial n_k)_{T,P,nj} \qquad j \neq k.$$

- A partial molar property indicates how an extensive property varies with changes in the molar composition at constant T and P.

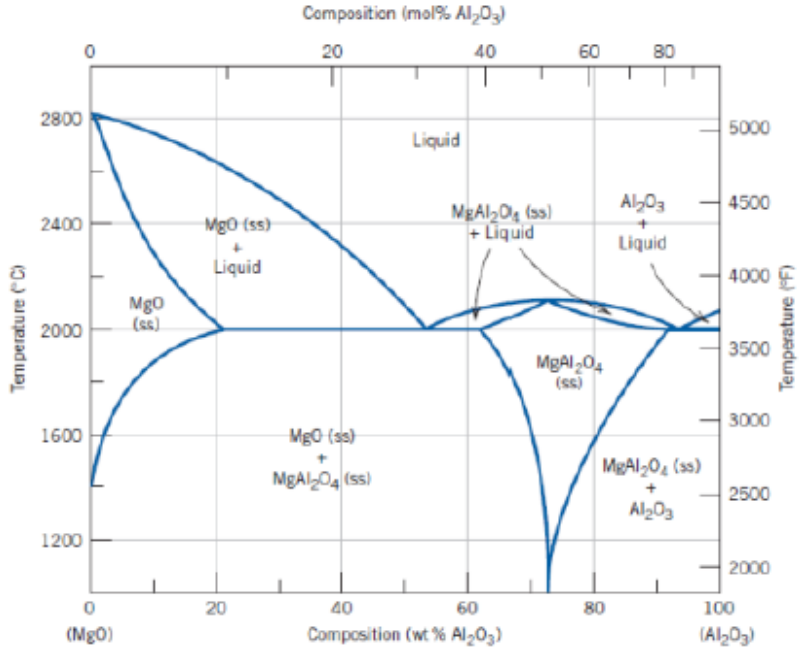
Properties

- Essentially a partial molar property is the partial derivative of the extensive property with respect to the amount (number of moles) of the component of interest.
- Every extensive property of a mixture has a corresponding partial molar property.



Component

- **The composition of a system is described by its components**
  - a single component system – ‘unary’
  - a two component system – ‘binary’ ($MgO + Al_2O_3$)
  - a three component system – ‘ternary’
  - a four component system – ‘quaternary’



Source: http://www.transtutors.com

Components and species

- **A component is any combination of atoms which defines the amounts of a system and can be added or taken away independently – i.e. it cannot be an ion or an electrically charged radical of any kind**
  - Components of a water – table salt solution are H_2O and NaCl, not Cl^- and Na^+ formed by the dissociating salt, because they are not possible to add into water independently
- **Species is any detail of the system which can be used to describe its microstructure**
  - Typically an atom, ion (Fe^{2+}), molecule ($CO_2(g)$) or radical ($OH\bullet$)

Composition coordinates

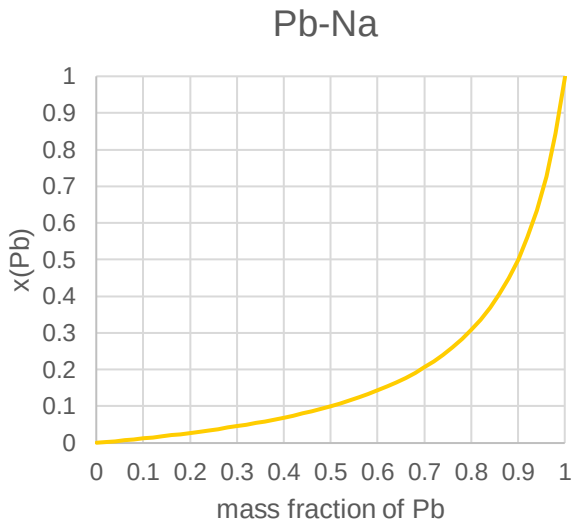
- Composition coordinate = how to present phase composition.
- The common composition coordinate in industrial cases is mass fraction (or weight-%).
- Correspondingly, the mass fraction m_i (or w_i) is defined as

  $m_i \equiv M_i/\Sigma_k M_k$, where k = 1...N.
- The thermodynamic composition coordinate always is atom or molar fraction scale and it is defined with the amounts n_i as

  $x_i \equiv n_i/\Sigma_k n_k$, where k = 1…N.

Composition coordinates

- **As by definition, $n_i \equiv M_i/N_i$, where N_i is molar mass of substance i, its mass fraction is not a linear function of mole fraction.**
  - this fact leads to severe need of coordinate transformations which in practice are carried out by computational software (e.g. HSC Chemistry).



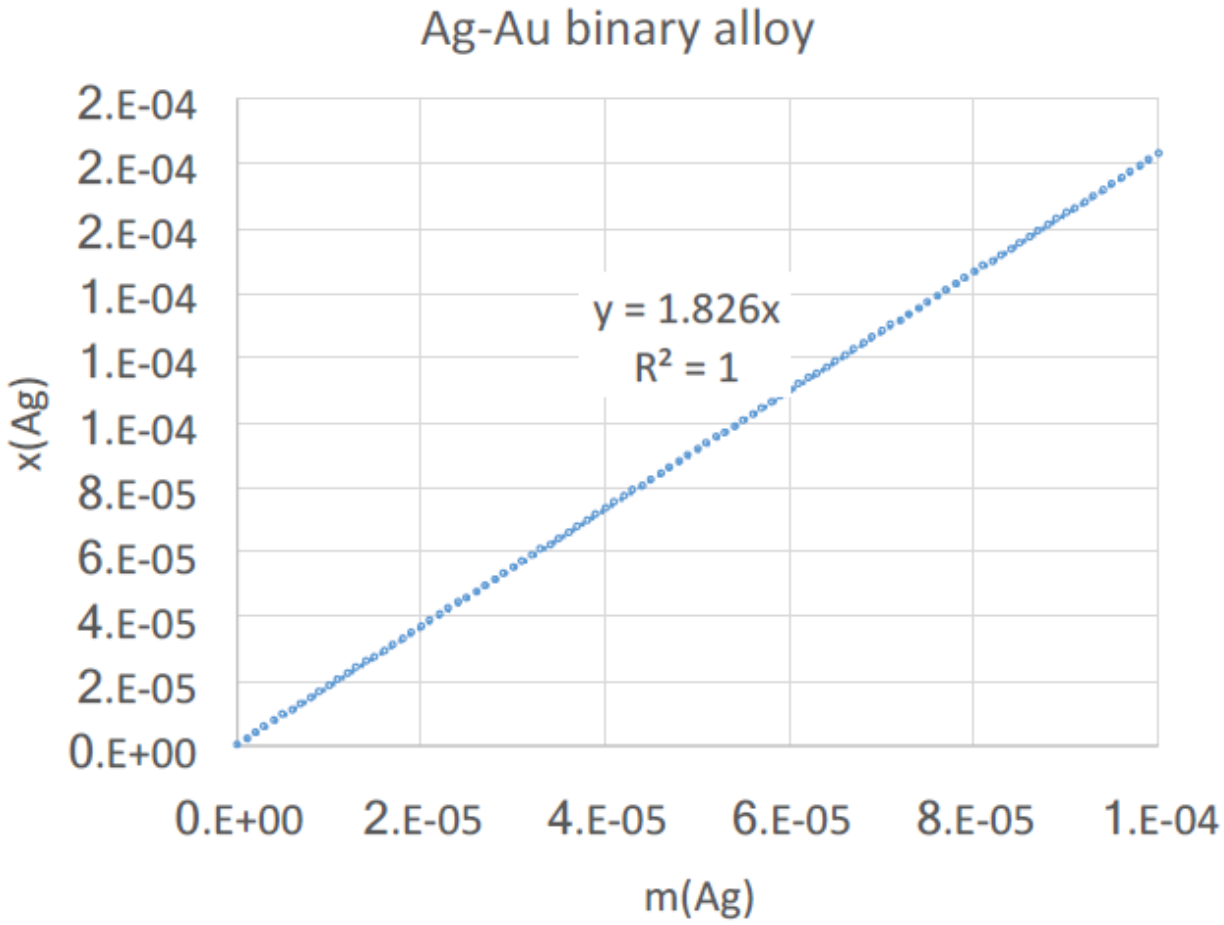
Composition coordinates

- Only in very dilute solutions we get an approximate linearisation between the molar fraction and mass/weight fraction
- Thus, in general the following holds

  $x_i \neq \alpha \times m_i$
- But as a limiting value in (very) dilute solutions one can derive the relation

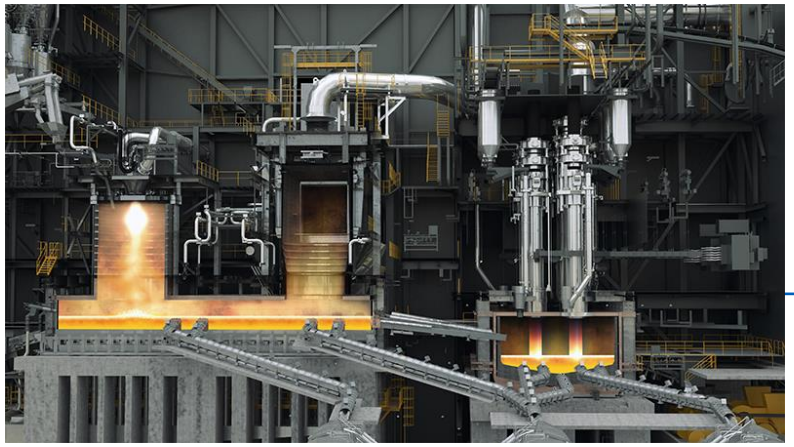
  $x_i = \alpha \times m_i$

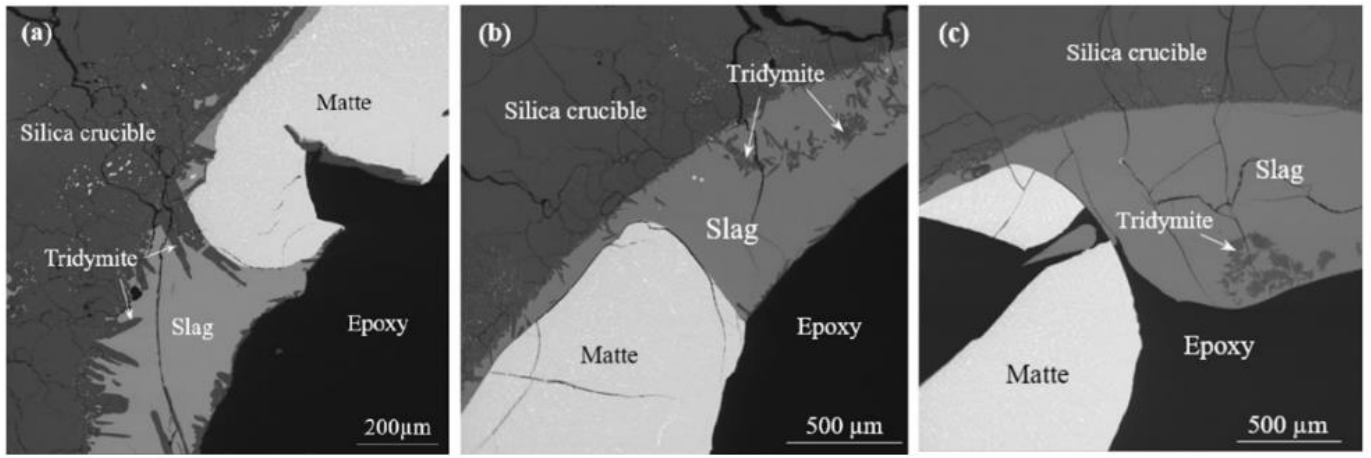
  $m_i, x_i \rightarrow 0$



Phase

- **Phase is physically and chemical uniform (homogenous) ‘volume’, separated from the other phases by a boundary surface**
- **A region of material that is chemically uniform, physically distinct, and often mechanically separable from other phases**
  - Smelting fyrnace: matte, slag, gas
  - Leaching reactor: solid, liquid, gas



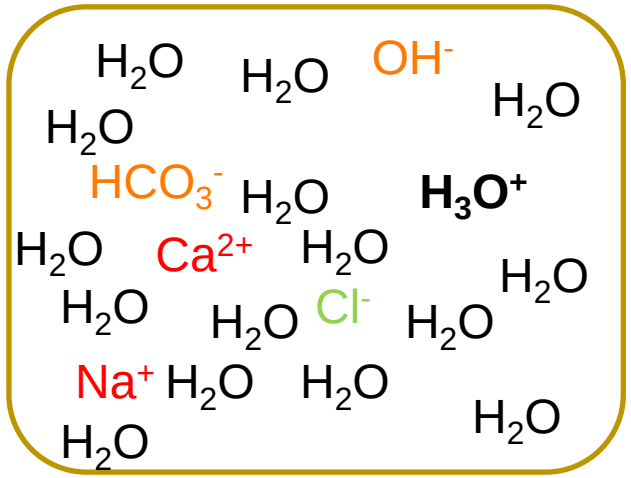


Equilibrium of Copper Matte and Silica-Saturated Iron Silicate Slags at 1300 ° C and of 0.5 atm (aalto.fi)

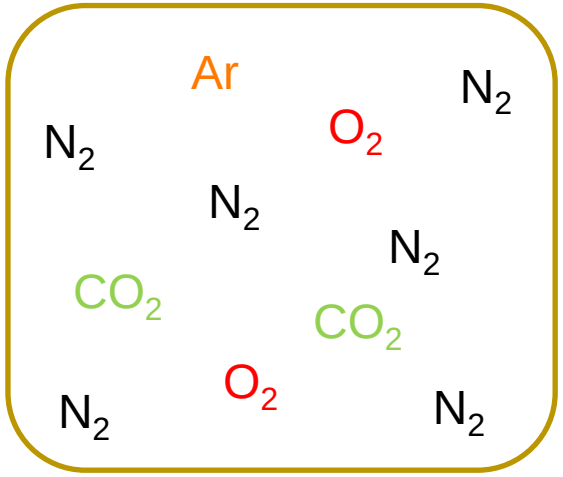
Some basic definitions

Phase: a homogeneous part of the system
- can be described by state functions

Examples



Sea water: water with dissolved salts



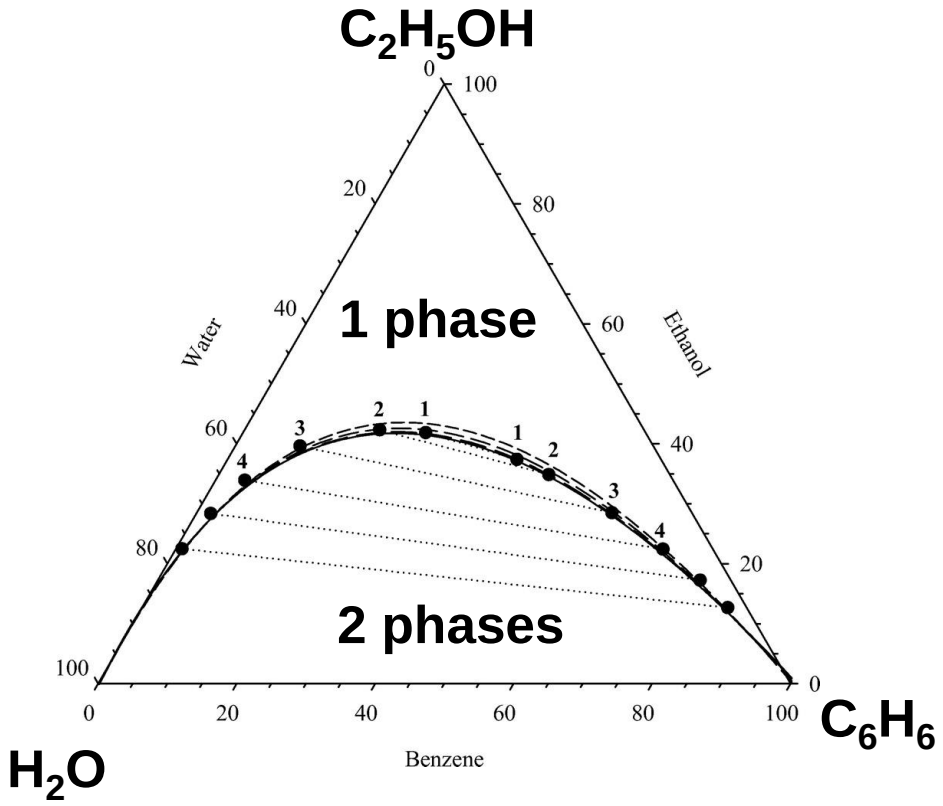
Air: Gas phase containing several gas species

Silicate mineral - plagioclase $CaAl_2Si_2O_8$-$NaAlSi_3O_8$

Phase

- **Liquid water + water vapor**
  - two phases (different structural properties)
- **Liquid oil + liquid water**
  - two phases (different chemistries)
- **Oxygen gas + nitrogen gas**
  - one phase (miscible solution)
- **Liquid water + liquid methanol**
  - one phase (miscible solution)

Phase



Ethanol-water: **1 phase**
Ethanol-benzene: **1 phase**
Benzene-water: **2 phases**

Phase

- State of matter is a distinct form in which matter can exist, usually solid, liquid, gas, and plasma.
- Phase transition = change in state of matter.
- During a phase transition certain properties of the medium change, often discontinuously.
- Phase transitions are results of a change of external conditions, such as temperature, pressure, composition etc.

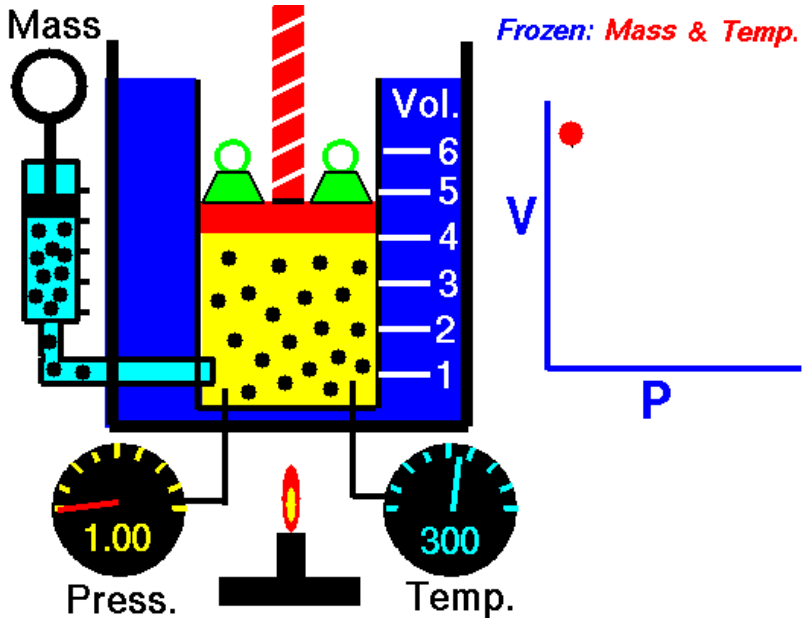
Process – change of state

- **By definition, a process 1 → 2 causes a change in state variable *F* which is the difference of the end and start points as $\Delta F \equiv F(2) - F(1)$**
  - a transformation at constant temperature = isothermal transformation or process - $\Delta T=0$.
  - a transformation at constant pressure = isobaric transformation – $\Delta P=0$.
  - a transformation in constant volume = isochoric transformation – $\Delta V=0$.
    - *In addition, you may find also the following expressions: an isentropic process and an isenthalpic process etc.*

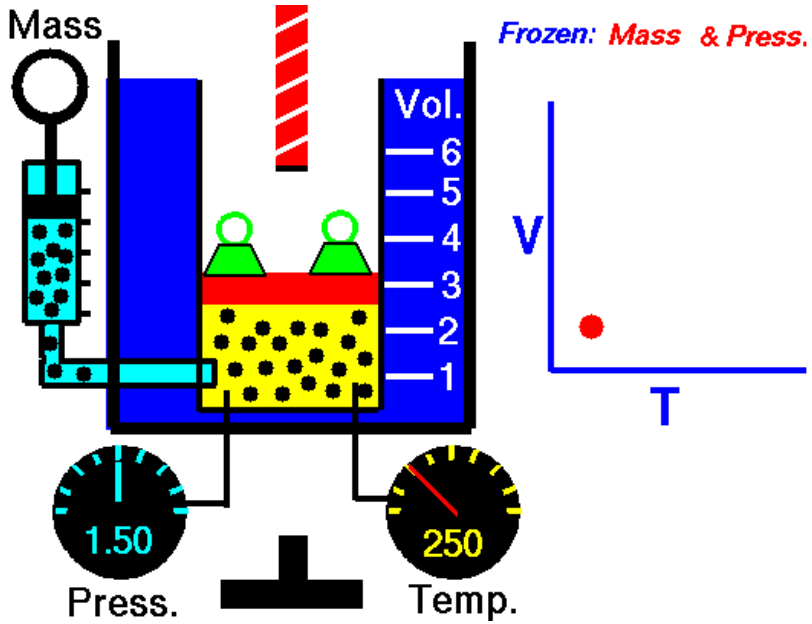
Equation of state of gases

- **Boyle's law (1660) at constant temperature**
  - $p \times V = \text{constant}$
- **Gay-Lussac law (1802) fixed mass or volume**
  - $p/T = \text{constant}$
- **Charles' law (published by Gay-Lussac 1802) in constant pressure**
  - $V/T = \text{constant}$
- **Dalton's law (1801): in gas mixtures total pressure is sum of partial pressures**
  - $p_{tot} = p_1 + p_2 + \ldots = \Sigma\, p_i$
  - $p_i = p_{tot} \times x_i$

Equation of state of gases



Boyle's law



Charles' law

Ref. https://www.grc.nasa.gov/www/k-12/airplane/Animation/frglab.html

Equation of state of gases

- **Combined gas law**
- $(V \times p)/T = \text{constant}$
- **Avogadro's law (1811): in same pressure and temperature a volume of gas contains an equal number of gas molecules' or**
  - $V \times p = n \times R \times T$
- **R = gas constant 8.3144598(48) $J \cdot mol^{-1} \cdot K^{-1}$**
- **R is a combination of the constant in Boyle, Charles and Gay-Lussac laws.**

Equation of state of gases

- More accurate measurements have shown that the above 'laws' are valid only in ideal gases.
- Later it has been proven that they are valid in all gases when $P \rightarrow 0$.
- *An important observation:* all 'simple' gases and their mixtures behave at high temperatures like ideal gas or they obey the relation $pV=nRT$.

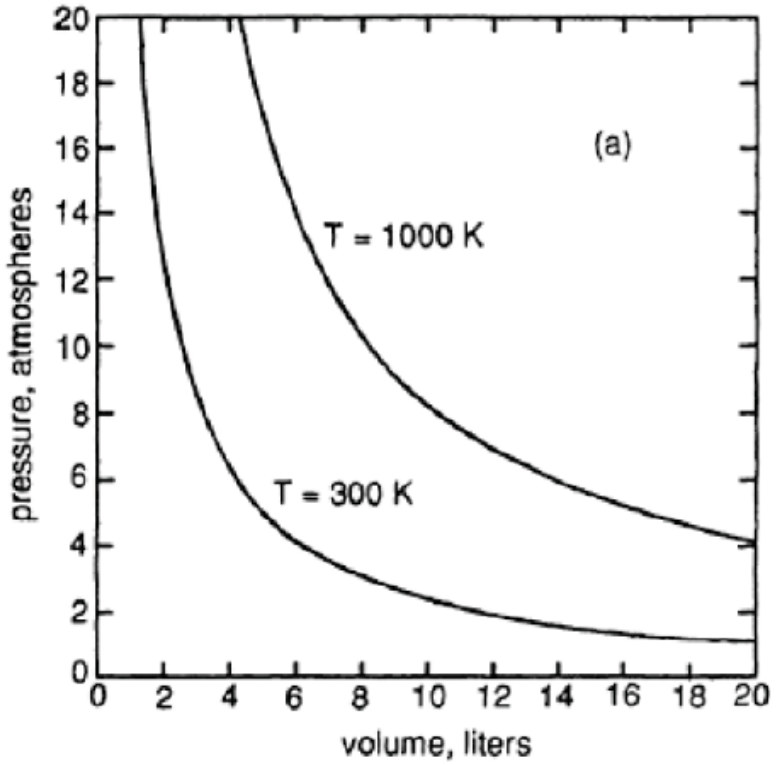
Ideal gases

- Ideal gas coefficient of thermal expansion

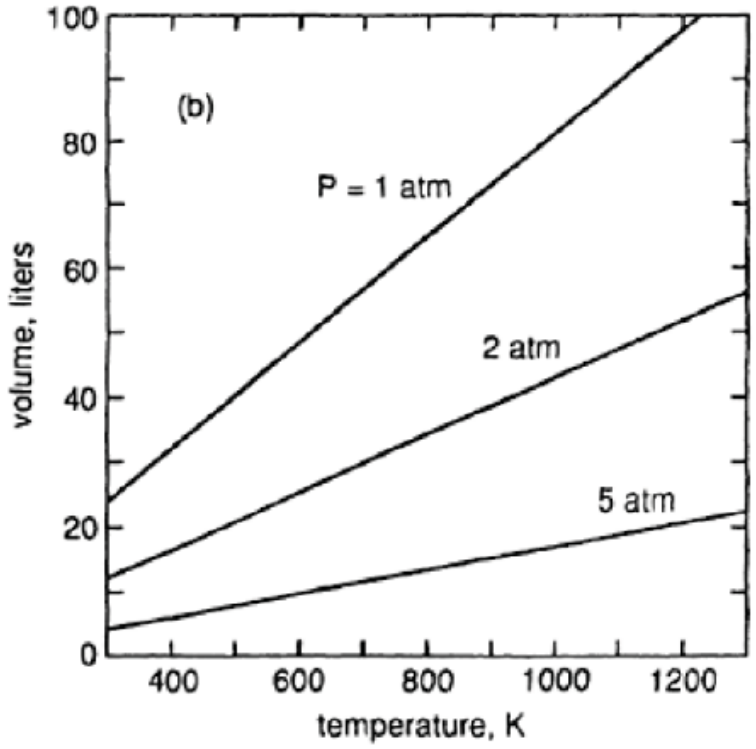
$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_p$$

- V_0 is the volume of the gas at 0 °C.
- A hypothetical gas was invented, which obeys Boyle's and Charles' laws exactly at all temperatures and pressures.
- This hypothetical gas is called the ideal gas, and it has a value of α = 1/273.15.
- At T = -273.15 °C the volume of the gas is zero.

Ideal gases



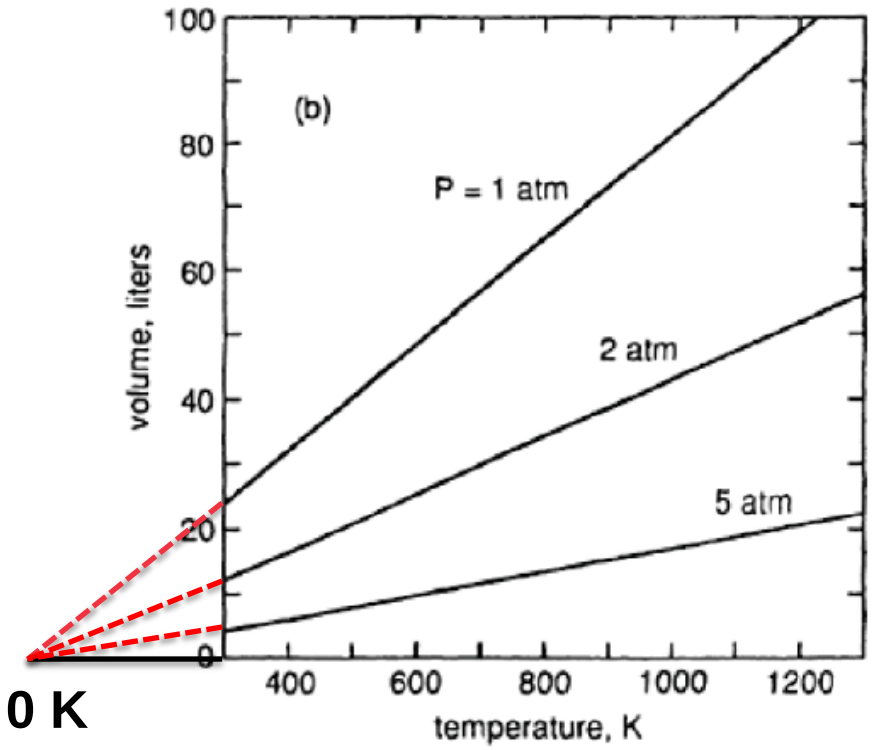
Boyle's law



Charles law

Source: D.R.Gaskell, Introduction to the Thermodynamics of Materials

Ideal gases



Charles law

Source: D.R.Gaskell, Introduction to the Thermodynamics of Materials

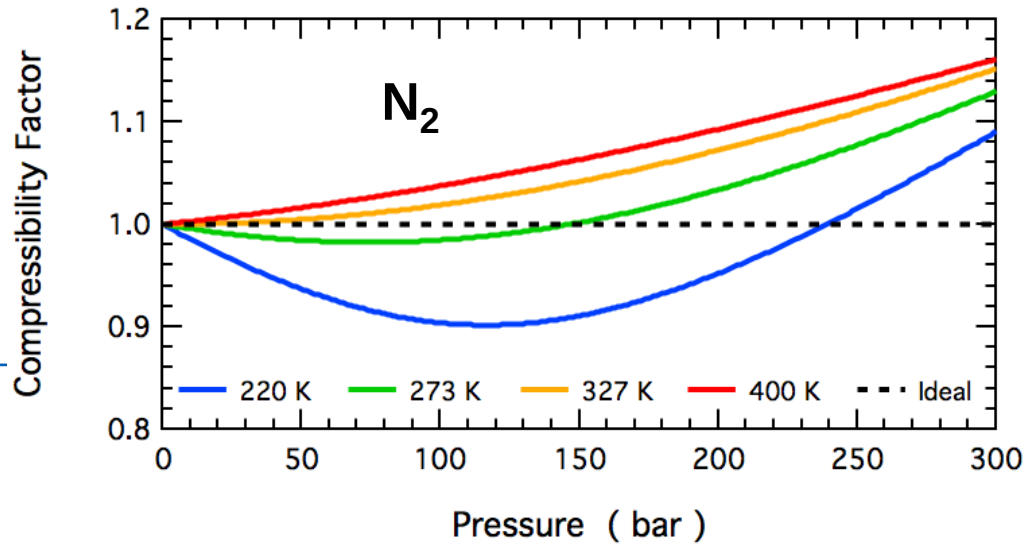
Ideal gases

- Ideal gas consists of non-interacting particles, and hence the atoms of an ideal gas can be separated from one another without work.
- Ideal gas law pV = RT is very simple.
- Therefore ideal gas is used in thermodynamic analysis and discussions.

- From Avogadro's hypothesis the volume per mole of all ideal gases at 0 °C and 1 atm is 22.414 liters.
- Standard temperature and pressure - STP.

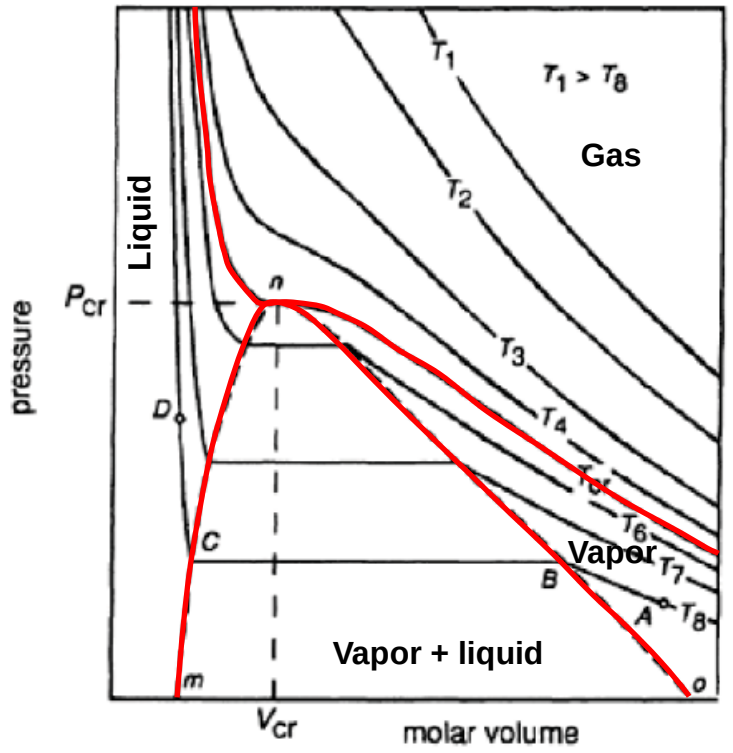
Real gases

- Real gas molecules occupy space and have interactions.
- The deviation from ideality is described by the compressibility factor Z.
- Z = PV/nRT
- For ideal gas Z = 1.
- For real gas Z is dependent on two selected variables like Z = f(P,T)



Real gases

- At high temperatures real gas behaves like an ideal gas.
- When at certain temperature pressure approaches condensation the P,V –behaviour is no more of ideal gas.
- Practical solution for this deviation are so called virial equations.



Source: D.R.Gaskell, Introduction to the Thermodynamics of Materials

van der Waal's equation

- **Improvement of the ideal gas law**
- **Considers two factors not included in the ideal gas law**
  - Particles in the gas occupies a finite volume
  - Particles in the gas can interact with each other
- **For one mole of gas**

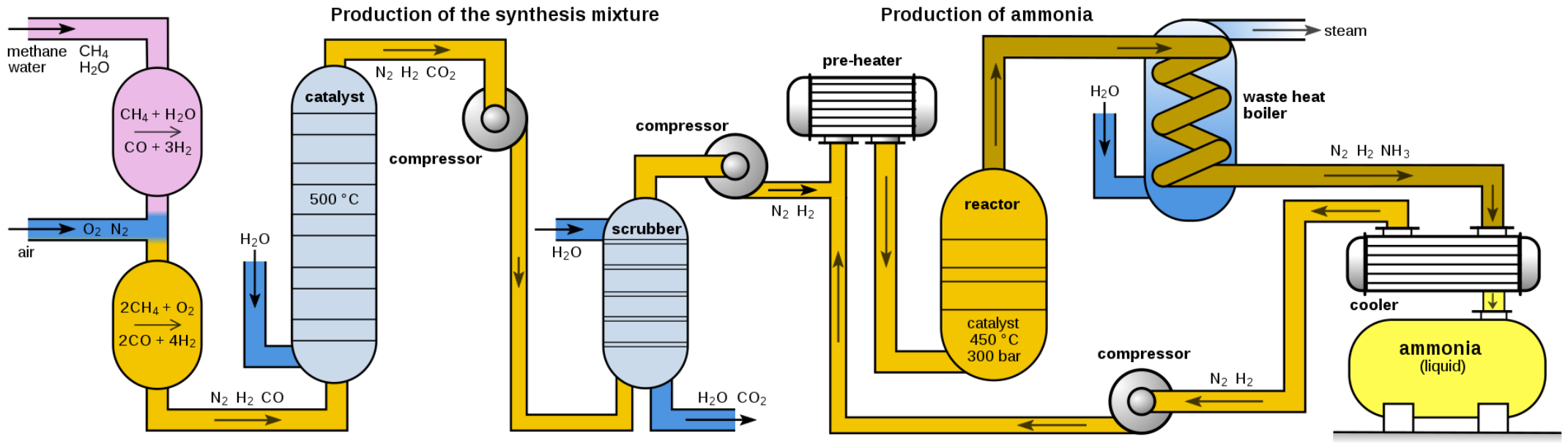
$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Correction term for particle interactions

Volume of particles

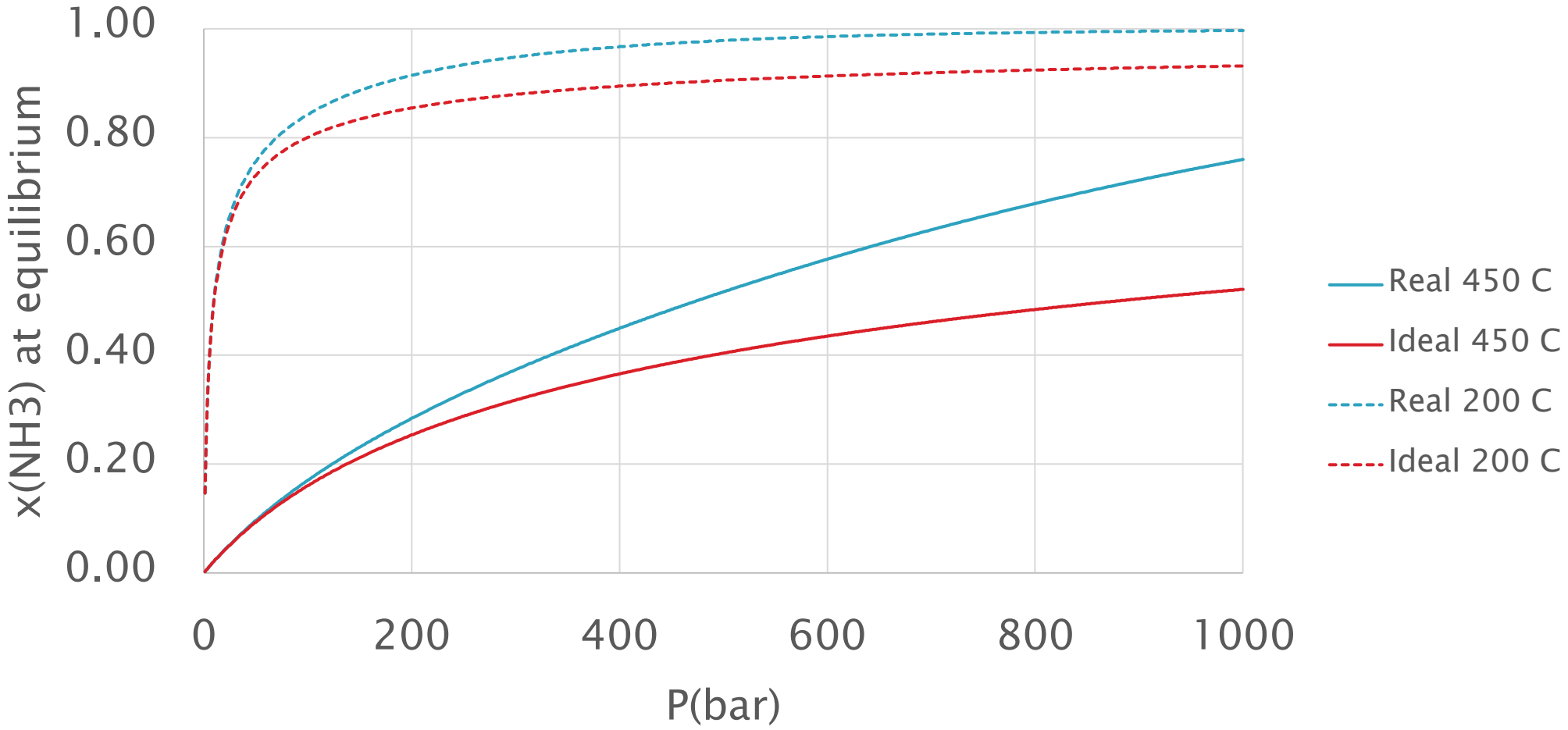
Example: ideal vs real gas–ammonia synthesis

- For the Haber–Bosch process to produce NH_3 from N_2 and H_2, catalytic high–T, high–P process is needed



Equilibrium calculated with Factsage software: ideal vs real gas

$$N_2 + 3\ H_2 = 2\ NH_3$$



State of equilibrium

- **Thermal Equilibrium**
  - The temperature throughout a system is uniform.
- **Mechanical Equilibrium**
  - No change in pressure with time and no movement of material.
- **Phase Equilibrium**
  - The mass of each individual phase does not change with time.
- **Chemical Equilibrium**
  - The chemical composition of a system does not change with time.

State of equilibrium

- The state of equilibrium is a property of a system where all its (experimentally) measurable properties, e.g. pressure, volume and temperature, are constant (as a function of time) now and also *after the system has been isolated* from its surroundings.

- If its properties prior to isolation were constant but change post it as a function of time, the system was *in a steady state condition* prior to its isolation.

0^{th} law of thermodynamics

- 1^{st} law of thermodynamics (1850): Energy is conserved, internal energy change = heat + work.
- 2^{nd} law (1824): Total entropy can only increase over time for an isolated system.
- 3^{rd} law (1906-1912): The entropy of a system at absolute zero is a well-defined constant. Later in 1923: The entropy may be zero for perfect crystalline substances.
- 0^{th} law (1931): If two systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

0^{th} law of thermodynamics

- If two systems A and B are in thermal equilibrium (i.e. do not change thermal energy or heat) with a third system C, they at the same time are in thermal equilibrium with each other.
- The statement defines the state variable called (thermodynamic) temperature.

0th law of thermodynamics

- **Principles to determine temperature quantitatively, or how to construct a thermometer:**
  - The temperature of an object can affect some physical property of the object, such as the length of a solid or the gas pressure in a closed vessel.
  - Two objects are in thermodynamic equilibrium when they have the same temperature.
  - If two objects of different temperatures are brought into contact with one another, they will eventually establish a thermodynamic equilibrium.

0th law of thermodynamics

- Thermocouple based on Seebeck effect E = f(T).
- Thermometer, expanding liquid.