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Executive Summary

This report outlines experimental and analytical procedures for the characterisation of chemically active materials in solar fuel production cycles. The procedures were developed as part of Task 8.1 - Tests procedures to assess the performance of materials for solar fuel production. The work at ETHZ focused on developing procedures for kinetic characterization of the reversible redox reactions utilized in two step thermochemical fuel production cycles. The procedures are based on isothermal relaxation methods and include general guidelines for planning the study, performing the experiments, and analysing the data. They are presented with a number of examples which share our know-how in performing kinetic studies, identify good kinetic data, and suitably analysing the results. At ENEA the focus was on procedures for characterising the decomposition reaction of metal sulphates, which can be utilized in solar hydrogen production cycles. The procedures developed use TGA/DTA to characterize, and in particular to determine the SO_2 yield (as opposed to SO_3) without the need for downstream gas analysis. A high SO₂ yield is essential for the thermal efficiency of the cycle, and the procedure developed can be used to quickly screen metal sulphates.



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1. Test procedures for kinetic characterisation of thermochemical redox cycle materials

In this section experimental and analytical procedures are outlined for the kinetic characterization of reversible solid gas redox reactions, which are utilized in fuel production for the splitting of H_2O and CO_2 . The procedures have been developed at ETHZ and are specifically for use with TGA, which are widely available among the RIs in the consortium and in the thermochemical research community. The major sources used to develop the procedures were the classical literature on solid gas kinetics [Levenspiel, 1999], data analysis guidelines from ICTAC Kinetics Committee recommendations for collecting and performing kinetic computations on thermal analysis data [Vyazovkin *et al.* 2011 & 2014], and the authors experience in characterising redox materials. The procedures under development are based around isothermal relaxation kinetic studies. The procedures include:

- 1. Best practice experimental guidelines for obtaining the kinetic data.
- 2. Identifying good and bad kinetic data.
- 3. Data analysis methods based around the iso-conversional method and simple model fitting.

Good kinetic data refers to measuring rates which are controlled by some physical kinetic mechanism within the sample being tested, such as surface reactions, solid state diffusion, gas phase diffusion within a pellet/granule etc. Bad kinetic data refers to kinetic rates which are limited by the experimental system, such as mass transfer limitations, thermodynamic mass transfer limitations, heat transfer limitations, gas switching times etc. Guidelines for identify these regions are not easy to find in the literature and their inclusion in the procedures should be of benefit to many

¹ For thermodynamic characterization of these materials the authors have been co-operating with a similar initiative in the USA funded by the DOE and titled HydroGEN. Within this project protocols are being formulated for the thermodynamic characterization of the partial reduction metal oxides used in fuel production. Brendan Bulfin (ETHZ) has been in close contact with Ellen Stechel (Arizona State University) who is leading this project. SFERA partners had the opportunity to complete a survey about the protocols and procedures and offer their input. With this transatlantic co-operation the protocols proposed can have a larger impact on this field of research.



researchers in this field.

In this report we outline the experimental procedure in quite general terms, before showing a number of examples, together with analysis of results and finally we summarise the overall procedure for the experimental and data analysis steps.

1.1. Experimental measurement procedures

The thermogravimetric analysis (TGA) system used to perform the experiments was a Netzsch STA 409 CD with a configuration as illustrated in Figure 1. In this system a solid sample is placed on the sample holder inside the furnace tube with a set of three mass flow controllers (MFC) that can be used to change flow and type of gas atmosphere around the sample. The sample holder is connected to a mass balance, which is used to measure the exchange of mass between the gas and the sample. There are certain limitations introduced by the system itself that need to be considered when analysing kinetic data. These include mass flow rates, the gas switching time as seen at the sample, and the time resolution of the data.



Figure 1. The TGA setup used to perform the kinetic analysis. The configuration of this system is important in understanding gas switching times and mass transfer effects.



There are two main options for collecting kinetic data in such a system; 1) isothermal relaxation experiments and 2) constant temperature ramp experiments [Vyazovkin *et al.* 2011, 2014]. The kinetic procedures elaborated here use the isothermal relaxation route, as the data collected is much easier to analyse. Constant temperature ramp kinetic experiments are difficult to interpret because of the number of changing variables. The following properties all change with temperature: thermodynamic equilibrium, gas phase diffusion coefficients, gas concentrations and flow rates, and of course the intrinsic kinetics of the sample. Rapid heating rates also introduce errors in the temperature measurement due to thermal inertia of the sample. For these reasons there are many sources in the literature cautioning against the use of constant temperature ramp kinetic experiments [Šesták 2015].

The basic principle of isothermal relaxation kinetics is to bring a sample to constant temperature and then switch the gas environment to induce a reaction. The sample is then not in equilibrium with the gas phase and will begin to undergo a reaction until equilibrium is reached. The materials we look at in this study undergo reversible redox reactions, where oxygen is the species exchanged between the solid and gas phases, as in the generic reactions;

$$MO_{\rm x} \leftrightarrow MO_{{\rm x}-\delta} + \frac{\delta}{2}O_2,$$
 (1)

$$\delta H_2 + MO_x \leftrightarrow MO_x + \delta H_2 0.$$
⁽²⁾

There are many applications which make use of such reversible redox reactions; chemical looping process [Lou *et al.* 2018], oxygen separation [Vieten *et al.* 2016], thermochemical heat storage [Carillo *et al.* 2019], and thermochemical fuel production [Romero & Steinfeld 2012]. The reactions can release stoichiometric amounts of oxygen as in the case of many transition metal oxides, for example copper oxide,

$$2\mathrm{Cu}0\leftrightarrow\mathrm{Cu}_20+\tfrac{1}{2}\mathrm{O}_2. \tag{3}$$

In this case there are two distinct solid phases which differ in their oxidation state. There are also non-stoichiometric reactions as in the case of perovskites and cerium dioxide

$$\operatorname{CeO}_2 \xrightarrow{\delta(p_{O_2},T)} \operatorname{CeO}_{2-\delta} + \frac{\delta}{2}O_2.$$
 (4)



These non-stoichiometric materials are the state of the art for thermochemical fuel production cycles [Bulfin 2017].

For the kinetic procedures we can distinguish between the oxidation and reduction reaction and consider them separately. For oxidation kinetics each kinetic experiment has three procedure steps:

- 1. The metal oxide is thermally and/or chemically reduced so that it is in the oxygen deficient state $MO_{x-\delta}$.
- 2. Under an inert atmosphere bring the sample to the desired temperature for the oxidation reaction. The temperature should be stabilized before Step 3.
- 3. Switch the gas flow from inert to the desired oxidizing gas, i.e., oxygen, steam carbon dioxide. The mass changes and gas composition can then be measured to monitor the progress of the reaction.

For reduction kinetics the procedure is very similar:

- 1. The metal should be brought to the desired oxidised state MO_x in an oxidising environment.
- 2. The sample should then be brought to the desired temperature for the oxidation reaction which typically requires an oxidising atmosphere to preserve the oxidised state. The temperature should be stabilized before Step 3.
- 3. Switch the gas flow from the oxidising gas to the desired reducing environment, which can be a sweep gas (providing low oxygen partial pressure) or a reducing gas such as hydrogen. The mass changes and gas composition can then be measured to monitor the progress of the reaction.

In both cases the conditions at, which Step 3 can take place are a crucial point in selecting the range of experimental measurements. In this step we need to switch to a state where the reactions are thermodynamically favourable and there is sufficient mass transfer to feed/take up the gas phase the reactants require/release. The equilibrium condition for the stoichiometric reactions is

$$\Delta_{\mathrm{r}}G^{\circ}(T) + \frac{1}{2}RT \ln\left(\frac{p_{\mathrm{O}_{2}}}{p^{\circ}}\right) = 0, \qquad (5)$$

where $\Delta_r G^\circ$ is the standard change in Gibbs free energy for the reaction. For the oxidation reaction to be favourable in an oxygen atmosphere we must have,





$$p_{0_2} > \exp\left(\frac{-\Delta_r G^\circ}{2RT}\right). \tag{6}$$

And for the reduction reaction to be favourable we must have,

$$p_{O_2} < \exp\left(\frac{-\Delta_{\rm r}G^\circ}{2RT}\right). \tag{7}$$

This sets some hard constraints on the range of oxygen partial pressure and temperature in which we can perform our experiments, and it can be used to select a suitable experimental range. In the case of non-stoichiometric systems, the thermodynamics also depend on the non-stoichiometry $\Delta_{\rm r} G^{\circ}(\delta)$, which actually adds a degree of flexibility to the conditions the reaction can proceed at, since the equilibrium non-stoichiometry responds elastically to the conditions. In the case of reactions with steam as in Equation 2, the equilibrium condition becomes

$$\Delta_{\rm r} G^{\circ}(T) + RT \, \ln\left(\frac{p_{\rm H_2}}{p_{\rm H_2O}}\right) = 0. \tag{8}$$

For the reduction reaction to be favourable we must have

$$\frac{p_{\rm H_2}}{p_{\rm H_2O}} > \exp\left(\frac{-\Delta_{\rm r}G^\circ}{RT}\right),\tag{9}$$

And for the oxidation reaction to be favourable we must have,

$$\frac{p_{\rm H_2}}{p_{\rm H_2O}} < \exp\left(\frac{-\Delta_{\rm r}G^\circ}{RT}\right). \tag{10}$$

Note that again this sets some constraints on the conditions of the experiments and the combination of these thermodynamic limits with the mass transfer of the system can lead to kinetic limitations [Davenport *et al.* 2017]. Here we refer to these as *thermodynamic mass transfer limitations*. These limitations are particularly interesting as they can result in apparent Arrhenius or anti-Arrhenius reaction rates, which can easily be mistaken for kinetics, but are in fact thermodynamic properties combined with the mass flow of the system.

When we select the conditions for our kinetic study, there are a number of considerations to make: (i) what are the conditions expected in the desired application, (ii) what are the thermodynamic constraints as outlined above, (iii) what do we hope to gain from the kinetic study. In applied studies we often only want an empirical kinetic model which can be used to investigate the performance in our desired



application. In such cases we should perform the kinetic study as close as possible to the conditions expected in the application, while also paying attention to thermodynamic constraints and ensuring we have *good* kinetic data. If on the other hand, we would like to learn something specifically about the intrinsic kinetics of the solid-state material and the mechanism of the reaction we can design the campaign accordingly. One method of doing so is using pure gases for the oxidation reaction, which ensures that gas phase diffusion and mass transfer effects are minimised giving the best chance of measuring intrinsic kinetics of the sample.

There are several good examples of this type of kinetic study applied to thermochemical fuel production cycles in the literature [Davenport et al. 2017, Ackerman et. Al. 2015]. In this report we show some examples and focus on the not so commonly reported *know-how* that we apply when planning and interpreting a kinetic study.

1.2. Examples

1.2.1. SrFeO₃

The perovskite oxide SrFeO3 exhibits an oxygen non-stoichiometry which depends on the temperature and partial pressure of oxygen, [Haavik et al. (2002), Holt et al. (1999), Yoo et al. (2017)]

$$\operatorname{SrFeO}_3 \xrightarrow{\delta(p_{O_2},T)} \operatorname{SrFeO}_{3-\delta} + \frac{\delta}{2}O_2.$$
 (11)

Such non-stoichiometric oxides are the materials of choice for thermochemical fuel production cycles. SrFeO3 based perovskites undergo lower temperature reduction, and have been extensively investigated as oxygen storage materials, which can be utilized in oxygen separation and production processes [Bulfin *et al.* 2019, Vieten *et al.* (2016), Bush *et al.* (2019)]. The lower temperature makes this material a very convenient choice for demonstrating the procedures.

Isothermal relaxation experiments of $\text{SrFeO}_{3-\delta}$ oxidation have shown rapid oxidation kinetics for temperatures above 673 K [Vieten et al. (2019)], where thermodynamic equilibrium was reached in approximately 1-2 min at 723 K [Bulfin et al. 2019]. However, at 523 K 300 hours was insufficient time for a dense disk of the reduced perovskite $\text{SrFeO}_{2.5}$ to reach equilibrium [Takeda et al. 1986]. These results suggest



that oxidation reaction kinetics can become a critical limitation for temperatures below 723 K.

Here we focus on the low temperature range, 450-750 K, and consider both the oxidation and reduction reactions of $SrFeO_3$. Full details of the presented kinetic studies on $SrFeO_3$ can be found in the publications by the authors [Bulfin *et al.* Jan & Nov 2020].

Oxidation kinetics - For the isothermal oxidation kinetics an 8 mm diameter pellet of SrFeO₃ weighing approximately 500 mg was prepared. In order to measure isothermal relaxation kinetics, the samples must be brought to a state where the nonstoichiometry is not at the equilibrium value. For oxidation kinetics, the samples were initially reduced under Ar 5.0 ($\approx 10^{-4} - 10^{-5}$ O₂) flow of 100 ml/min⁻¹ at 800°C. The samples were then cooled under the same Ar flow to the desired temperature, where re-oxidation is limited due to the lack of available oxygen. When the temperature has stabilised at the desired set point the gas flow is then switched to pure oxygen. The perovskite then begins to oxidise towards equilibrium and the resulting increase in mass was measured against time, giving an isothermal relaxation profile. Finally, the sample was brought to 400°C in synthetic air after each kinetic run, as a reference point. Figure 2 shows the raw TGA data for a number of these scans performed at different temperatures, where the rate can be seen to increase with temperature.



Figure 2. The TGA data of the isothermal oxidation relaxation kinetics of $SrFeO_3$ showing temperature, oxygen partial pressure and mass changes vs. time.



The procedure was repeated for temperatures in the range 450-750 K, to obtain a broad range of data. In order to analyse such data, it is convenient to use the conversion extent X, given by,

$$X = \frac{\delta_0 - \delta(t)}{\delta_0 - \delta_\infty}.$$
 (12)

where δ_0 is the non-stoichiometry at time zero and δ_{∞} is the equilibrium value which the reaction is converging upon. We then have $X \in (0,1)$ where 0 corresponds to no reaction having taken place and 1 means we have reached chemical equilibrium. A quick check of the effect of temperature on the oxidation reaction can be obtained by looking at the half-time of the reactions defined by, $X(t_{1/2}) = 0.5$.



Figure 3. The half-time plotted against $\frac{10^3}{RT}$, on a logscale to show the temperature dependence. The dashed grey line encloses the good kinetic data, that is suitable for further analysis.

From Figure 3 we can see that below 550 K, which is the data highlighted by the grey dashed line, the half-time shows a very strong temperature dependence, which is a good indication that we are measuring actual kinetics. Above 550 K the temperature dependence becomes much less steap. The half-time in this region is around 10 seconds for the 500 mg pellet. The total mass change to reach the X = 0.5 is on the order of 5 mg or 1.56×10^{-4} mol of O_2 , and the oxygen supply rate of 100 ml min⁻¹ corresponds to 7.34×10^{-5} mol s⁻¹ of O_2 . So, the minimum half-time by



mass transfer limitations is just over 2 seconds. Given that the gas switching time in this system is around 20 seconds [Bulfin *et al.* Jan 2020 - ESI], we conclude that the kinetics above 550 K are controlled by physical limitations of the experimental apparatus, *i.e.*, gas supply rate and the time it takes for the sample to see a complete switch from argon to oxygen.

We can analyse the *good* data above 550 K by assuming that the kinetics obey a general reaction,

$$\frac{dX}{dt} = c_{0_2}^n k(T) f(X), \tag{13}$$

and further that the temperature dependence is Arrhenius,

$$k(T) = k_0 \exp\left(\frac{-E_a}{RT}\right). \tag{14}$$



Figure 4. Left: Conversion extent X vs. time for temperatures in the range 453-553 K in steps of 10 K. Right: Plots of $\frac{dX}{dt}$ vs. $\frac{10^3}{RT}$ at fixed X which yield the activation energy as the slope of the lines.

The iso-conversional method can then be applied to determine E_a as shown in the right-hand side of Figure 4. It is important again to exclude rate data from these fits that takes place during the gas switching time, which was estimated to be the first 20 seconds for this system. On the right-hand side of Figure 4 we can see that the slopes at all values of conversion extent are similar and activation energy was found to be $E_a = 92 \pm 17$ kJ mol⁻¹. Since the kinetics were performed in pure oxygen, the rate



should not be limited by any gas phase transport, and this apparent activation could be related to an intrinsic property of the material. Further analysis of other samples led us to conclude that solid phase diffusion of oxygen was the rate limiting step in this case. The data was also fit with a simple model $f(X) = (1 - X)^m$ to fully describe the kinetic rates.

Reduction kinetics - For the reduction reaction the non-equilibrium state required for relaxation kinetics was achieved only by switching the gases. The samples were brought to the desired temperature set point in a pure oxygen flow of 200 ml min⁻¹, giving $p_{0_2} \approx 1$ bar. When the temperature had stabilised the gas, flow was then switched to 190 ml min⁻¹ Ar and 10 ml min⁻¹ synthetic air (20% O₂) giving $p_{0_2} \approx 0.01$ bar. The more reducing atmosphere will cause the sample to lose oxygen, proceeding towards equilibrium with the resulting decrease in mass measured against time. Finally, the samples were brought to 450°C in pure oxygen after each kinetic run, as a reference point.



Figure 5. The TGA data of the isothermal reduction relaxation kinetics of $SrFeO_3$ showing temperature, oxygen partial pressure and mass changes vs. time.

The reduction kinetics were measured at isothermal conditions by switching the atmosphere from pure oxygen to a 1% oxygen in inert gas mixture. A temperature range 573-723 K at intervals of 25 K, was found to yield good kinetic data, with a



strong temperature dependence as seen in Figure 5. Below 573 K the kinetics were becoming too slow to measure and above 723 K the half-time was approaching $t_{1/2} < 20$ s, where gas switching at the sample will begin to play the major role in the rates measured.



Figure 6. Conversion extent X vs. time for temperatures in the range 573-723 K in steps of 10 K. Right: Plots of $\frac{dX}{dt}$ vs. $\frac{10^3}{RT}$ at fixed X which yield the activation energy as the slope of the lines.

We can further analyse the data by assuming that the kinetics obey a general reaction,

$$\frac{dX}{dt} = k(T)f(X),\tag{15}$$

and further that the temperature dependence is Arrhenius,

$$k(T) = k_0 \exp\left(\frac{-E_a}{RT}\right).$$
(16)

In this case the dependence on oxygen concentration is dropped as we are looking at the rate at which oxygen leaves the sample. On the right-hand side of Figure 6 we can see that the slopes at all values for conversion extent are similar and activation energy was found to be $E_a = 144 \pm 16 \text{ kJ mol}^{-1}$. We conclude that the kinetic regime for the reduction reaction is different from the oxidation reaction, with a much larger energy barrier, and by process of elimination it must be surface reaction controlled.

Oxidation at lower p_{0_2} - SrFeO₃ has excellent potential in oxygen separation



processes, where it can effectively remove trace oxygen to very low partial pressures. In a recent study, we showed that when combined with pressure swing adsorption it can offer a promising route to high purity nitrogen production from air [Bulfin *et al.* Nov 2020]. For oxygen as a dilute gas in nitrogen the kinetic regime could be quite different to that seen above due to a more complex mass transfer in the gas phase within and around pellets/granules. Therefore, an isothermal relaxation kinetic study was performed for the oxidation of an SrFeO₃ pellet at T_{ox} = 623 K, under various oxygen concentrations.



Figure 7. The TGA data of the isothermal oxidation relaxation kinetics of $SrFeO_3$ showing temperature, oxygen partial pressure and mass changes vs. time.

For this study, an 8 mm diameter pellet weighing 800 mg was prepared and placed in the TGA. For the relaxation study the pellet was first reduced at the conditions proposed in the process; 873 K under a gas flow with an oxygen partial pressure of $p_{0_2} = 0.01$ bar. The pellet was then cooled to 623 K and oxidised under different oxygen partial pressures in the range 1 – 0.01 bar, as shown in Figure 7. To analyse the data, we no longer look at temperature dependence but rather oxygen concentration. First, we verify that the rates are not mass transfer limited, i.e., $\frac{dm}{dt} \ll \dot{n}_{0_2} M_{0_2}$. We can then analyse the data by assuming that the kinetics obey a general reaction,

$$\frac{dx}{dt} = k \ c_{O_2}^n (1 - X)^m. \tag{17}$$



Figure 8. Left: Conversion extent X vs. time for oxygen partial pressures in the range 0.01-1 bar. Right: Plots of $\frac{dX}{dt}$ vs. 1 - X at fixed to determine the value of m.

A log-log plot of $\frac{dx}{dt}$ vs. 1 - X should then yield lines with slope *m*. This can be seen in the right side of Figure 8 where at low partial pressures (0.1 - 0.01) we can see that the data all have similar slopes of approximately m = 0.8. However, as we increase the partial pressure above 0.1 the slope becomes steeper giving a larger *m*, which indicates that the reaction regime is changing. This is reasonable as when we approach pure oxygen, the nitrogen gas is no longer present as a 'blocking species', and gas phase transport can take place via pressure gradients, rather than dilute species diffusion. To obtain a kinetic model suitable for modelling the application we therefore limit our model fitting to oxygen partial pressures below 0.2 bar. This data was then fit and used in development of a validated reactor model for this process [Bulfin *et al.* Nov 2020].

$1.2.2. CuO/Cu_2O$

A good example which can be used to highlight thermodynamic mass transfer limitations is that of the copper oxide redox cycle. This material undergoes stoichiometric reduction,

$$2\mathrm{Cu}0\leftrightarrow\mathrm{Cu}_20+\frac{1}{2}\mathrm{O}_2,\tag{18}$$

and has been investigated for thermochemical heat storage [Gigantino et al. 2020]. The



thermodynamics of the stoichiometric reduction reaction must be taken into account when planning the study. The reduction kinetics of this material offer a good example of thermodynamic mass transfer limitations in kinetics. For the reduction reaction we have the equilibrium condition,

$$p_{O_2,eq} = \exp\left(\frac{-\Delta_r G^\circ}{2RT}\right).$$
 (19)

We can achieve this at isothermal conditions switching from an oxygen containing gas with $p_{0_2} > p_{0_2,eq}$ to an inert sweep gas so that $p_{0_2} < p_{0_2,eq}$ and the reaction proceeds. An experimental plan satisfying this condition at a range of different temperatures is illustrated in Figure 9.



Figure 9. A plot of $p_{0_2,eq}$ vs. T where the experimental plan with the starting point and the set point used to induce non-equilibrium and perform a relaxation kinetic experiment at a number of temperatures.

This equilibrium condition also puts a constraint on the maximum possible rate of the reaction, as oxygen can only leave the sample up to a partial pressure of $p_{O_2,eq}$. We have a sweep gas flow to carry away the oxygen and the maximum oxygen flow rate is obtained limited by the equilibrium partial pressure of oxygen giving,



$$p_{\rm O_2,eq} = \frac{n_{\rm O_2,max}}{n_{\rm sweep} + n_{\rm O_2,max}} p.$$
(20)

Rearranging gives

$$\dot{n}_{0_2,\text{max}} = \dot{n}_{\text{sweep}} \frac{p_{0_2,\text{eq}}}{p - p_{0_2,\text{eq}}},$$
 (21)

This gives a maximum rate of mass loss given by

$$\left(\frac{dm}{dt}\right)_{\max} = \dot{n}_{\text{sweep}} \frac{p_{\text{O}_2,\text{eq}}}{p - p_{\text{O}_2,\text{eq}}} M_{\text{O}_2}.$$
(22)

Note that the partial pressure has an exponential dependence on temperature so that this rate limitation will appear very similar to an Arrhenius type rate dependence.



Figure 10. A plot of $\frac{dm}{dt}$ vs. T where showing the theoretical mass transfer limitation according to Equation 22, experimental data at a range of conversion extents.

However, this rate limitation is independent of kinetics and is only limited by the flow



rate of the sweep gas. Figure 10 shows experimental data for CuO based granules according to the study plan described in Figure 10. It can clearly be seen that the measured rates follow closely this thermodynamic mass transfer limitation. We should not further analyse this data as it is only dependent on the thermodynamics and the gas flow rates. We could conclude that in a practical application at these conditions the reaction would likely be limited by heat and/or mass transfer within the system.

1.3. Summary of procedures

Here we summarise the procedure for performing isothermal relaxation kinetic studies of the reversible redox cycles of a metal oxide,

$$MO_{\rm x} \leftrightarrow MO_{{\rm x}-\delta} + \frac{\delta}{2}O_2.$$
 (23)

Planning the study – An initial plan for which conditions to perform the relaxation kinetics can be made by following some simple steps:

- 1. Use the thermodynamics of the reactions to identify a suitable condition for the experimental analysis. The gas switching step must make the reactions thermodynamically favourable. See Figure 9 for an example of this.
- 2. If the study is to gain insight on intrinsic material kinetics, pure gases should be used for the oxidation reactions. If the study is aimed at developing an empirical kinetic model for an application, then the study should be performed as close to the applications operating conditions as possible.

As can been for $SrFeO_3$ above, the study in pure oxygen was not suitable for modelling the behaviour of this material in a trace oxygen separation process. A different kinetic regime was seen at lower oxygen concentrations which highlights the importance of choosing the correct study conditions.

Identifying good and bad data - When the study is complete there are a number of things to check to ensure that we are analysing good kinetic data.

 Determine the gas switching time as seen at the sample in the system. This depends on MFC response times, and diffusion along the flow. See Bulfin *et al.* Jan 2020 for an approximate method for calculating this time. Data obtained



within the gas switching time should be omitted from the analysis.

- 2. For oxidation reactions check for mass transfer limitations i.e., $\frac{dm}{dt} \sim \dot{n}_{O_2} M_{O_2}$. A quick experimental test is to change the flow rate \dot{n}_{O_2} and if this proportionally (or significantly) changes the rate then the kinetics are mass transfer limited.
- 3. Check for thermodynamic mass transfer limitations, *i.e.*, $\frac{dm}{dt} \sim \dot{n}_{sweep} p_{O_2,eq}(T)$ for reduction or $\frac{dm}{dt} \sim \dot{n}_{O_2}(p p_{O_2,eq}(T))$ for oxidation. Again, a quick experimental test is to change the flow rate of the sweep gas or the oxidation gas and if this changes the rate of reaction proportionally then the kinetics are mass transfer limited. It is important to be aware that these types of limitations can show Arrhenius like dependence.
- 4. A log-log plot of $t_{1/2}$ vs. 1/RT can be useful in identifying changes in rate limiting regime. For example, from kinetic controlled to mass transfer controlled. Or from one rate limiting mechanism to another.

Finally, when the *good* data has been identified it can be analysed using the iso-conversional method, and suitable empirical models can be fit to the data [ICTAC].

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2. Test procedures for characterising the decomposition of metal sulphates

In the SFERA III WP8 framework, ENEA is involved in the thermodynamic and kinetic analysis of metal sulphur compounds decomposition. Given that the purpose of the task is to develop "performance testing of materials used in solar fuel production reactors, in terms of stability, thermodynamic and kinetic performance", it was settled to share the measurements protocols and to the test solid materials used as intermediate species in thermochemical water-splitting cycles (WSTC). In this respect, ENEA agreed to test metal sulfates used as oxygen source in WSTC presenting a maximum temperature of 900°C. In literature the experimental works on sulfates decomposition are mostly focused on sulfates conversion into the corresponding oxides through TGA analysis, not detecting and distinguishing the produced SO_2 and/or SO_3 [Mu *et al.* 1981]. In water-splitting cycles based on sulfates, the yield of the sulfate decomposition into SO_2 and O_2 , and consequently the cycle thermal efficiency, can only be evaluated by distinguishing the produced SO_2/SO_3 gases.

The sulphate decomposition into the corresponding oxide, sulphur dioxide and oxygen, is part of a cyclic process proposed by ENEA [Prosini *et al.* 2008, Giaconia *et al.* 2009, Prosini *et al.* 2009], based on the Sulphur-Iodine cycle, aimed at hydrogen production via water splitting, where the H_2O molecule is converted into hydrogen and oxygen by using recyclable and inorganic compounds as intermediates; this process basically consists of two separate sections, the sulphuric and hydriodic sections, where, respectively, oxygen and hydrogen are produced.

More in detail, to reduce the temperature level of the endothermic reactions and facilitate the subsequent separation processes, an intermediate metal oxide was adopted by ENEA; the metal oxide is reacted with sulphuric acid to produce the correspondent metal sulphate, which, in turn, is decomposed into sulphur dioxide and oxygen.

The objectives of the procedure here proposed for evaluating sulfates conversion into SO_2 in absence of detection of evolving gases (SO_2/SO_3) are:



- building a database of different sulfates, ranked on the base of their SO₂ generating «efficacy»;
- ii) describing the SO₂ generating efficacy in terms of semi-empirical kinetics parameters, obtained through the fitting of experimental DTA/TGA curves and following a simplified approach («integration» approach), regardless of the rigorous kinetics of the sulfate decomposition.

The procedures here proposed to determine the thermodynamic properties of this reactive system were carried out by thermo-gravimetric analysis TGA/DTA.

2.1. Theoretical aspects

The so named Sulphur-Iodine (S-I) cycle can be considered as one of the most studied thermochemical process in the scientific literature, and is schematically composed of the following reactions:

| S-I cycle |
|---|
| Bunsen reaction (exothermic, T: 80-120°C): |
| $2H_2O_{(l)} + x/2 I_{2(l)} + SO_{2(g)} \rightarrow H_2SO_{4(aq)} + 2HI_{(aq)}$ |
| Hydriodic acid decomposition (endothermic, T: 300-450°C): |
| $2\mathrm{HI}_{(\mathrm{aq, g})} \mathrm{I}_{2(\mathrm{g})} + \mathrm{H}_{2(\mathrm{g})}$ |
| Sulfuric acid decomposition (endothermic, T: 800-900°C): |
| $H_2SO_{4(aq)} \rightarrow H_2O_{(g)} + SO_{3(g)} \rightarrow H_2O_{(g)} + SO_{2(g)} + \frac{1}{2}O_{2(g)}$ |

In order to avoid the use of halogenated species in the cycle, several alternatives have been proposed in the literature over the years. A first one is the well-studied "Westinghouse" cycle, where an electrochemical step is present:

| Westinghouse cycle |
|---|
| Cathodic production of hydrogen: |
| $2H_2O_{(l)} + SO_{2(g)} \rightarrow H_2SO_{4(aq)} + H_{2(g)}$ |
| Sulfuric acid decomposition (endothermic, at 800-900°C): |
| $H_2SO_4(aq) \rightarrow H_2O(g) + SO_3(g) \rightarrow H_2O(g) + SO_2(g) + \frac{1}{2}O_2(g)$ |



Another, presumably less studied, but, in any case, potentially very interesting process, involves a photocatalytic hydrogen production step:

| Photocatalytic production of hydrogen from ammonium sulphite |
|---|
| Photocatalytic production of hydrogen: |
| $(NH_4)_2SO_3 + H_2O \rightarrow (NH_4)_2SO_4 + H_2$ |
| Ammonium sulphate decomposition: |
| $(NH_4)_2SO_4 \rightarrow 2 NH_3 + H_2SO_4$ |
| Sulfuric acid decomposition (endothermic, at 800-900°C): |
| $H_2SO_{4(aq)} \rightarrow H_2O_{(g)} + SO_{3(g)} \rightarrow H_2O_{(g)} + SO_{2(g)} + \frac{1}{2}O_{2(g)}$ |
| Ammonium sulphite formation: |
| SO_2 + 2 NH ₃ + H ₂ O \rightarrow (NH ₄) ₂ SO ₃ |

It is worth noticing that, in all the processes above reported, the same identical step is present for oxygen production, namely, sulphuric acid decomposition into water and sulphur trioxide, and, in turn, SO_3 splitting into SO_2 and O_2 .

The present ENEA work focuses on a modification of this step. Though some interesting experimental activities were dedicated in the past to the development of solar reactors for sulphuric acid decomposition, the management of solar receivers operating in the presence of corrosive acid at high temperature is still a challenging issue. The proposed modified process can be schematized as following:

| ENEA modification - metal sulphur compounds decomposition | | |
|--|--|--|
| Sulphate decomposition M=Fe, Zn, Co (etc) | | |
| $M_x(SO_4)_y \to M_xO_y + ySO_2 + \frac{y}{2}O_2$ | | |
| Reaction between the obtained metal oxide and sulphuric acid | | |
| $M_x O_y + y H_2 S O_4 \rightarrow M_x (S O_4)_y + y H_2 O$ | | |
| Again, sulphate decomposition. | | |

Several oxide/sulphate components can be potentially feasible for this process and Iron compounds are considered in this report. The main requirement is the capacity for the oxide to react with sulphuric acid producing the corresponding metal sulphate,



which, in turn, must present a decomposition temperature below $1,000^{\circ}$ C. In order to strip the obtained SO₂ and O₂ from the reaction environment, air is used as carrier gas; indeed, the employment of other gases is too expensive on a large scale.

2.2. Analytical procedure

The sulphate decomposition can be considered as a two-step reaction as following:

$$MSO_4 \rightarrow MO + SO_3 \qquad \Delta H_1(T) \text{ is unknown}$$
 (24)

$$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2 \qquad \Delta H_2(T) \text{ and } \Delta G_2(T) \text{ from NIST [Stern 2020]}$$
 (25)

while the conversion *X* is defined as:

$$X = \frac{\text{molSO}_2}{\text{molSO}_3 + \text{molSO}_2}$$
(26)

From TGA/DTA analysis it is possible to measure the enthalpy of the overall decomposition ΔH_{tot} (T) at a fixed temperature T:

$$\Delta H_{\text{tot}} (T) = \Delta H_1(T) + X \Delta H_2(T)$$
(27)

Assuming a constant value for ΔH_1 (independent from temperature), the equation (27) becomes as follows:

$$\Delta H_{\text{tot}}(T) = \overline{\Delta H_1} + X \,\Delta H_2(T) \tag{28}$$

In order to correlate the conversion X to temperature, a semi-empirical approach is adopted, looking for a mathematical correlation which is based on the assumption that the 2^{nd} reaction has a first order kinetic law:

$$-\frac{dP_{SO_3}}{dt} = k P_{SO_3}; -\frac{dC_{SO_3}}{dt} = k C_{SO_3}$$
(29)

$$-\int_{C_{SO_3,IN}}^{C_{SO_3}} \frac{dC_{SO_3}}{C_{SO_3}} = \int k * dt$$
(30)

$$ln\left(\frac{C_{SO_3_IN}}{C_{SO_3}}\right) = k * t \tag{31}$$

$$X = \frac{C_{SO_3_IN} - C_{SO_3}}{C_{SO_3_IN}} = 1 - \frac{C_{SO_3}}{C_{SO_3_IN}}$$
(32)

$$ln\left(\frac{1}{1-X}\right) = k * t \tag{33}$$

$$k = Ae^{-\frac{E_a}{RT}}$$
(34)

$$X = 1 - \frac{1}{e^{(t*A*e^{-\frac{E_a}{RT}})}}$$
(35)

Through the proposed procedure the experimental DTA curve is integrated, determining ΔH_{tot} (T) and also t react, which corresponds to total sulfate decomposition time, at several temperatures. For each test, by combining Eq. 28 and 35, it is possible to obtain $\overline{\Delta H_1}$, X, and consequently the empirical parameters E_a and A by fitting (using Matlab *fsolve* function).

In the present work ENEA proposes to apply the above-mentioned procedure to investigate Iron sulfate decomposition at 625°C, 650°C, 675°C and 700°C.

2.3. Experimental measurement procedures

The onset temperature, reaction heat and time, are determined by using a thermobalance system (TGA/DSC 1, Mettler Toledo; air as carrier gas at 1 bar of pressure). The measurements are carried out setting a blank test using alumina crucibles with



no cap (70 µl), followed by a dehydration step and a series of heating ramps and isotherms on about 50 mg of $Fe_2(SO_4)_3$ for each test. Before each temperature step, the instrument is calibrated by using the melting temperatures and the latent heats of two different standards: Indium and Aluminium. The temperature program applied for each test is reported in Table 1.

| | Temperature (°C) | Temperature (°C) | time (min) | Rate (°C/min) | Air flow (ml/min) |
|-----------------------|----------------------|---------------------|---------------|------------------|----------------------|
| Dehydration | step | | 1 | | 1 |
| Ramp | 50 | 400 | | 20 | 10 |
| Isotherm | | 400 | 30 | | 10 |
| Sulfate decomposition | | | | | |
| Ramp | 400 | 625650 – 675 700 | | 100 | 10 |
| Isotherm | 625-650 – 675-700 | | 60 | | 10 |

Table 1. Temperature program for each test

2.4. Results and discussion

Following the analytical procedure described in the previous paragraph, Iron (III) sulphate was used to test the validity of the proposed method. In particular, four isothermal levels were selected (Table 1), according to experimental data obtained in previous works [Tizzoni *et al* 2015]. In all tests, after an initial step necessary to ensure the sample dehydration, it was required to reach the sulphate decomposition temperature as fast as possible. Figure 11 and Figure 12 represent, respectively, an example of TGA/DTA pattern and the numerical integration performed over the isothermal.

In fact, it was evidently needed to calculate the sulphur dioxide formation at a determined temperature, and, for this reason, the degradation before the reaching of the set point was an undesirable effect, to be minimized as much as possible. However, this issue is always present and becomes of particularly relevance especially at the higher temperatures, that is 675°C and 700°C.





Figure 11. Example of TGA/DTA analysis of the Iron sulfate decomposition. From top to bottom: thermo-gravimetric pattern, heat-flow and temperature ramp of the experiment. The test was carried out under atmospheric air, with a flow of 10 Nml/min. The first endothermic peak, from 50° C to 400° C, is related to the loss of water; the second endothermic peak represents the heat absorbed during sulphate decomposition.



Figure 12. Example of numerical integration.



Figure 13 shows the typical shapes of the endothermic peaks obtained at the four different decomposition temperatures. In any case, the peak starting point was taken at the time correspondent to the beginning of the isotherm, while the peak ending point was considered where no more mass loss was detectable. Clearly, the peaks width decreases with temperature, making easier the integration of the curves obtained at 625°C and 650°C. Actually, as described below, this is the reason for the better accuracy of the conversion values calculated over those isotherms. In order to calculate the conversion figures with a good precision, ten different experiments were carried out for each isothermal level, and both the average values and the imprecision were determined.



Figure 13. DTA analysis of the Iron sulfate decomposition: typical shapes of the endothermic peaks obtained at the four different decomposition temperatures, a)625°C, b)650°C, c)675°C and d)700°C. The tests were carried out under atmospheric air, with a flow of 10 Nml/min.

Figure 14 and Table 2 show the obtained results, that are also compared with the data presented in a previous work, where a direct measurement of SO_2 and SO_3 was performed [Tizzoni et al. 2015].





Figure 14. ΔH_{tot} (T) integrated values at several temperatures.

| Table 2. Experimental results compared with the data obtained in a previous |
|---|
| work 6 by a direct measurement of SO_2 and SO_3 [Tizzoni <i>et al.</i> 2015]. |
| |

| INPUT data | | | | | | OUTPUT data | | | |
|------------|--------|---|---------------------------|---------------------------------|--|----------------------------|-------------|-------|---------------------------------|
| Test n. | Т (°С) | ΔH _{TOT} (T)measured [kJ/mol] | t _{react} (s) | ΔH ₂ (T) [kJ/mol] | $\frac{\overline{\Delta H_1}}{[kJ/mol]}$ | E _a [kJ/mol] | A | x | X [Tizzoni el al 2015] |
| 1 | 625 | 115.22 | 281.90 | 98.180 | 170 | 274 | 1.1010 | 0.277 | |
| 2 | 650 | 166.20 | 160.50 | 98.078 | 170 | 274 | 1.10^{10} | 0.393 | 0.400 |
| 3 | 675 | 183.82 | 72.70 | 97.975 | 170 | 274 | 1.10^{10} | 0.440 | 0.440 |
| 4 | 700 | 148.41 | 4.10 | 97.770 | 170 | 274 | 1.1010 | 0.554 | - |

From Table 2 it is evident that a good accordance has been found, regarding the conversion, between the present work results and past measurements up to 675°C; the tests at 700°C show a higher error for the reaction enthalpy, likely due to the difficulty of performing a fully accurate integration of the DTA peaks obtained, as discussed above.

Analysing the obtained results, it is possible to assume that the reactions studied are under kinetic control; overall this method allows a fast semi-quantitative determination of the SO_2/SO_3 ratio without using time consuming direct analytical



methods. The results demonstrate the suitability of the TGA/DTA system for investigating the yield of inorganic steps involved in hydrogen production cycles.

2.5. Summary of procedures

The procedure here adopted can be schematized as following:

Identification of the problem:

- 1. The energy efficiency, calculated as the hydrogen LHV divided by the total heat duty, of a sulphur-based water splitting thermochemical cycle is directly related to the production rate of sulphur dioxide (and therefore oxygen), in the process highest temperature step.
- 2. Besides a direct sulphuric acid decomposition, a very interesting alternative is the formation of a metal sulphate to be used in place of H₂SO₄.

Schematically, a direct decomposition:

$$H_2SO_{4(aq)} \rightarrow H_2O_{(g)} + x SO_{3(g)} + y SO_{2(g)} + y/2 O_{2(g)}$$
 (36)

can be modified this way:

$$MO + H_2SO_4 \rightarrow MSO_4 + H_2O \tag{37}$$

$$MSO_4 \to MO + x SO_3 + y SO_2 + \frac{y}{2}O_2$$
 (38)

3. In general, a direct measurement of SO_2 or oxygen is necessary to determine the rate of sulphur dioxide produced with respect to the total decomposition products. Actually, it is possible to define a conversion parameter as following:

$$X = \frac{y}{x + y} \tag{39}$$

4. From TGA/DTA analysis it is possible to measure the enthalpy of the overall decomposition ΔH_{tot} (T) at a fixed temperature T, and to relate this value with



the conversion in SO_2 ; the sulphate decomposition can be considered as a twostep reaction as following:

$$MSO_4 \rightarrow MO + SO_3 \quad \Delta H_1(T) \text{ is unknown}$$
 (40)

$$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2 \quad \Delta H_2(T) \text{ and } \Delta G_2(T) \text{ from NIST [Stern 2020]}$$
 (41)

Assuming a constant value for ΔH_1 (independent from temperature):

$$X = \frac{\Delta \text{Htot}(\text{T}) - \overline{\Delta H_1}}{\Delta H_2(\text{T})}$$
(42)

General measurement procedure (validated as described above):

- 1. It is necessary to employ a TGA system where the sensor is equipped with thermocouples in order to allow calorimetric measurements;
- 2. If the sensor does not permit a direct comparison with a reference empty crucible, it is preliminary required to perform a blank test, employing the same crucible eventually used for the sample with the same temperature method.
- 3. The heat flow obtained with the blank is subtracted to the one obtained with the sample. This peak is used to calculate the decomposition heat (ΔH_{tot});
- 4. To integrate the peak obtained in step 3, it is necessary to define its starting and ending points. The former is set considering the time at which begins the isotherm; the latter corresponds to the point at which no more mass loss is detectable (from TGA curve analysis).
- 5. At least ten experiments must be carried out at each isotherm, and the inaccuracy can be estimated as the double of the standard deviation for the average values.



2.6. References

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