AsTher®

Thermodynamic Database

Determination of the Substantial Composition of Input Materials Using Thermodynamic Calculations

To calculate the heat and mass balance of a process, we need to know which substances are used in the process. For example, the carbon demand in iron production depends on whether iron exists in the material as FeO, Fe_2O_3, or $FeCO_3$.

If the FeO content in the input material is known, we can
estimate the carbon demand and the heat balance according to the reactions $FeO + C = Fe + CO$
$2 FeO + C = Fe + CO_2$.

We usually only receive the elemental composition of the input material . For example, in the case of copper ores, the elemental concentrations (As, Cu, Fe, Sb, S) in the ore are declared, but it is unclear which substances are present in the input material , whether CuS, Cu_2S, FeS, FeS_2, $CuFeS_2$, etc.

For the battery paste resulting from lead recycling from used batteries, the As, Bi, Cu, Pb, S, and Sb concentrations are specified. Lead exists in the battery paste as PbO, PbO_2, $PbSO_4$, etc., and partly in elemental form. Only when we know the concentrations of these lead compounds can we calculate the heat and mass balance.

Phase analysis of the input material to determine their substantive composition is costly and often unreliable. In most cases, the state of the mixture is approximately in the range of minimum free energy and maximum entropy. Therefore, the possible composition of the input material can be estimated with sufficient accuracy using thermodynamic calculations. The calculated compositions can occasionally be verified by phase analysis.

We encounter this problem less frequently in ores or natural substances, since a complete elemental analysis is usually available. The possible combination of elements almost always results in only a specific substance composition.

The calculation method for determining the substance composition varies for each specific case. If the supplied input material are produced in processes at high temperatures, oxidation during cooling and storage must be taken into account.

In general, calculations are carried out taking into account the following criteria or restrictions:

Minimum Gibbs free energy: If a material to be used in a process has been stored in a specific environment for an extended period of time, the substance's composition can be estimated using thermodynamic calculations based on an approximate equilibrium state. That is, the state with the minimum Gibbs free energy (or with the minimum free enthalpy).

Maximum entropy: Several possible compositions with the minimum free energy are determined within the range of possible fluctuation. The state with the highest possible entropy is assumed to be the most probable.

The oxygen potential in the environment of the formation process or during storage of the material must be comparable to the oxygen potential in the calculated state.

The elementary sum must approximately correspond to the value of 100% in the calculated state.

The material must originate from only one process . The substantial composition of a material mixture from two or more processes cannot be determined using thermodynamic calculations based on elemental analysis. The mixture must have been formed under the same conditions and within the same time period.

The criteria listed above are not the "Five Commandments," nor are they a "categorical imperative." In certain special cases, a criterion may be ignored. However, if a criterion is ignored, we must provide a good reason for ignoring it. For example, if the molar ratio of Fe/O=1/1 [mol/mol] in a mixture consisting of iron and oxygen and without elemental iron, the mixture most likely consists of FeO.

mixture	Fe (s) [mol]	Fe2O3 (s) [mol]	Fe3O4 (s) [mol]	FeO (s) [mol]
1	**0.25**	0	0.25	0
2	**0.22**	0	0.22	0.12
3	**0.066**	0.066	0	0.802
4	0	0	0	**1**

It is assumed that the composition calculated according to the above criteria is not an exact, but only an approximate, representation of the actual composition of a mixture. Moreover, elemental analyses of a material do not produce identical results. From the elemental analysis, we can roughly estimate which elements are used in a process. This also applies to the calculated substantial composition of the material.

If we create the heat and mass balance of a process with the composition of the input materials calculated according to the above criteria, we achieve sufficient agreement with the measured data of the process.

1. Gibbs free energy as a criterion for determining the possible state

In a thermal process, a liquid phase (e.g. slag) consisting primarily of the elements Fe, Si, and O is formed at 1500°C.
The elemental analysis in % mass [kg/kg]:
Fe %: 54.8
Si %: 13.78
Based on this measurement, the oxygen concentration O% is approximately 31.4.
The following table shows the calculation of the relative mole number of the elements.

	w [kg/kg]	M [g/mol]	n [mol/kg]=w/M	rel. mol= n_i/n_{Si}
Fe	0.5481	55.85	9.81	2
Si	0.1378	28.01	4.91	1
O	*0.314*	*16*	*19.63*	*4*
sum	1			

Tab. 1.1 : Calculation of the relative number of moles according to the relative mass [kg/kg].

The relative molar composition of the mixture according to Table 1.1 is $\mathbf{Fe_{2n}\,Si_n\,O_{4n}}$. Depending on the relative molar mass of the elements, numerous compositions are possible.
The mixture most likely consists of the substances Fe(s), FeO(s), Fe_2O_3(s), Fe_3O_4(s), SiO_2(s), and Fe_2SiO_4(s).

The following table shows three selections from the numerous possible compositions as examples.

substance	I	. . .	II	. . .	III
FeO [mol]	2	. . .	1	. . .	0
SiO_2 [mol]	1	. . .	0.5	. . .	0
Fe_2SiO_4 [mol]	0	. . .	0.5	. . .	1
Total [mol]	3		2		1

Tab. 1.2 : Three selections of the possible substantial compositions of the mixture according to the elemental analysis in Tab. 1.1

The molar Gibbs free energy of a substance in a mixture

$$\bar{G}_i=\bar{G}_i^0+R\cdot T\cdot\ln a_i \qquad (1)$$

The Gibbs free energy of the mixture

$$G=\sum_i n_i\cdot\bar{G}_i=\sum_i n_i\cdot\left(\bar{G}_i^0+R\cdot T\cdot\ln a_i\right) \qquad (2)$$

In an approximately ideal mixture, the Gibbs free energy is

$$\bar{G}_i = \bar{G}_i^0 + R \cdot T \cdot \ln x_i \qquad (3)$$

The Gibbs free energy of the possible states is shown below.

		I	II	III
	$\bar{G}_i^0 [J/\mathrm{mol}]$	$n_i \cdot \left(\bar{G}_i^0 + R \cdot T \cdot \ln x_i\right)$	$n_i \cdot \left(\bar{G}_i^0 + R \cdot T \cdot \ln x_i\right)$	$n_i \cdot \left(\bar{G}_i^0 + R \cdot T \cdot \ln x_i\right)$
Fe2SiO2	-2 036 422	0	-1,028,429	-2 036 422
FeO	-474 164	-960 283	-484,382	0
SiO2	-1 088 870	-1 105 065	-554,653	0
sum		-2 065 348	**-2,067,464**	-2 036 422

Tab. 1.3 : Free enthalpy of the melt according to the selected substantial compositions in Tab. 1.2.

According to the calculation results, the most probable state is the second of the selected states, since it is the state with the lowest free energy.

The above combinations result in the following mass concentration in %

substance	I	. . .	II	. . .	III
Fe_2SiO_4 [%]	0.00	. . .	50.00	. . .	100.00
FeO [%]	70.51	. . .	35.26	. . .	0.00
SiO2 [%]	29.49	. . .	14.74	. . .	0.00
sum	100.00		100.00		100.00

Tab. 1.4: Possible relative concentrations [kg/100 kg] of the substances in the mixture according to Tab.1.3.

In the above calculation, only three substances are taken into account, and only three possible substantial calculations are performed.

Such calculations are usually carried out using a corresponding application for thermodynamic calculations, in which the substantial composition of the mixture is determined with sufficient accuracy, taking into account all process-relevant substances and with minimal Gibbs free energy.

The results of such a calculation are presented in tabular form below.

According to the calculation, the most likely state is between choices I and II.

	w% [kg/kg]	x [mol/mol]
Fe (l)	0	0
Fe2SiO4 (l)	**22.7**	**0.090**
Fe3O4 (l)	1.03	0.0036
FeO (l)	**53.5**	**0.60**
FeSi (l)	4.12E-08	3.96E-10
Si (l)	0	0
SiO2 (l)	**22.8**	**0.31**

Table 1.5 : Most likely composition of the liquid phase at 1500°C
according to thermodynamic calculations
based on the elemental analysis in Table 1.1. (FeOSi.eql)

2. Entropy as a criterion for determining the possible state

In the calculations to determine the substantial composition of the mixtures, the state with the highest possible entropy is assumed to be the most probable.
The entropy of a substance in a mixture

$$\bar{S}_i = \bar{S}_i^o - R \cdot \ln a_i \quad (4)$$

The entropy of the mixture

$$S = \sum n_i \cdot \bar{S}_i = \sum n_i \cdot \left(\bar{S}_i^o - R \cdot \ln a_i \right) \quad (5)$$

This includes:
$\bar{S}_i^o [J/\mathrm{mol}]$: molar entropy of a substance as a pure substance

The following table shows the elemental analysis of a mixture resulting from the recycling of car batteries (so-called "battery paste"). The remaining mass is predominantly oxygen, and exists in the form of metal oxides or metal sulfates.

element	Mass%[kg/kg]
Bi	0.01
Cl	0.1
Cu	0.1
Fe	0.1
N/a	0.1
Pb	83
S	2.5
Sb	1
SiO2	0.75
sum	87.66

Tab. 2.1: Elemental composition of battery paste

substance	**Mass.% [kg/kg]**
Bi2O3 (s)	0.011
CuO(s)	0.125
Fe2O3 (s)	0.143
Na2SO4 (s)	0.109
NaCl (s)	0.164
Pb2SiO4 (s)	3,273
PbCl2 (s)	0.001
PbO (s)	26,096
PbO.PbSO4 (s)	40,585
PbO2 (s)	26,409
PbSiO3 (s)	1,695
PbSO4 (s)	0.044
Sb2O3 (s)	1,198
SiO2 (s)	0.002
sum	99,857

Tab. 2.2: Substantial composition of the paste with additional oxygen mass of approximately
12.2[kg O/100 kg paste] (battery paste.25C.eql)

The calculations vary the oxygen content of the mixture and calculate the possible substantive compositions. The calculation results are presented in the following graphs.

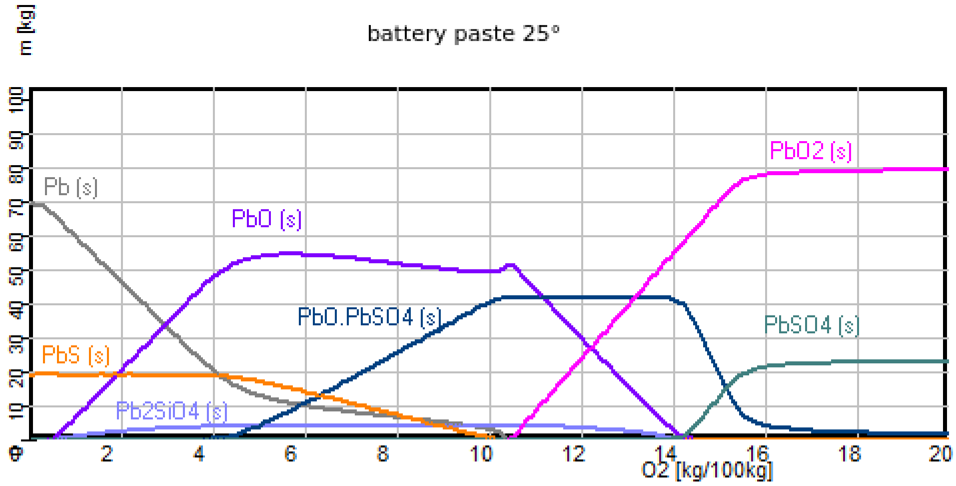

Fig. 2.1 : Possible Pb compounds depending on the oxygen mass in the paste mixture of 100 [kg] (battery paste.25C.eql)

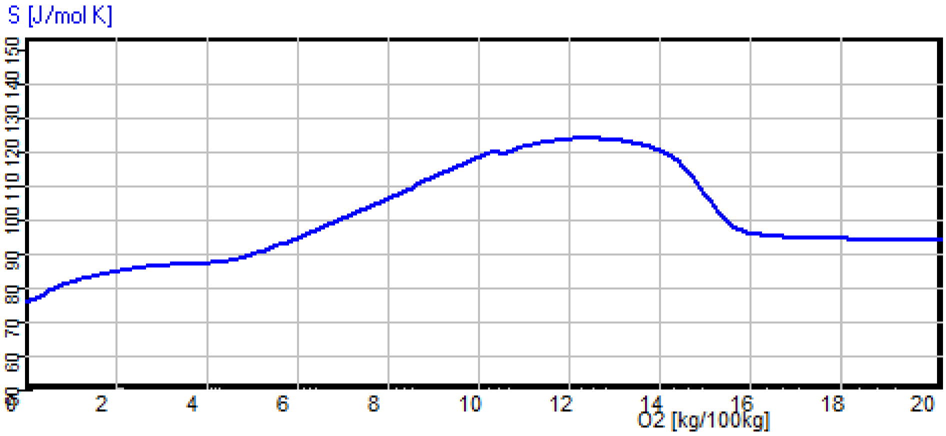

Fig. 2.2: Molar entropy of the paste mixture as a function of the oxygen mass in the paste mixture of 100 [kg] (battery paste.25C.eql)

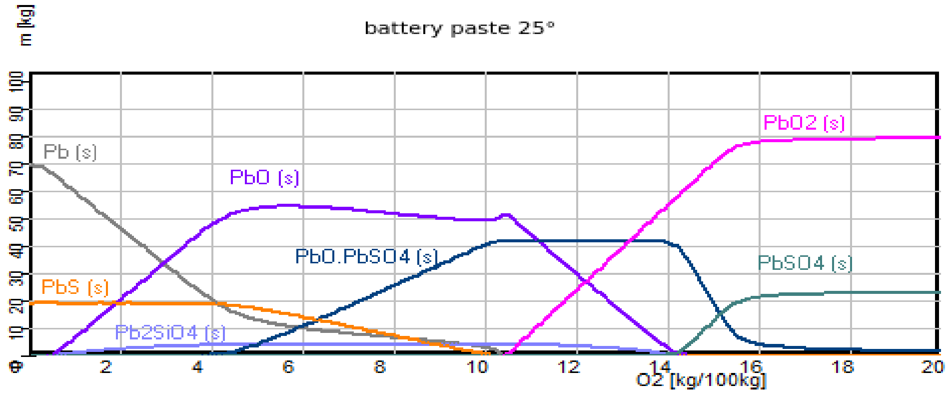

Fig. 2.3: Sum of the mass of the calculated compounds as a function of the oxygen mass in the paste mixture (battery paste.25C.eql)

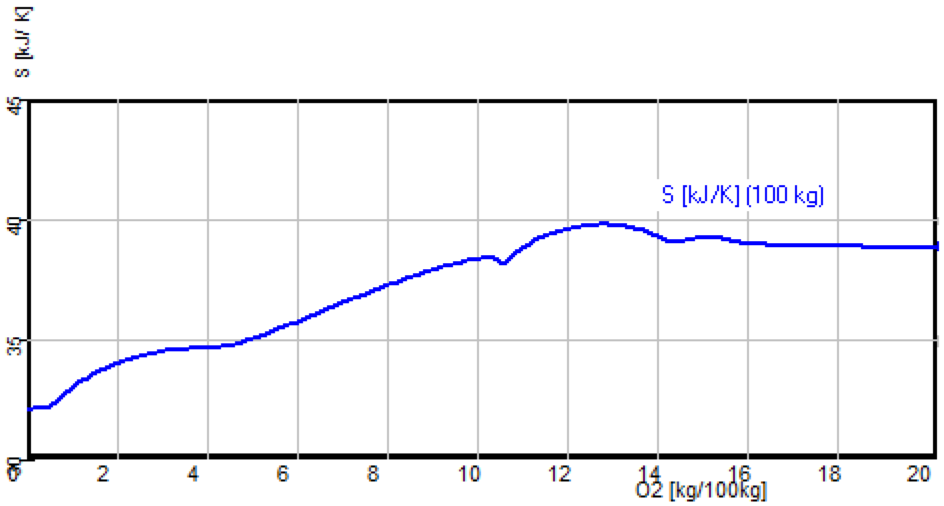

Fig. 2.4: Entropy of the paste mixture as a function of the oxygen mass in the paste mixture (battery paste.25C.eql)

The main reason for considering the substance composition at the highest entropy level is that the highest entropy level is statistically the most probable. The statistical significance of entropy is demonstrated in the exercises. However, it is also necessary to consider whether the calculated substance composition is also practically possible.
It is unlikely that PbS, for example, exists in battery paste.

The possibility cannot be ruled out that the calculated composition at the highest entropy state simultaneously corresponds to an elemental sum of the percentage mass fractions of approximately 100%. Such coincidences are often found in multiple calculations.

3. O_2 potential as a criterion for determining the possible state

If we want to estimate the possible composition of a mixture (e.g., a slag from a thermal reduction process) through thermodynamic calculations, we must know, among other things, the oxygen content of the mixture. The oxygen content in the mixture corresponds to the chemical potential of the oxygen in the mixture's environment.

Molar free energy of a substance is also called chemical potential μ.

The chemical potential of a substance in a liquid phase is defined by

$$\mu_{i(l)}=\bar{G}_{i(l)}=\bar{G}^o_{i(l)}+R\cdot T\cdot\ln a_i=\bar{G}^o_{i(l)}+R\cdot T\cdot\ln\left(x_i\cdot\gamma_i\right) \tag{6}$$

The definition of the chemical potential of a substance in a gas phase:

$$\mu_{i(g)}=\bar{G}_{i(g)}=\bar{G}^o_{i(g)}+R\cdot T\cdot\ln f_i=\bar{G}^o_{i(g)}+R\cdot T\cdot\ln\left(\phi\cdot y_{i(f)}\right) \tag{7}$$

If $\bar{G}_{i(l)}=\bar{G}_{i(g)}$, no reaction takes place. This is the equilibrium state. We speak of "the chemical potential of i in the system": μ_i.
In equilibrium, the following applies:

$$\mu_i=\mu_{i(l)}=\mu_{i(g)}$$

$$\mu_i=\mu_{i(l)}=\bar{G}^o_{i(l)}+R\cdot T\cdot\ln a_i \tag{8}$$

$$\mu_i=\mu_{i(g)}=\bar{G}^o_{i(g)}+R\cdot T\cdot\ln f_i \tag{9}$$

In an oxidic melt, the MeOx concentration corresponds to an O_2 partial pressure or an O_2 potential in the gas phase according to the reaction

MeOx(l) = Me(l)+ x/2 O_2 (g)

$$K=\frac{f_{O2}^{x/2}\cdot a_{\mathrm{Me}}}{a_{\mathrm{MeOx}}}$$

The term " **oxygen potential in the melt"** means the molar free energy of the oxygen in the gas phase, which would coexist with the MeOx concentration in the melt at equilibrium.

During reduction processes, $P_{O_2}<10^{-7}$ [bar], O_2 is very rare in the gas phase. Therefore, the term "O_2 potential" or "Pco/Pco $_2$ ratio" is often used in the vicinity of the slag, based on the reaction

$CO + 1/2\ O_2 = CO_2$

.

Example

Determination of the substantial composition of the flue dust:
The exhaust gases from the reduction process of the battery paste are first combusted at 800°C and then cooled in a boiler to 350°C. The O2 partial pressure in the boiler is approximately 1 bar.

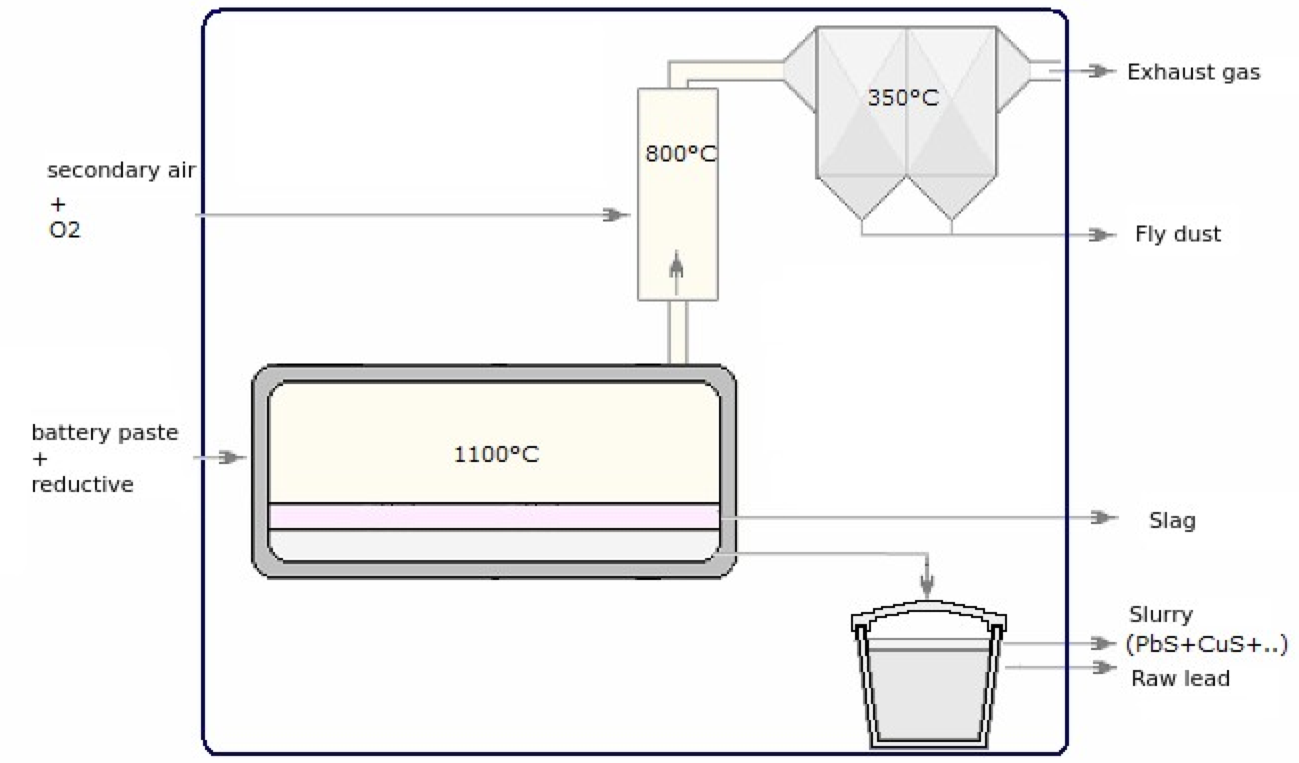

Fig.3.1: Schematic representation of the process for Pb recycling from battery paste.

	Mass % [kg/kg]
Ace	1
CD	6
Cl	0.4
Pb	62
S	9
Sb	0.5
Tl	0.1
Zn	1.2
sum	80.2

Table 3.1: Elemental composition of the flue dust in the boiler. The missing mass is almost entirely oxygen. (Flue Dust 350C.eql)

In the calculations, the amount of oxygen in the dusts is varied, and the possible substantial composition of the dusts is calculated based on an approximate thermodynamic equilibrium state in the boiler. Figure 1.3.2 shows the calculation results.

battery paste

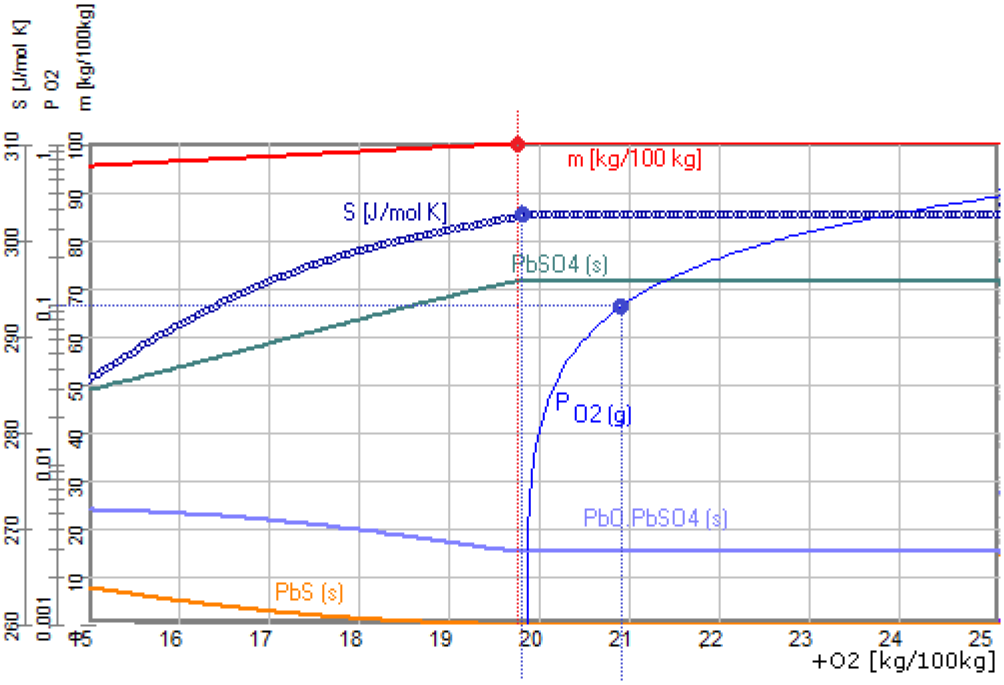

Fig.3.2 : Possible content of PbO (s), PbS (s), PbSO4 (s), PbO.PbSO4 (s) in 100 kg of flue dust depending on the oxygen content of the dust at 350[°C] and 1 [bar].

According to calculations, the maximum oxygen content is
19.9 [kg oxygen/100 kg mixture].
This condition can be achieved when PO_2 is >0.01 [bar]. An increase in the O_2 partial pressure no longer affects the O_2 content of the dust (saturation).

	m [kg]
As2O5 (s)	1.53
CdCl2 (s)	0.798
CdO (s)	5.20
CdSO4 (s)	1.78
PbCl2 (s)	0.288
PbO (s)	0.17
PbO.PbSO4 (s)	1:30 p.m.
PbO2 (s)	0.00
PbSO4 (s)	74.89
Sb2O3 (s)	0.598
TlCl (s)	0.12
ZnO (s)	1.49
ZnSO4 (s)	0.00
	100.

Tab. 3.2: Substantial composition of the flue dust in the boiler at 350°C and 1 bar according to the elemental analysis in Table 3.1.

If the flue dusts are reused in a process after cooling (e.g. down to 25°C), the possible substantial composition must be determined again at 25°C.
The following example shows the composition as a function of temperature below 1 [bar] at an O_2 partial pressure of Po_2 =0.2 [bar].

T [C]	PO2 [bear]	CdO [%]	CdSO4 [%]	CdCl2 [%]	PbO [%]	PbO.PbSO4 [%]	PbSO4 [%]	TlCl [%]	ZnO [%]
100	0.21	5.93	0.42	0.93	0.02	10.67	78.34	0.12	1.49
200	0.21	5.65	0.95	0.88	0.05	11.75	76.96	0.12	1.49
300	0.21	5.34	1.51	0.83	0.12	12.80	75.55	0.12	1.49
400	0.21	5.06	2.02	0.77	0.22	13.72	74.30	0.12	1.49

Tab. 3.3: Main components of flue dust in an equilibrium state as a function of temperature below 1 [bar] and PO2 = 0.2 [bar].

If the calculations produce a large fluctuation, then the decision depends on how the cooling occurs, whether with sufficient air and turbulence or with the exclusion of air.
If cooling is rapid, the composition at 350°C can also be assumed for 25°C.

4. Natural substances

The substantial composition of natural substances (e.g. ores) can almost always be determined starting from a thermodynamic equilibrium state, because the formation of the substances takes place over a long period of several thousand years.
Since a complete elemental analysis is usually available for ores, often only a certain substantial composition results from the combination of elements.

The following presents calculation results for determining the substantial composition of the soil from the coal mine based on elemental analysis.

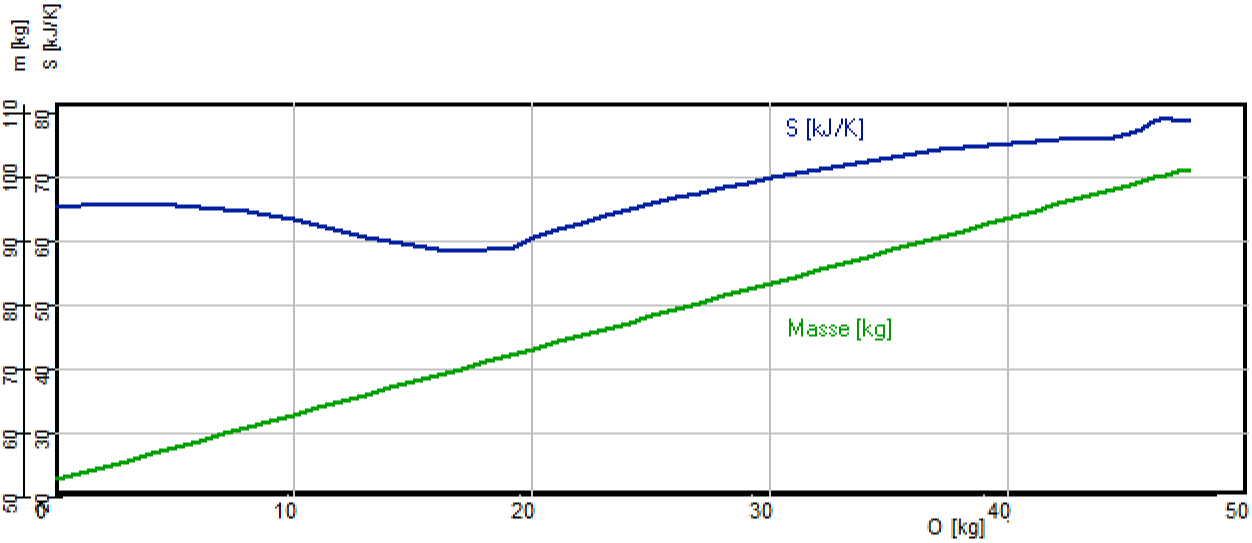

Fig. 4.1 : Entropy and mass of the soil from the coal mine as a function of the oxygen content in the mixture at 25°C and 1[bar]

Measured elemental composition of the Earth

element	Mass [%]
Si	27.11
Al	13.76
Fe	4,197
K	4,981
Ti	0.599
Mg	0.603
N/a	0.742
P	0.0873
C	0.546
sum	52.63

Calculated substantial composition at maximum entropy of the mixture1.27

	m [%]	*a*
Al2O3 (s)	4.97	0.04708
Al2SiO5 (s)	33.44	0.1997
C (s)	0.546	0.04398
Fe (s)	0.637	0.01107
Fe2SiO4 (s)	1,163	0.00553
FeO (s)	0.144	0.00194
FeSiO3 (s)	6,649	0.04881
K2Si2O5 (s)	12.73	0.05745
K3PO4 (s)	0.600	0.00273
MgSiO3 (s)	2,485	0.02395
Na2SiO3 (s)	1,965	0.01556
SiO2 (s)	32.77	0.52778
TiO2 (s)	1,000	0.0121
sum	99.09	0.99769

(RuhrCoalSand.eql)

Calculating the entropy of a system according to statistical thermodynamics

The following example shows the physical meaning of entropy and why the maximum entropy state should be considered for the calculation or estimation of the substantial composition.

In a system, there are 7 particles, 4 possible energy states: 2, 4, 6, 8 [J].

Probability or number of possible distributions: $\Omega=(\Sigma n_i)!/(\Pi n_i!)$,

Energy of the system: $E=\Sigma(n_i\cdot E_i)=34[J]$,

Entropy: $S=k\cdot\ln\Omega[J/K];\bar{S}=R\cdot\ln\Omega[J/\mathrm{mol}\cdot K]$,

<table>
<tr><th>Possibility</th><th>Probability Ω, Energy E and Entropy Σ</th></tr>
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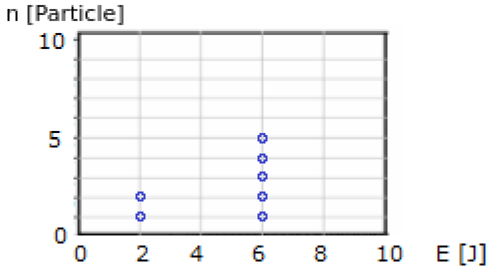

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$$\Omega=\frac{(2+0+5+0)!}{2!\cdot0!\cdot5!\cdot0!}=21$$
$$E=2\cdot2+0\cdot4+5\cdot6+0\cdot8=34[J]$$
$$S=8.314\cdot\ln(21)=25.3[J/\mathrm{molK}]$$

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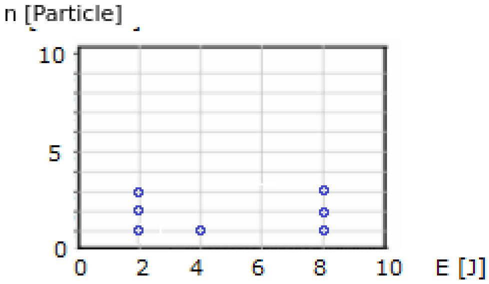

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$$\Omega=\frac{(3+1+0+3)!}{3!\cdot1!\cdot0!\cdot3!}=140$$
$$E=3\cdot2+1\cdot4+0\cdot6+3\cdot8=34[J]$$
$$S=8.314\cdot\ln(140)=41.1[J/\mathrm{molK}]$$

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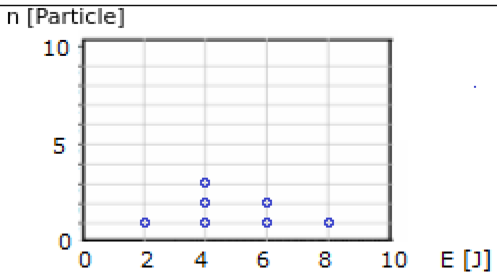

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$$\Omega=\frac{(1+3+2+1)!}{1!\cdot3!\cdot2!\cdot1!}=420$$
$$E=1\cdot2+3\cdot4+2\cdot6+1\cdot8=34[J]$$
$$S=8.314\cdot\ln(420)=50.2[J/\mathrm{molK}]$$

most possible state

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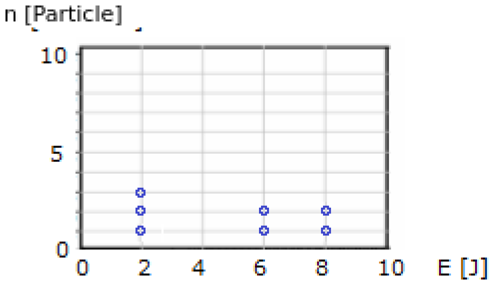

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$$\Omega=\frac{(3+0+2+2)!}{3!\cdot0!\cdot2!\cdot2!}=210$$
$$E=3\cdot2+0\cdot4+2\cdot6+2\cdot8=34[J]$$
$$S=8.314\cdot\ln(210)=44.5[J/\mathrm{molK}]$$

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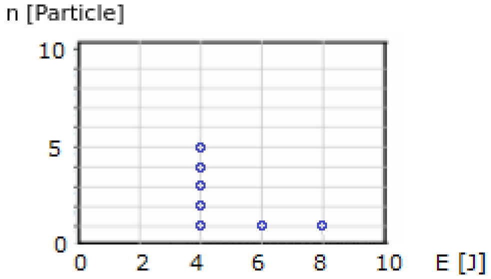

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$$\Omega=\frac{(0+5+1+1)!}{0!\cdot5!\cdot1!\cdot1!}=42$$
$$E=0\cdot2+5\cdot4+1\cdot6+1\cdot8=34[J]$$
$$S=8.314\cdot\ln(42)=31.1[J/\mathrm{molK}]$$

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Compare Boltzmann distribution with the most probable distribution at Ω=420