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Кафедра высокотемпературных процессов, материалов и алмазов

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THERMODYNAMICS, KINETICS AND CALCULATIONS

on METALLURGICAL PROCESSES

ТЕРМОДИНАМИКА, КИНЕТИКА И РАСЧЕТЫ

МЕТАЛЛУРГИЧЕСКИХ ПРОЦЕССОВ

Допущено учебно-методическим объединением по образованию в области металлургии в качестве учебного пособия для студентов высших учебных заведений, обучающихся по направлению 150100 – Металлургия

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Great advances have taken place in metallurgical processes during the past several decades. Modern, energy saving iron- and steel making or direct reduction technologies as well as copper and other non-ferrous metals production are some examples of the recent progress.

Energy and environmental issues have been generally considered as the main driving forces for this development. It is, however, clear that the key factor for the progress has been better knowledge of the basic phenomena in the processes. It means both thermodynamic bases of the prevailing phases and the reactions as well as chemical kinetics and transport phenomena in the reaction system, i.e. transport of heat, mass and momentum. All these are needed to create a representative model or a series of submodels to describe and to simulate the process.

This book is mostly directed to thermochemical and thermodynamic properties of phases and reactions. However, in some parts also structure of phases e.g. slags are discussed as well kinetic and mass transport phenomena.

This book was written as a joint project of professors at National University of Science and Technology «MISIS» and at Helsinki University of Technology (HUT). Its purpose is to be a general text book for undergraduate or postgraduate students who have metallurgy as their main subject. It is also suitable for self-studying as it has in each chapter, first a fairly thorough theoretical description of the problem followed by calculation examples and plenty of working examples and control questions.

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ПРЕДИСЛОВИЕ

Книга "Термодинамика, кинетика и расчеты металлургических процессов" является результатом совместной работы русских и финских ученых и объединяет опыт теоретической подготовки инженеров-металлургов и инженеров-исследователей металлургических процессов в Национальном исследовательском технологическом университете «МИСиС» и в Технологическом университете г. Хельсинки (Финляндия), издание отражает большой прогресс в металлургии за последние два десятилетия.

Термодинамика, термохимия и кинетика высокотемпературных процессов составляют теоретическую основу процессов получения и рафинирования металлов. На этой основе книга позволяет освоить проведение теоретического анализа сложных металлургических систем и процессов и их моделирование, формулировать и решать задачи, имеющие практическое значение. В книгу включены теория, модели и расчеты металлургических систем и процессов.

В главе "Термохимия" приведены методы расчета энергетических равновесий при высоких температурах.

В главе "Химическая термодинамика пирометаллургических систем и процессов" изложены основные теоретические положения равновесий химических реакций в металлургических системах, включающих металлическую, шлаковую и газовую фазы, и решения практических задач. Термодинамика металлических растворов и взаимодействие в системе металл-газ даны на примерах систем медь-сера и медь-сера-кислород, вакуумного рафинирования меди и обезуглероживания хромсодержащего расплава на основе железа. На основе традиционных и новых термодинамических моделей оксидных расплавов применительно к металлургическим шлакам (ионные и полимерные ионные модели силикатных растворов) приведены расчеты активности компонентов основных и кислых шлаков. Представлены методика и результаты электрохимических измерений в оксидных расплавах и шлаках, расчеты активности оксида железа и парциальных мольных величин компонента по результатам электрохимических измерений. Рассмотрены примеры расчетов реакций между металлом и шлаком: раскисление, десульфурация и дефосфорация стали, а также распределение элементов между медью и шлаком, медным штейном и шлаком.

В главе "Кинетика гетерогенных металлургических процессов» показано использование теоретических представлений о скоростях сложных процессов взаимодействия в системах металл-шлак-газ, теории и критериев подобия для оценки коэффициентов массопереноса. Рассмотрены кинетические модели процессов обезуглероживания и окислительного рафинирования стали и задачи с использованием модельных уравнений. Изложена кинетическая модель абсорбции азота расплавами на основе железа из низкотемпературной плазмы и выполнены расчеты по уравнениям модели.

В главе «Наноматериалы» изложены основные закономерности получения наноматериалов. Приведены примеры расчетов образования зародышей при получении наноразмерных частиц, а также процессов взаимодействия с их участием.

Дополнительно к изучению теории и овладению методами физико-химических расчетов книга позволит освоить физико-химическую и металлургическую терминологию на английском языке, на котором издается большая часть периодической литературы, журналов и книг по металлургии. В конце книги имеется англо-русский словарь терминов.

INTRODUCTION

The most important applications of thermochemistry and thermodynamics in metallurgy are determination of **energy balances** and **equilibrium properties** of whole reaction systems or their crucial parts in order to derive **energy and material requirements and optimal thermomechanical and chemical conditions** for processes.

Real metallurgical (chemical) processes are quite rarely isothermic, i.e. take place at constant temperature. The most common and convenient simplification for thermochemical processes is, however, an isothermal one. Another useful and common approach is isobaric as most metallurgical processes take place at constant pressure, which often is atmospheric. The overwhelmingly most common thermodynamic abstraction for metallurgical processes is to treat them as a single isobaric-isothermic process or as a set of isobaric-isothermic processes. In some cases isochoric i.e. constant volume approach is the most proper one as for processes taking place in closed pressurized chambers (autoclaves) or extremely rapid, explosionlike reactions.

Industry processes are either 1) continuous, steady-state processes which means that physicochemical and thermodynamic properties of the reaction system will vary along the length of a reactor but not with time. 2) nonsteady-state, batch processes in which the charge is treated in one stage and its composition and temperature are continuously changing.

The final properties of the reaction system are often decisive and it is often enough to carry out the thermochemical and thermodynamic analyses only for the final (and initial if necessary) state of the process. All isobaric or isochoric continuous or batch processes can also be presented as a series of separate nonisothermal thermomechanical and isothermal chemical changes. So, isothermal thermodynamic analysis can be employed almost without restriction to the nonisothermic metallurgical processes.

There are available several computer programs for computing thermomechanical effects and equilibrium compositions of high temperature reaction systems. However, as the main task of this book is to help students to understand and apply physical chemistry as a tool for solving problems in metallurgy and material technology the exercises in this book are aimed mainly for manual computing.

Theoretical analyses of many metallurgical processes include thermodynamic calculations of interactions in slag-metal liquid systems. Activities of slag components should be calculated previously.

Liquid slag is considered as an ionic solution. By comparing it with real liquid slags one can find out the reasons for deviations and create more complex models: polymeric models of silica melts, models of regular ionic solutions for basic and acid slags. These models are discussed below. There are some complicated models of subregular oxide solutions (Lumsden and Shiro-Banya models), which are not given in this book. The study of thermodynamic models allows to approach critically one or another model for calculation of the component activities of a slag, to determine and to specify model parameters on the base of phase diagrams and electrochemical measurements in slags.

Kinetic calculations of metallurgical processes help to reveal mechanics and durations of real processes. It is of great importance to choose correct kinetic equations. In some complicated cases it is convenient to use the criteria of similarity for calculations of mass transfer coefficients. There are examples of kinetic calculations: ferrous oxide reduction from slag melts by solid carbon, kinetic models of steel decarburization process and steel oxidizing refining process and nitrogen absorption by melts from low temperature plasma.

1. THERMOCHEMISTRY

1.1 SHORT BASIS OF CALCULATION OF ENERGY BALANCES

Thermochemical analysis and calculations are employed for determining energy balances of processes as whole or of their particular parts or zones in order to derive energy consumption or heat evolution and exchange with the environment (energy loss), etc. Energy balances give basis also for computation of reaction temperatures and temperature distribution in reaction environments.

A material system can exchange energy with its environment in the form of heat or work. Energy exchange take place with the expense of kinetic energy of atoms, molecules or lattice, phase transformations (solid state phase transition, melting, evaporation) and chemical reactions (including dissolution, solution formation and chemisorbtion). Energy balances are computed either for isobaric as usual or isochoric conditions.

The thermodynamic function employed in thermochemical analysis of chemical reaction systems undergoing isobaric changes is enthalpy, H . For an isochoric process energy exchange equals to the changes in internal energy, U (or E).

In **Fig. 1.1.1** the principles of an isobaric energy (heat) balance are presented schematically. The basic principle for an energy balance is: **energy and matter transferred into the system equals to the sum of the energy and matter transferred from the system in different forms and accumulated inside the system.**

There are different ways to establish an energy or heat balance even when the basis for all them is basically the same. The method presented here is based on the computation of enthalpy of input and output substances and phases relative to pure elements at some reference temperature for which frequently room temperature is chosen. Another method is to compute the physical heat contents of input and output matter, and the extents of expected chemical reactions and the heats liberated/absorbed in them. Other methods are between these two extremes. As enthalpy and internal energy are state properties there are no other restrictions for construction the heat balance but the same reference is employed for both input, output matter.

The enthalpy of a phase relative to pure elements at the reference temperature can be divided in two categories. The isobaric chemical heat content consists of heats of formation of all individual compounds present in the phase as well as heat of formation of solution (heat of mixing). The isobaric physical heat content consists of all heat absorbed in heating up the individual substances to the temperature, concerned including heats absorbed in phase transformations (solid-solid transformation, melting and evaporation).

The quantities readily available for the most common substances are **isobaric heat capacities, $C_p(T)$, standard enthalpies of phase transformations and formation of chemical compounds**. The corresponding isochoric quantities **the isochoric heat capacity function, $C_v(T)$** and the corresponding **internal energy changes (ΔU or ΔE)** can be readily computed from the isobaric ones. Several data compilations and computer databases give directly the "absolute enthalpies" of elements and compounds i.e. the sum of physical and chemical heat contents which are tabulated relative to elements at room temperature. Data for thermal effects involved in solution formation is very limited except for dilute molten or solid alloys of some common metals.

For an isobaric process, in which the heats absorbed or evolved equal to the enthalpy changes we have, accordingly

$$\Delta H_{ph} = \overset{\text{I}}{\Sigma(H_T - H_{T^\circ})_i} = \overset{\text{II}}{\Sigma n_i \int C_{p_i} dT + \Sigma n_i \Delta_{tr} H_i} \quad (1.1.1)$$

in which $(H_T - H_{T^\circ})_i$, C_{p_i} and $\Delta_{tr} H_i$ are the molar heat content, heat capacity and heat of phase transformation of an element, compound or solution, present in the input or output.

Accordingly, the first term (I) is the sum of heats absorbed by homogeneous phases in heating, the second term (II) is the sum of isothermal heats absorbed in phase transformations which take place in substances between the reference temperature and the input or output temperatures.

Chemical heat is the sum of heats of formation of compounds and solutions they form.

$$\Delta H_{ch} = \overset{\text{I}}{\Sigma n_i \cdot \Delta_f H^\circ_i} + \overset{\text{II}}{\Sigma H^{mix}} \quad (1.1.2)$$

The first term on the right side of equation is the sum of heats of formation of all compounds from elements and the second term is the sum of heats of mixing (formation of solution from its components) of all solution phases.

Pure energy (Q_p) can be transferred into the reactor or reaction zone by conduction and radiation of heat or by direct transformation of other forms of energy into heat inside the reactor - e.g. resistive, inductive, arc, plasma, electron beam heating and other methods to transform electric energy into heat. The accumulation of heat in non steady state processes may take place by direct increase of heat content of substances or with the expense of accumulation of substance in the reactor or reaction zone.

The most serious problem in calculation of energy balances for high temperature processes is often the lack of thermochemical data for solutions, heat capacities, heats of mixing, solidification, devitrification etc. Accurate values for heats of mixing for metallurgical solutions are not commonly available. In some cases they are given within the total heat content of the given molten phase measured relative to room temperature or some other reference temperature. As heats of mixing are small relative to heats of reactions they can often be neglected without causing any serious error in heat balance.

The procedure presented in the following examples for computing energy balances of isobaric processes is valid for isochoric ones when enthalpy (H) and isobaric heat capacity (Cp) functions are substituted by internal energy (U or E) and isochoric heat capacity (Cv) functions. Relations between the isobaric and isochoric thermochemical functions are as follows:

For chemical reactions

$$\Delta_r U^\circ_T \approx \Delta_r H^\circ_T - \Delta n_g \cdot RT \quad (1.1.3)$$

For heat capacities of condensed substances

$$C_v(T) \approx C_p(T) \quad (1.1.4)$$

and of perfect (ideal) gases

$$C_v(T) = C_p(T) - R \quad (1.1.5)$$

Δn_g is the change in number of moles of gaseous reaction components in reaction and R is the common gas constant = 8.314 J·mol⁻¹·K⁻¹ (1.987 cal·mol⁻¹·K⁻¹)

The first step in construction of energy balance of a chemical process is to establish a stoichiometric material balance, which gives the amounts, stoichiometric forms of substances and phases in the feed and product of process concerned. There are several ways to construct and compute an energy balance the main differences depending on the choice of reference state for substances and on the forms of available enthalpy data. It is not always reasonable to choose room temperature for the reference temperature and pure elements for the standard state of substances. If the material system includes exceptionally stable compounds, which do not undergo any chemical changes in processes concerned there is no need to compute the standard heats of formation at room temperature as they are equal on input and output side of the energy balance and cancel, accordingly, each other.

Methods to establish energy balances for high temperature processes are better visualised in the following examples.

Worked example 1

Adiabatic reaction temperature of titanium carbide synthesis

In "combustion synthesis" or "self propagating high-temperature synthesis" (SHS), ceramic materials are synthesised by applying the heat of reaction to generate high temperatures necessary to complete solid-solid reactions. For synthesis the specimens pressed from a mixture of reagent powders are placed into a reaction chamber, which is evacuated or spooled with an inert gas, the specimen is electrically ignited and the combustion reaction goes through the specimen very rapidly.

We want to know, what is the theoretical maximum temperature (adiabatic reaction temperature) which can be achieved when titanium carbide is synthesised by SHS from a stoichiometric mixture of titanium powder and carbon black? Synthesis reaction is:



Adiabatic reaction temperature corresponds to the conditions when the reaction rate is very high relative to the rate of heat transfer from the reaction zone to the environment and all heat evolved is absorbed by the reaction product. If combustion takes place in a mechanically open reactor in which the total pressure equals the atmospheric one this heat equals to the enthalpy of formation of one mole of TiC, $\Delta_f H^\circ_{298}(\text{TiC})$. The principle of calculation of adiabatic reaction temperature is schematically presented in **Fig. 1.1.2** and **table 1.1.1** in the form of simple heat balance 0.5 kg of TiC synthesised from a stoichiometric mixture of titanium powder and carbon black.

Table 1.1.1. Material & energy (heat) balance.

IN: (reagents at room temperature)					
subst.	amount		T	"phys.heat"	"chem.heat"
	kg	mol		$n_i(H_T - H_{298})_i$	$n_i \Delta_f H^\circ_{298}$
Ti(s)	0.400	8.34	298	8.34·0	8.34·0
C(s)	0.100	8.34	"	8.34·0	8.34·0
$\Sigma =$				0	0
OUT: (products at final temperature T_{ad})					
TiC	0.500	8.34	298	$8.34(H_{T_{ad}} - H_{298})$	$8.34 \cdot \Delta_f H^\circ_{298}$
$\Sigma =$				$8.34((H_{T_{ad}} - H_{298}) + \Delta_f H^\circ_{298})$	

From the material and heat balance we get the following simple equation:

$$\begin{array}{ccc}
 \text{IN} & & \text{OUT} \\
 0 = 8.34((H_T - H^\circ_{298})_{\text{TiC}} + \Delta_f H^\circ_{298}(\text{TiC})) & & \\
 0 = (H_T - H^\circ_{298})_{\text{TiC}} + \Delta_f H^\circ_{298}(\text{TiC}) & & (1.1.6)
 \end{array}$$

From Eq. 1.1.6 we get further

$$\Delta_f H^\circ + \int_{298}^{T_m} C_{p_{\text{sol}}}^{(T)} dT + r \cdot \Delta_m H^\circ_{\text{TiC}} + \int_{T_m}^{T_{\text{ad}}} C_{p_{\text{lig}}}^{(T)} dT = 0 \quad (1.1.6')$$

in which T_m and T_{ad} are the melting temperature of TiC and the adiabatic (maximum) temperature of reaction, r is the mole ratio of molten to total amount of reaction product (TiC). If $r = 0$, $T_{\text{ad}} \leq T_m$; if $0 \geq r \leq 1$ $T_{\text{ad}} = T_m$ and if $r = 1$, $T_{\text{ad}} \geq T_m$.

By introducing data compiled in the end of example into the Eq. 1.1.6' we get

$$\begin{aligned}
 & -184,100 + \int_{298}^{3290} (49.95 + 0.979 \cdot 10^{-3} \cdot T - 14.77 \cdot 10^5 \cdot T^{-2} + 1.59 \cdot 10^{-6} \cdot T^2) dT + \\
 & + r \cdot 71,100 + \int_{3290}^{T_{\text{ad}}} 62.76 dT = 0 \\
 & -184,100 + \left| \begin{array}{l} 3290 \\ 298 \end{array} \right. (49.95T + 0.979 \cdot 10^{-3} / 2 \cdot T^2 + 14.77 \cdot 10^5 \cdot T^{-1} + 1.59 \cdot 10^{-6} / 3 \cdot T^3) + \\
 & + r \cdot 71,000 + \left| \begin{array}{l} 298 \\ T_{\text{ad}} \end{array} \right. 62.76T = 0
 \end{aligned}$$

We first compute the energy needed to heat one mole of TiC up to the melting temperature in order to check the magnitude of r . Solution of Eq. 0.6' gives for r a value of 0.16. I.e. the adiabatic reaction temperature is equal to the melting temperature of TiC and 16 percent of TiC is melted. 11.5 kJ of energy released per mole of TiC in the reaction 1 is left in excess when one mole of TiC is heated up to its melting temperature whereas 71.1 kJ is needed for complete melting of TiC.

$$\mathbf{T_{\text{ad}} = 3290\text{K} = 3017^\circ\text{C}; r = 0.16}$$

Thermochemical data for calculations

$$\begin{aligned}
 \text{TiC}^1: \Delta_f H^\circ_{298} &= 4.184 \cdot (-44) \text{ J/mol} = -184,100 \text{ J/mol} \\
 \Delta_m H_{3290} &= 4.184 \cdot 17,000 = 71,100 \text{ J/mol} \\
 C_p(T)_{\text{sol}} &= 4.184 \cdot (11.939 + 0.234 \cdot 10^{-3} T - 3.531 \cdot 10^5 T^{-2} + 0.451 \cdot 10^{-6} T^2) \text{ J/mol}; \\
 C_p(T)_{\text{liq}} &= 4.184 \cdot 15 \text{ J/mol}
 \end{aligned}$$

Worked example 2

Adiabatic reaction temperature of combustion synthesis of titanium nitride

Titanium nitride is synthesised from titanium powder and gaseous nitrogen under high pressure by SHS-method. A 0.2 kg specimen loosely pressed from titanium powder is placed into a pressure chamber of 2 dm³. Reaction chamber is filled by pressurised nitrogen to 18 MPa at room temperature and the charge is electrically ignited. What would be the theoretical maximum temperature in the reaction zone and the corresponding pressure in the reactor under adiabatic conditions ?

Relation between the real process and its thermochemical model used for computing the maximum adiabatic temperature is as follows:

Heat released in the chemical reaction



is assumed to be completely absorbed by the reaction product TiN and remaining gas (N₂). As reaction takes place in a closed vessel the reaction system does not perform any work against the external pressure and thermochemical conditions of the process are isochoric. Heat of reaction which equals to the change of the internal energy of the titanium nitride formation ($\Delta_f U^\circ$) heats up the reaction product (TiN) and the remaining nitrogen gas.

The change of the mole number of gaseous species, Δn_g , is according to the reaction equation 2 equal to - 0.5. If we consider nitrogen to behave as a perfect gas even at 18 MPa the amount of nitrogen in the reaction chamber is according to the ideal gas law ($PV = nRT$) equal to $n_{\text{N}_2} = 1.8 \cdot 10^7 \cdot 0.002 \cdot 8.314^{-1} \cdot 298^{-1} = 14.53 \text{ mol}$

Table 1.1.2. Heat & Material balance

IN: (internal energy of reactants at 298K)					
subst.	amount kg/m ³	mol	T	"phys.heat" $n_i(U_T - U_{298})_i$	"chem.energy" $n_i \cdot \Delta_f U^\circ_{298}$
Ti	0.200 kg	4.184. 18..	298	4.18·0	4.18·0
N ₂	0.002 m ²	14.53	"	14.53·0	14.53·0
$\Sigma =$				0	+ 0
OUT: (internal energy of products at T_{ad})					
TiN	0.258 kg	4.18	T _{ad}	$4.18(U_{T_{ad}} - U_{298})_{\text{TiN}}$	$4.18 \cdot \Delta_f U^\circ_{298}$
N ₂		12.44	"	$12.44(U_{T_{ad}} - U_{298})_{\text{N}_2}$	5.99·0
$\Sigma =$				$4.18(U_{T_{ad}} - U_{298})_{\text{TiN}} + 12.44(U_{T_{ad}} - U_{298})_{\text{N}_2} +$	
				$4.18 \cdot \Delta_f U^\circ_{298}$	

From the energy balance $U_{in} = U_{out}$ we get

$$0 = n_{TiN} \cdot \Delta_f U_{298}^\circ + n_{TiN} (U_{T_{ad}} - U_{298})_{TiN} + n'_{N_2} (U_{T_{ad}} - U_{298})_{N_2} \quad (1.1.7)$$

and further according to Eq. 1.1.1

$$n_{TiN} \cdot \Delta_f U_{298}^\circ + n_{TiN} \left(\int_{298}^{T_m} C_v(T)_{sol} dT + r \cdot \Delta_m U_{TiN} \right) + n'_{N_2} \int_{298}^{T_{ad}} C_v(T)_{N_2} dT = 0 \quad (1.1.7')$$

where r is the molar ratio of molten to the total reaction product (TiN) and n'_{N_2} is the amount of the remaining nitrogen and $\Delta_m U_{TiN}$ is the isobaric heat of fusion of TiN.

(Notice that $\Delta_m H_{TiN} \approx \Delta_m U_{TiN}$!)

By introducing the tabulated values of thermochemical properties of reactants (from the end of this example) into Eq. (1.1.7') we get

$$4.18(-336,620) + 4.18 \left(\int_{298}^{3223} (49.83 + 3.93 \cdot 10^{-3}T - 12.38 \cdot 10^5 T^{-2}) dT + r \cdot 62,760 + \int_{3223}^{T_{ad}} 66.94 dT \right) + 12.44 \left(\int_{298}^{T_{ad}} (19.00 + 4.27 \cdot 10^{-3}T) dT \right) = 0$$

Integration gives

$$1,407,072 = 4.18 \left(\int_{298}^{3290} (49.83T + 3.93 \cdot 10^{-3}/2 T^2 + 12.38 \cdot 10^5 T^{-1}) + r \cdot 62,760 + \int_{298}^{T_{ad}} 66.94T + 12.44 \int_{298}^{T_{ad}} (19.00T + 4.27 \cdot 10^{-3}/2 T^2) \right)$$

The solution of equation gives for the adiabatic reaction temperature

$$T_{ad} = 2863K = 2590^\circ C$$

When inserting the values $V = 0.002 \text{ m}^3$, $n_{N_2} = 12.44 \text{ mol}$, $R = 8.314 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $T_{ad} = 2863 \text{ K}$ to the state equation of ideal gas $PV = nRT$ we get for pressure corresponding to fully adiabatic conditions

$$P_{ad} = 12.44 \cdot 8.314 \cdot 2863 / 0.002 = 162 \text{ MPa} (= 1597 \text{ atm})$$

As the time for combustion wave to propagate through the specimen may be few seconds, a substantial part of the heat evolved will be transferred to the walls of reaction chamber and the mean temperature of nitrogen gas will be markedly lower than the adiabatic temperature. The actual pressure prevailing in the chamber after the completion of combustion will, accordingly, not reach the level of the calculated pressure value.

Thermochemical data used for calculations:

$$\begin{aligned} \text{TiN: } \Delta_f H_{298}^\circ &= 4.184(-80,750) \text{ J/mol} = -337,860 \text{ J/mol} \\ \Delta_m H_{3223} &= 4.184 \cdot 15,000 \text{ J/mol} = 62,760 \text{ J/mol} \\ C_p(T)_{\text{sol}} &= 4.184(11.91 + 0.94 \cdot 10^{-3} T - 2.96 \cdot 10^{-5} T^2) \\ C_p(T)_{\text{liq}} &= 4.184 \cdot 16 = 66.94 \text{ J/mol} \end{aligned}$$

From the given isobaric functions we get the corresponding isochoric ones (see Eqs. 3 to 5)

$$\begin{aligned} \Delta_f U_{298}^\circ &= -337,860 - (-0.5) \cdot 8.314 \cdot 298 = -336,620 \text{ J/mol} \\ C_v(T)_{\text{sol}} &\approx C_p(T)_{\text{sol}} = 49.83 + 3.93 \cdot 10^{-3} \cdot T - 12.38 \cdot 10^{-5} \cdot T^2 \text{ J/mol} \\ C_v(T)_{\text{liq}} &\approx C_p(T)_{\text{liq}} = 66.96 \text{ J/mol} \end{aligned}$$

$N_2(g)$: $C_p(T) = 4.184(6.66 + 1.02 \cdot 10^{-3} T) \text{ J/mol}$, and for corresponding isochoric heat capacity (Eq. 5)

$$C_v(T) = 27.61 + 4.27 \cdot 10^{-3} T - 8.314 = 19.00 + 4.27 \cdot 10^{-3} T$$

Worked example 3

Energy balance of the deoxidation of anode copper

After oxidising refining (fire refining) oxygen content of anode is too high for electrolysis and copper should be deoxidised. Vaporised propane is one of the employed deoxidants. The main deoxidation reactions for propane are



and



We want to know if the deoxidation reaction is endothermic or exothermic and what would be the end temperature when molten copper is deoxidised with propane at 1200°C from 0.80 to 0.15 wt-% of oxygen. Based on the experience from an industrial anode furnace we assume that hydrogen is consumed completely in deoxidation reaction but 1/3 of carbon passes unreacted through the melt. For simplicity we neglect the heat loss, i.e. it is presumed to be equal to zero.

As copper is not oxidising we get for the amount of oxygen in copper in the end of deoxidation period; $m_{[O]} = (0.15/100) \cdot (992/0.9985) = 1.49 \text{ kg}$. The amount of oxygen transferred from one ton of copper by hydrogen and carbon is, accordingly, $8 \text{ kg} - 1.49 \text{ kg} = 6.51 \text{ kg} = 0.407 \text{ kmol}$.

According to the reactions 4 and 5 one mole of hydrogen and carbon are consumed in reduction of one mole of oxygen. From four moles of hydrogen and three moles of carbon released in decomposition of one mole of propane one mole carbon is not reacting and accordingly, six moles of oxygen are removed from the melt by one mole of propane. This gives a value of $0.407/6 = 0.0678$ kmol/2.98 kg C_3H_8 for one ton of anode copper under the given conditions.

Initial temperature of copper, 1200°C is chosen for the reference temperature. Propane is computed to decompose at room temperature. As the final temperature was assumed to be close to the initial (= reference) temperature the constant Cp-values corresponding the reference temperature, 1473K, are used in computing the heat absorption by reaction products and copper.

Table 1.1.3. Material balance per 1 metric ton of anode copper

IN			OUT		
substance	kg	kmol	substance	kg	kmol
Cu(l)	992	15.61	Cu	992	15.61
[O]	8	0.500	[O]	1.49	0.093
$C_3H_8(g)$	2.98	0.0678			
$H_2(g)$		0.271	$H_2O(g)$		0.271
C_{gr}		0.203	$CO(g)$		0.136
			C_{gr}		0.0678

Table 1.1.4. Energy balance for one metric ton of anode copper;
Reference temperature = 1473K (1200°C)

substance i	amount kmol	Temp. K	$n_i(H_T - H_{T^0})$ kJ	$n_i \cdot \Delta H$ kJ
IN:				
Cu(l)	15.61	1473	0	0
[O]	0.500	1473	0	0.50·(-85,350)
C ₃ H ₈ (g)	0.0678	298	0	0.0678·(-103,850)
H ₂ (g)	0.271	298	$0.271 \int_{298}^{1473} C_{p(T)_{H_2}} dT$ = 0.271·(-35,584)	0
C _{gr}	0.203	298	$0.203 \int_{298}^{1473} C_{p(T)_C} dT$ = 0.203·(-22,594)	0
Σ			-14,230	49,716
OUT:				
Cu(l)	15.61	T	15.61(T-1473)C _{pCu}	0
[O]	0.093	T	0	0.093·(-85.35)
H ₂ O(g)	0.271	$\frac{1473+T}{2}$	$0.271 \cdot \frac{T-1473}{2} \cdot C_{p_{H_2O}}$	0.271·(-250.45)
CO(g)	0.136	$\frac{1473+T}{2}$	$0.136 \cdot \frac{T-1473}{2} \cdot C_{pCO}$	0.136·(-115.16)
C _{gr}	0.0678	T	0.0678(T-1473)C _{pC}	
Σ			(T-1473)(15.61C _{pCu} + 0.136C _{pH₂O} + 0.0678C _{pCo} + 0.0678C _{pC})	-91,471
Heat loss				0

From the heat balance we get the following equation interconnecting the amount of heat released in chemical reactions at 1200°C and the amount of heat absorbed in heating up copper, carbon, carbon monoxide and water vapour up to end temperatures. Temperature chosen for computing the heat content of gaseous products (leaving the reactor continuously) is the mean temperature between the initial temperature 1473 and the end temperature T.

$$\text{IN} \quad \text{OUT}$$

$$-14,230/\text{kJ} - 49,716/\text{kJ} = \Sigma n_i(H_T - H_{1473}) - 91,471/\text{kJ}$$

$$27,525/\text{kJ} = \sum n_i(H_T - H_{1473})$$

$$27,525 = (15.61 \cdot 31.38 + 0.271 \cdot 45.78/2 + 0.136 \cdot 33.96/2 + 0.0678 \cdot 23.62)(T - 1473)$$

from which we get for the end temperature **1528K = 1255°C**

Thermochemical data

Heat capacities:

$$C_{gr}: \quad J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_p = 0.109 + 38.94 \cdot 10^{-3}T - 1.481 \cdot 10^{-5}T^2 - 17.38 \cdot 10^{-6}T^3$$

$$C_p(1473) = 23.62$$

$$H_2(g): \quad C_p = 27.28 + 3.26 \cdot 10^{-3}T + 0.502 \cdot 10^{-5}T^2$$

$$CO(g): \quad C_p(1473) = 33.96$$

$$H_2O(g): \quad C_p(1473) = 45.78$$

$$Cu(l): \quad C_p(1473) = 31.38$$

Standard heats of formation:

	$\Delta_f H^\circ / \text{kJ/mol}$	T/K	Ref.
$C_3H_8(g)$:		298	1
$H_2O(g)$:	-250.467	1473	2
$CO(g)$:	-115.164	1473	2

The standard Gibbs energy change for the reaction



$$\Delta G^\circ_4 = -20\,400 + 4.43 \cdot T \text{ cal/mol, } ^3$$

As in general $\Delta G = \Delta H - T \cdot \Delta S$, we get from the above equation an approximate value for the molar heat of formation of an infinitely diluted solution of oxygen in molten copper

$$\Delta H^\circ = -20.400 \text{ kcal} = 85.35 \text{ kJ.}$$

¹ M. Kh. Karapetyants, **Chemical Thermodynamics**. MIR, Moscow 1978.

² Barin, I., Knacke O., **Thermochemical properties of inorganic substances**. Springer-Verlag Berlin et al., 1973.

³ Sigworth, G.K., Elliot, J.F., **The Thermodynamics of dilute copper alloys**. Can.Met.Quart. 13 (1974) 3, 455-461.

Worked example 4

Energy balance of coal gasification in molten iron

In some new developments for coal gasification molten, high carbon iron is applied as the reaction environment for gasification reactions (e.g. Molten Iron Puregas or MIP-process). Oxygen and coal powder are blown into the iron melt. Desulphurisation can be performed by blowing lime powder into the reactor with oxygen used for gasification sulphur being absorbed in highly basic slag. Extra heat can be absorbed with by water, hydrocarbons or lime injected into the melt. In order to determine consumption of cooling agent one has to establish a heat balance for the reactor.

Principles of coal gasification reactor are described schematically in **Fig. 1.1.3**. Pulverised coal with lime powder and pure oxygen are injected into molten iron through bottom tuyeres or top lances. Coal is thermally decomposed to carbon and volatile species, carbon is dissolved in the iron melt, coal gangue reacts with lime and forms a basic slag which also absorbs the major part of sulphur. Carbon reacts in molten iron with oxygen and water vapour and is converted into carbon monoxide. Slag is continuously or timely tapped and stored. Steam is used in this example for balancing the heat generated in carbon conversion.

The main processes are, accordingly:

1. Coal cracking reactions, which release carbon, hydrocarbons, hydrogen, carbon monoxide, nitrogen and sulphur;
2. Dissolution of carbon
$$\text{C(s)} = [\text{C}]_{\text{Fe}} \quad 6$$
3. Oxidation of dissolved carbon by oxygen
$$\text{O}_2(\text{g}) + 2[\text{C}]_{\text{Fe}} = 2\text{CO}(\text{g}) \quad 7$$
and water vapour
$$\text{H}_2\text{O}(\text{g}) + [\text{C}]_{\text{Fe}} = \text{H}_2(\text{g}) + \text{CO}(\text{g}) \quad 8$$
4. Dissolution and slagging of sulphur:
$$\text{S}_2(\text{g}) = 2[\text{S}]_{\text{Fe}} \quad 9$$
$$[\text{S}]_{\text{Fe}} + \text{CaO}(\text{s}) = (\text{CaS})_{\text{slag}} + [\text{O}]_{\text{Fe}} \quad 10$$

The main task in establishing a heat balance is to determine the oxygen to cooling agent ratio. The work temperature of the reactor is 1500°C.

Following specifications and simplifications are committed for establishing the material and energy balance for the process:

- Coal, lime and oxygen are injected at room temperature (25°C = 298K), steam at 350°C (623K);
- Process temperature is 1500°C (1773K) at which all products (gas and slag) are assumed to leave the reactor;
- Carbon content of molten iron at 1500°C is kept as 3.5 wt-%;
- Heat losses are (pilot reaction) 0.170 GJ/ton coal;
- Gangue substances react with the lime and form basic slag which absorbs all sulfur in the form of calcium sulfide. Iron losses in slag are assumed to be compensated by iron oxides fed into the reactor with coal;
- Dust formation is neglected;

- Conversion of all carbon and hydrogen bearing substances into carbon monoxide and hydrogen is complete;
- As the process is continuous it should also proceed under steady state conditions, i.e. there will be no accumulation of materials or heat inside the reactor, and temperature and material distribution within the reactor will not change with the time.

Calculation of the material balance

Compositions and quantities of reactant materials are given in **Table 1.1.5**. Material balance for 1 metric ton of coal presented in **Table 1.1.6** is established on the base **Table 1.1.5** according to the specifications and simplifications given above.

Table 1.1.5. Compositions and quantities of input materials (coal, lime, steam and oxygen gas) per 1 metric ton of coal

Substance	C	H*	N	O*	S	H ₂ O	Al ₂ O ₃	SiO ₂	Fe	Ca O	O ₂	N ₂
	kg	kg	kg	kg	kg	kg	kg	kg	kg	kg	m ³	m ³
Coal/ 1000 kg	87	30	10	30	8	?	31	41	3.5	-	-	8.01
Lime/ 86 kg										86		
Transp gas/80m ³ (NTP)												80
Steam/ kg(350° C)						Z(?)						
Oxygen/ m ³ (NTP)											Y(?)	
Total:	87						31	41	3.5	86		88.0
	0											1

*H₂O + CH₄

**Oxygen in easily reducible compounds like H₂O and Fe-oxides

To establish a stoichiometric material balance one has to know or choose the chemical (mineralogical) composition of input and output substances and phases. It was assumed here that hydrogen, oxygen and sulphur are present in coal as methane, water and element sulfur. Material balance in kg per metric ton of coal is presented in **Table 1.1.6**. The chosen chemical forms substances in coal gangue and cooled slag are listed in **Table 1.1.7**, the choice being more or less arbitrary. The stoichiometric material balance is presented in **Table 1.1.8**.

Calculation of the heat balance

Physical and chemical enthalpies of gaseous components are computed using Cp functions and standard heats of formation given in **Table 1.1.10**. The chemical enthalpies of the chosen coal gangue and slag components are presented in **Table 1.1.7**. The heat content of molten slag room temperature as the standard state is computed separately (next paragraph) according to Voskoboinikov's equation for heat capacity function. The unknown amounts of oxygen and water vapour are solved from material and heat balances.

Heat content of slag

V.G. Voskoboinikov et al.⁴ has established an equation for composition dependence of heat capacity of blast furnace type slags from the measured heat contents of large number of industrial slags. Equation gives the apparent mean specific heat capacity of molten slag at 1623-1873K relative to room temperature and slag composition (ref. 4)

$$C_{293}^T = [0.63 \cdot 10^{-2} \cdot (T-293) - 2.0 \cdot 10^{-6} (T-293)^2 - 3.67 + 0.067(1 - \% \text{CaO} / \Sigma \%_{\text{ox}})] \text{ kJ/kg} \quad (1.1.8)$$

in which %CaO and $\Sigma \%_{\text{ox}}$ refer to calcium oxide content and the sum of contents of other oxides in slag, respectively, presented in weight per cent scale. For the coal gasification slag we get %CaO/ $\Sigma \%_{\text{ox}} = 0.761$ which gives at 1500°C the following value for the apparent mean specific heat capacity relative to 298K (25°C)

$$C_{293}^{1773} = 1.26 \text{ kJ/(kg} \cdot \text{K)}$$

and for the heat content of slag at 1500°C:

$$(H_{1773} - H_{298})_{\text{slag}} = m_{\text{slag}} \cdot C \cdot \Delta T = 166.5 \cdot 1.29 \cdot 1475 = 317 \text{ MJ}$$

Chemical enthalpy of gangue, slag and lime

Gangue and slag were assumed to be mainly composed of silicates. Concentrations of chosen gangue and slag forming constituents as well as their thermochemical properties at 298K are given in **Table 1.1.7**.

⁴Voskoboinikov's results cited by Onayev, I.A., **Fiz. Khim. Svoistva Shlakov Tsvetnoi Metallurgii**. Nauka, Alma-Ata, 1972.

Solving the O₂/H₂O(g)-ratio in the injection gas mixture

Steam (Z) and oxygen (Y) consumption for one metric ton of coal are solved from the heat and material balances.

Heat balance equation (from **Table 1.1.9**):

$$H_{in} - H_{out} = Q_{hl} \text{ (heat loss)}$$

$$-3117 - 230.4 \cdot Z/18 - (-5519 + 45.4 \cdot Z/18) = 179 \text{ (MJ)}$$

$$Z = 145.1 \text{ kg}$$

Oxygen (O₂) balance equation:

$$2.843 + Z/36 + Y/22.4 = 38.062 \text{ kmol}$$

$$Y = 698.6 \text{ m}^3\text{(NTP)}$$

Tables of material and heat balances and thermochemical data for calculations

Table 1.1.6. Material balance per 1 metric ton of coal

kmol	C	O ₂	N ₂	H ₂	S	Ca	Si	Al	Fe
IN									
Coal:	72.5	2.076*	.357	15.0	.249		.682	.608	.063
	0								
Lime:		.767				1.534			
Steam:		Z/36		Z/18					
Oxygen:		Y/22.4							
Transport gas:			3.569						
Σ	72.5	(2.843 + Z/36 + Y/22.4)	3.926	(15.0 + Z/18)	.249	1.534	.682	.608	.063
OUT:									
Slag:		1.812*			.249	1.534	.682	.608	.063
166.5kg									
Gas:	72.5	36.25	3.926	(15.0 + Z/18)					
		(in CO)							
Σ	72.5	38.062	3.926	(15.0 + Z/18)	.249	1.534	.682	.608	.063

*the total oxygen calculated as O₂

Table 1.1.6'. Composition of the product phases presented in the form of single compounds

Slag:	CaO	SiO ₂	Al ₂ O ₃	FeO	CaS	tot	
	72	41	31	4.5	18	166.5	/kg
	43.2	24.6	18.6	2.7	10.8	100	/wt-%
	49.7	26.4	11.8	2.4	9.7	100	/mol-%
Gas:	CO	H ₂	N ₂				
	72.5	15+Z/18	3.926	/kmol			

Table 1.1.7. "Chemical enthalpies" (standard Gibbs energies of formation) of coal gangue and slag at 298K (formation from elements)⁵

Compound	$\Delta_f H^\circ_{298}$ kJ/mol	IN/OUT	quantity y kmol	heat MJ
CaO(s)	-636	IN	1.534	-976
		OUT	-	-
CaS	-482	IN	-	-
		OUT	0.249	-120
SiO ₂ (s)	-904	IN	0.043	-39
		OUT	-	-
Al ₂ O ₃ ·2SiO ₂	-3380	IN	0.304	-1028
		OUT	-	-
3Al ₂ O ₃ ·2SiO ₂ (s)	-6830	IN	-	-
		OUT	0.004	-27
2CaO·SiO ₂ (s)	-2310	IN	-	-
		OUT	0.351	-811
2FeO·SiO ₂ (s)	-1485	IN	0.031	-46
		OUT	0.031	-46
2CaO·Al ₂ O ₃ ·SiO ₂ (s)	-4005	IN	-	-
		OUT	0.292	-1169
		IN		-2089
		OUT		-2173

⁵ Babushkin et al. **Thermodynamics of silicates**. Springer-Verlag, Berlin, 1985.

Table 1.1.8 The stoichiometric material balance: kmol/ton coal

Subs.	C	CO	H ₂	H ₂ O	CH ₄	O ₂	N ₂	S	CaS	CaO	SiO ₂	Al ₂ O ₃	3Al ₂ O ₃	2CaO	2FeO	2CaO	
												2SiO ₂	2SiO ₂	SiO ₂	SiO ₂	Al ₂ O ₃	SiO ₂
IN																	
Coal:	65.94			1.88	6.56		.36	.249			.043	.304					.031
Lime:										1.534							
Oxygen								$\frac{Y}{22.4}$									
:																	
Steam:				Z/18													
Transp. gas:								3.57									
Σ	65.94			1.88+	6.56		3.93	.249		1.534	.043	.304					.031
				Z/18			$\frac{Y}{22.4}$										
OUT																	
Slag:									.249				.004	.351	.031	.292	
Gas:	72.5	15.0+					3.93										
		Z/18															