Introductory Lecture 2:

Solar Driven Chemistry

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Biomass, coal, mineral oil are the natural storage materials of solar energy; they are produced via the photochemistry of photosynthesis. In combination with atmospheric oxygen the conserved chemical energy can be released. At present more than 90% of the world's primary energy demand is provided by such solar chemical resources. – The thermodynamic basis of the production of «artificial» chemical fuels is examined by solar process heat driven thermochemistry, by solar photon flux driven photochemistry, and by electrochemical processes using electric energy from solar thermal power generation or from photovoltaics. «Solar fuels» such as hydrogen, «solar chemicals» such as cement, «solar specific reactions» such as detoxification are discussed in this tour d'horizon.

Rudolf Sizmann: Born 1929 in Holland. Dr. rer. nat. in chemistry 1956. After working in chemical industry, 1962 habilitation at the Technische Universität (TU) München and lecturer in experimental physics. 1964–1965 Visiting Scientist Atomic Energy Research Establishment, Harwell UK. 1965 appointed Full Professor of Experimental Physics at Ludwig-Maximilians-Universität (LMU) München. 1969–1970 Visiting Professor at New York University. 1975–1977 Dean of the Faculty of Physics, LMU. 1980 Elected Member of the Bavarian Academy of Science. 1981 Visiting Professor at Tokyo University. 1986 Elected Member of the Deutsche Akademie der Naturforscher Leopoldina, Halle. 1987–1988 Chairman of the Physics Department, LMU. – Main research activities: nuclear solid state physics, conversion of solar radiation to process heat, chemical energy storage, applied solar thermal driven processes, e.g. refrigeration, air conditioning and desalination.

1. Introduction

There are three major paths along which solar radiation can be employed in the traditional structure of our energy economy[2] (see Fig. 1):
- by conversion to (process) heat,
- to electricity,
- to fuels and chemicals.

The *chemical path* (Table 1) has the advantage of producing transportable and long-term storable energy carriers. This is important because the daily and seasonal energy demand is rarely synchronous and geographically matched to incident solar radiation.

2. Photochemistry

For chemistry the radiation flux is directly available for use as a photon flux to drive quantum processes[1]. To produce fuels being energy carriers (Table 1) an endergonic photochemical reaction is required. In the manufacture of chemicals an enhanced energy content of the products is not necessarily a measure of their value: the particular chemical structure procured or the favorable reaction yield obtained via photochemistry can determine the economic importance.

The sun can be considered being a black-body emitter of 5777 K. Therefore, at short wavelengths of the spectrum, the chemical potential of the solar photon flux is remarkably high. The chemical potential

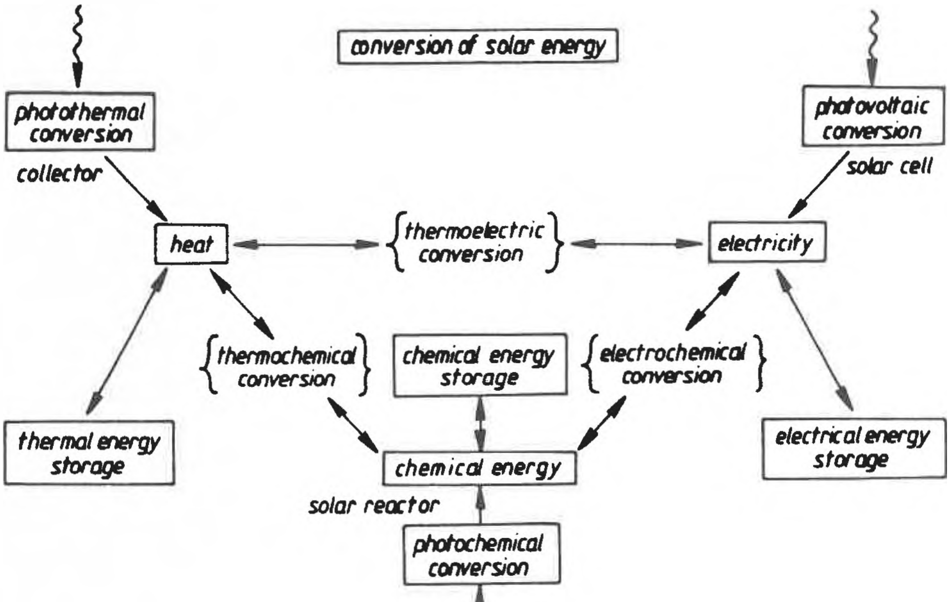

Fig. 1. Conversion paths of solar energy.

Table 1. Solar driven chemistry.

Energy Carriers = Fuels:	hydrogen, synthesis gas, ammonia, ... methanol, ... aluminium, ...
Chemicals:	calcining of limestone, ore reduction, ... water desalination, ... nylon 6, vitamins, ...
Reactions:	surface treatment (alloying), ... carbon fibers, ... detoxification, ...

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$\mu(\nu)$ is a measure of the driving force of absorbed radiation in photochemical processes[2]

$$E_\nu(\nu) = \frac{2\Omega^* h\nu^3}{c^2} \cdot \frac{1}{\exp\left(\frac{h\nu - \mu}{kT}\right) - 1}$$

E_ν is the spectral component ν of the solar spectrum (spectral flux density); Ω^* is the solid angle; T is the temperature of the system. We rearrange the equation

$$\mu(\nu) = h\nu - kT \cdot \ln\left(1 + \frac{2\Omega^* h\nu^2}{c^2 E_\nu(\nu)}\right)$$

$h\nu = hc/\lambda$ is the photon energy at frequency ν or wavelength λ. By optical concentration this high chemical potential is extended to longer wavelengths, finally covering all of the spectrum, i.e. all of the incident energy flux (Fig. 2).

The direct use of the solar photon flux requires absorption by the chemicals. For reasons due to bond structure, normally only a partial band width, if at all, of the total spectrum contributes to absorption. This reduces the energy efficiency of solar flux driven photochemical reactions.

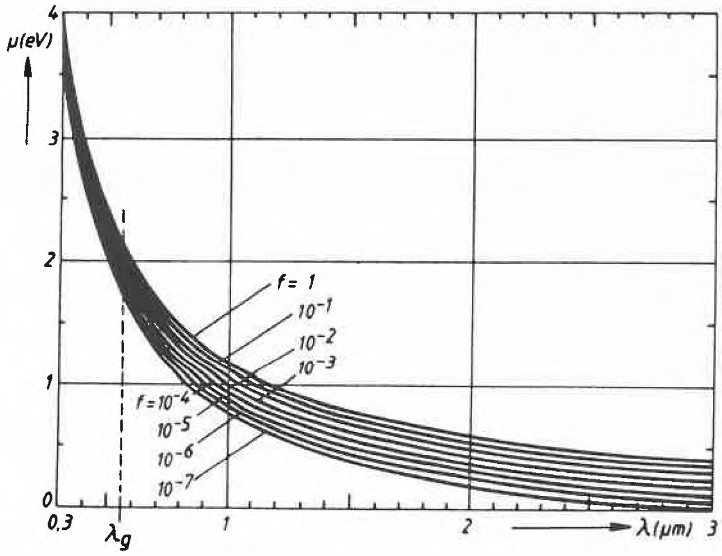


Fig. 2. Chemical potential of the solar photon flux. f denotes the dilution of the radiation, i.e. the ratio of the flux density to the maximum flux density at the surface of the sun.

3. Thermochemistry

The situation is different in endothermic thermochemical reactions. All materials couple to temperature changes[3]. The process heat is supplied by (blackbody) absorption of solar radiation in collectors or receivers. The temperature range available extends to over 2000 degrees if concentrators for the solar flux are employed. Fig. 3 shows temperature ranges of various industrially important thermochemical processes[4].

In this sense solar driven thermochemistry is essentially conventional thermochemistry (Fig. 4); the origin of the heat source is irrelevant to the coupled chemical process. However, there are solar pecularities: the high temperature level (e.g., attained with concentrated radiation in so-called direct absorption receivers), the high thermal flux density up to a theoretical maximum of 63 MW/m^2, the frequent transients because of the fluctuating incident solar radiation (by astronomical but more erratically by meteorological factors). The latter point calls either for back-up sources of heat supply or for heat storage. Conventional industrial thermochemical reactions are generally not suitable for transient operation: e.g., increased exergetic losses by heat transfer resistances; catalysts designed for optimum activity only in a narrow temperature range.

The adaption to such pecularities of solar driven thermochemical reactions appears rather to be a chemical engineering task than a fundamental research problem.

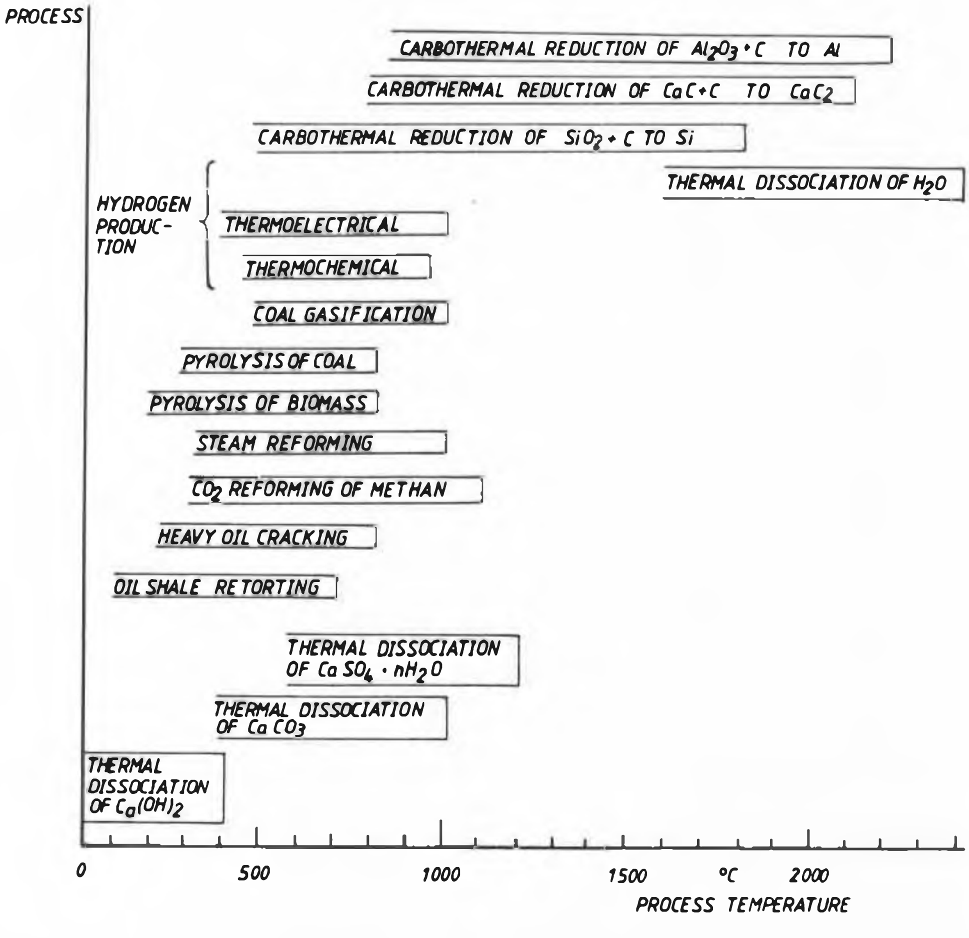


Fig. 3. Temperature ranges of industrial thermochemical processes.

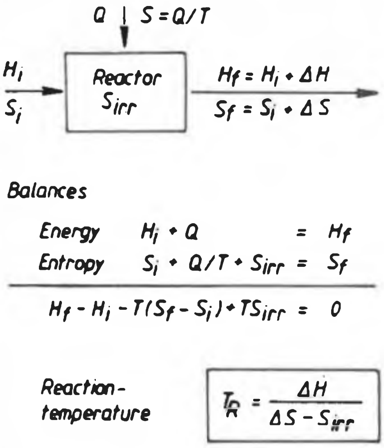


Fig. 4. One-stage thermochemical process. To match the enthalpy requirement ($Q = \Delta H$) simultaneously with the entropy requirement ($Q/T = \Delta S$) of the process, the temperature T has to be adjusted to the so-called reaction temperature T_R.

4. Thermo/Photochemistry

The situation is different in considering the combination of photochemistry and thermochemistry. The simultaneous presence of heat (thermal excitation) and of photon flux with characteristics of a 5777 K emitter produces a new and solar unique environment for chemical processes. At present, little is known about the advantages of such a hybrid energy input. By thermodynamic arguments it can be shown that the combination could be favorable for lowering the reaction temperature of endothermic processes (Fig. 5). On the other hand photoexcitation could change the kinetics in thermochemical processes, opening a new dominant reaction channel towards different and high-yield reaction products.

5. Electrochemistry

Electricity can be provided by solar process heat thermal power conversion or by the unique photovoltaic conversion of solar radiation. For reasons of transport and storage electrochemical processes can be employed to produce fuels and chemicals. Here we encounter again a conventional process: electrochemistry, in combination with a new energy source: solar produced electricity. The obvious peculiarity in this combination is the transient character of the source which – without recourse to any back-up sources – requires a new chemical engineering development of hitherto continuously running standard electrochemical processes.

6. Electro/Thermochemistry

The possible combination of electrochemistry and thermochemistry is obvious: both electricity and process heat can

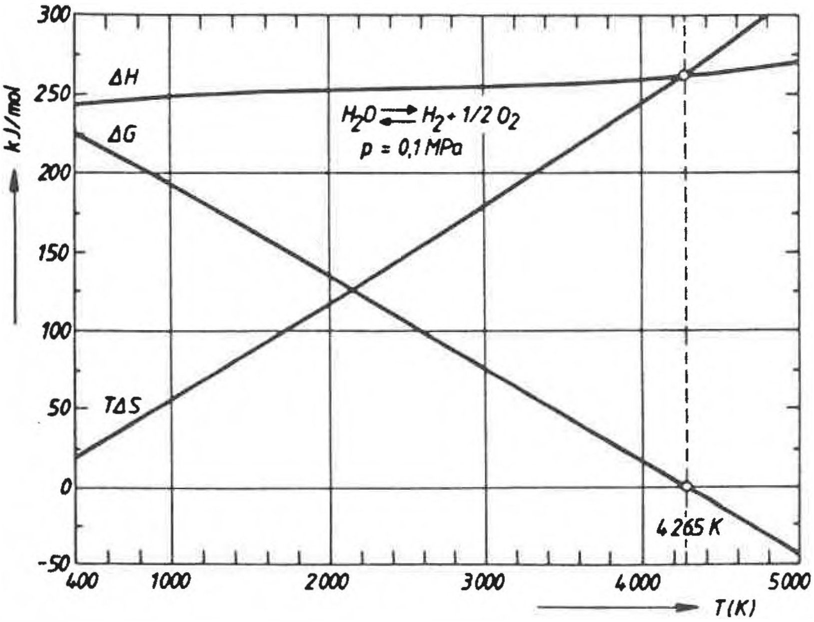


Fig. 6. ΔH, ΔS, and ΔG are reaction enthalpy, reaction entropy, and reaction Gibbs free enthalpy of water splitting. Note the decrease of ΔG with increasing temperature T; it is equivalent to the electric energy required in electrolysis of water vapor. The increase of TΔS with increasing temperature is equivalent to the increase of the endothermal heat of reaction.

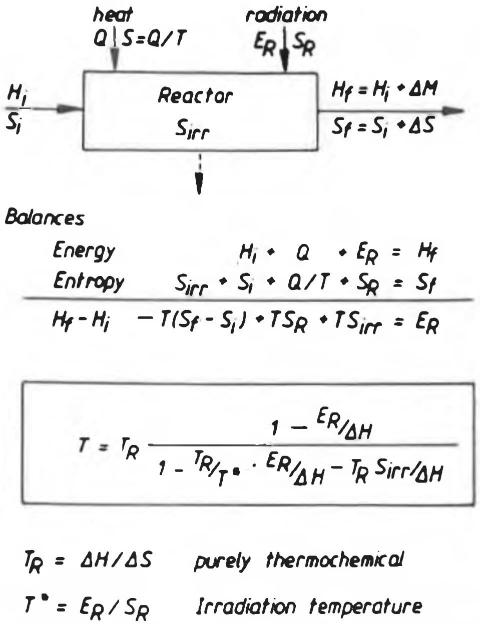


Fig. 5. Reaction temperature and irradiation.

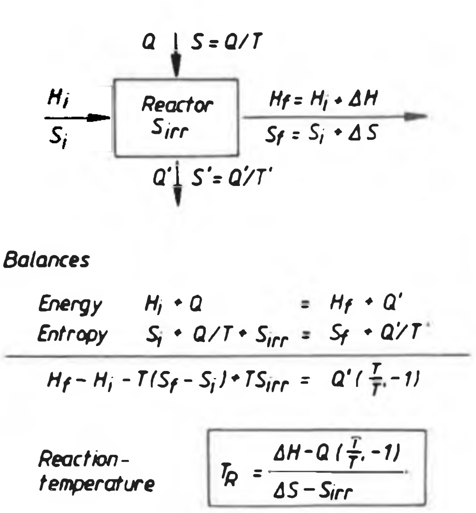


Fig. 7. General scheme of a two-stage thermochemical process. Compared to the one-stage process (Fig. 4) there is an additional degree of freedom: waste heat Q' is allowed to leave the reactor, carrying away surplus entropy of reaction. This allows a lower reaction temperature T_R.

be provided at the same time from incident solar radiation. Thermodynamics shows that such a combination reduces the level of reaction temperature required to drive an endothermic process or the amount of electricity necessary per unit reaction turnover[6].

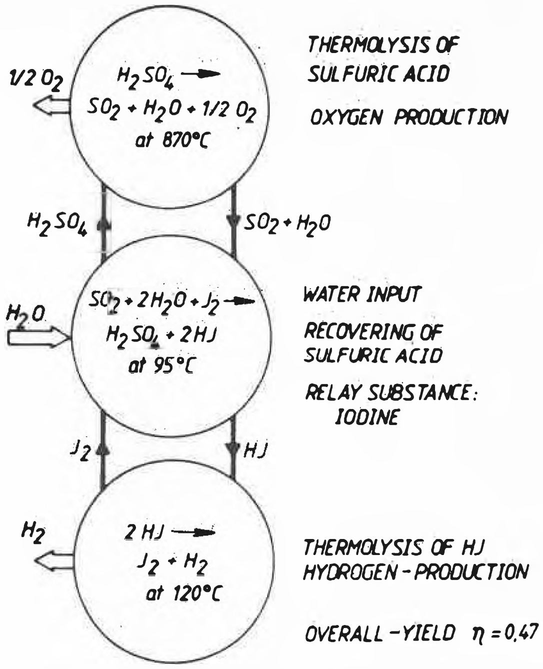


Fig. 9. General Atomic process of thermochemical water splitting in a three-stage reaction sequence. Entropy is removed in the exothermal reactions at the low temperatures, lowering the high temperature to about 1200 K. This temperature should be compared to the one-stage temperature of 4265 K (Fig. 6).

7. Photo/Electrochemistry

Still an open field is the solar unique combination of a photon flux in an electrochemical reaction. A reduction of electricity input can be expected but also, regarding complex systems, a change in the dominant type of electrochemical products.

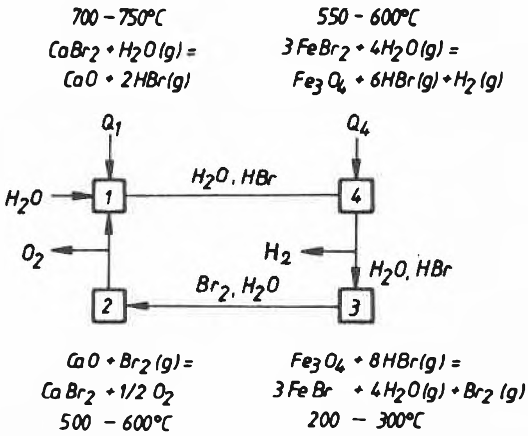
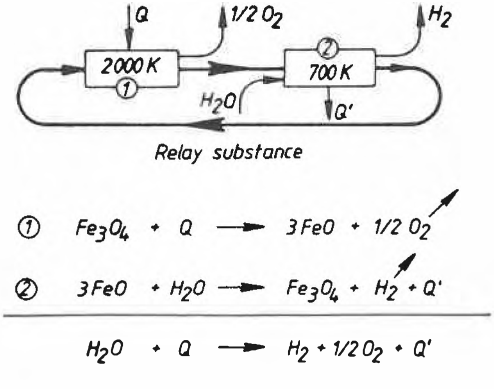


Fig. 10. UT-3 process of thermochemical water splitting. It is a four-stage process which allows to lower the high-temperature heat input to about 1000 K only. The process uses solid state – gas phase reactions.

8. Examples

An example which happens to apply to all of the mentioned solar directly and indirectly driven chemical processes is the decomposition of water to hydrogen and oxygen. Hydrogen production from water is one of the most important long-term goals in solar fuels production. High-temperature, high-pressure water electrolysis is an endothermic and at 1000 °C about $^1/_3$ less electricity consuming process as shown in Fig. 6. Purely thermochemical water vapour splitting (see Fig. 4) needs temperatures of the order of 3000 °C, which poses a severe materials problem[7]. Thermochemical multistep reactions have been proposed for reducing the reaction temperature[5, 8–10], see Figs. 7, 8, 9, and 10. The thermodynamically unavoidable price for lowering the reaction temperature is having nominally less yield per unit input of solar radiation energy.



① $Fe_3O_4 + Q \longrightarrow 3FeO + 1/2\ O_2\uparrow$

② $3FeO + H_2O \longrightarrow Fe_3O_4 + H_2\uparrow + Q'$

$H_2O + Q \longrightarrow H_2 + 1/2\ O_2 + Q'$

Fig. 8. Two-stage thermochemical reaction for water splitting as proposed by Nakamura[7], Bamberger[8], Richardson. The relay substance is iron oxide. Entropy is removed by an exothermal low-temperature reaction at 700 K. This reduces the required temperature of the high-temperature reaction to about 2000 K as compared to the one-stage temperature of 4265 K (Fig. 6).

Photochemical water decomposition is at present a research item of high topical interest. Natural photosynthesis producing biomass (or its derivatives) but also other valuable chemicals is the prominent example of a solar photon flux driven chemical process. It is particularly apt to demonstrate the various factors contributing to processing losses between the initial input (solar radiation) and the final product (e.g., ethanol). The general relation is

$$W_e = \int_0^\infty \eta^* G_\lambda d\lambda (1 - r)\frac{(g - 1)}{g} f$$

W_e is the usable output of the final product (in terms of heat of combustion per square meter of farming area); G_λ is the average spectral solar flux density; η^* is the photosynthetic efficiency for biomass produced in the plant,

$$\eta^* = \frac{\Delta H}{\int_0^\infty \int_{t^*} G_\lambda d\lambda dt}$$

ΔH is the heat of combustion of dry biomass; r is the fraction which remains as residue on the field after harvesting; g is the energy harvest factor (the ratio of energy content of the biomass over the energy expenditure for growing the biomass: planting, fertilizing, irregating, harvesting, transporting etc.); f is the conversion efficiency of the raw biomass to the final product (e.g., ethanol). Practical values are $\eta^* = 0.02$, $r = 0.5$, $g = 2$, $f = 0.8$. All the values are time averages over a natural vegetation period t^*. With an insolation of $\int_0^\infty G_\lambda d\lambda = 140$ W m^{-2} we obtain $W_e = 0.6$ W m^{-2} of average fuel production rate, equivalent to an energy efficiency of only 0.4%.

Improvement in natural photosynthetic efficiency appears to be most promising: different species of plants exhibit different efficiencies (see Fig. 11). Genetic engineering is the key issue in this context.

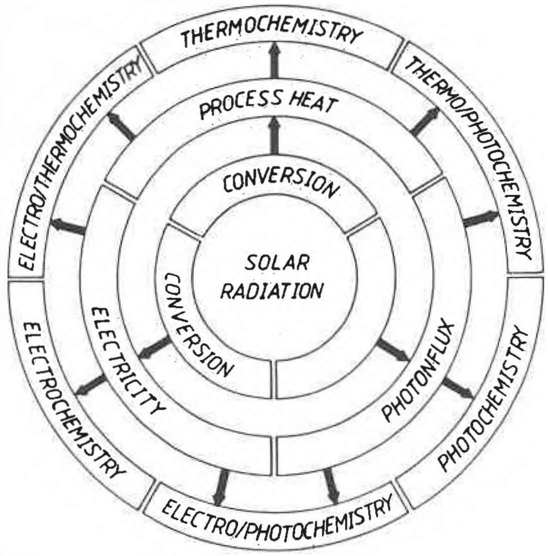


Fig. 12. Solar driven chemistry – the big challenge for chemists and chemical engineers.

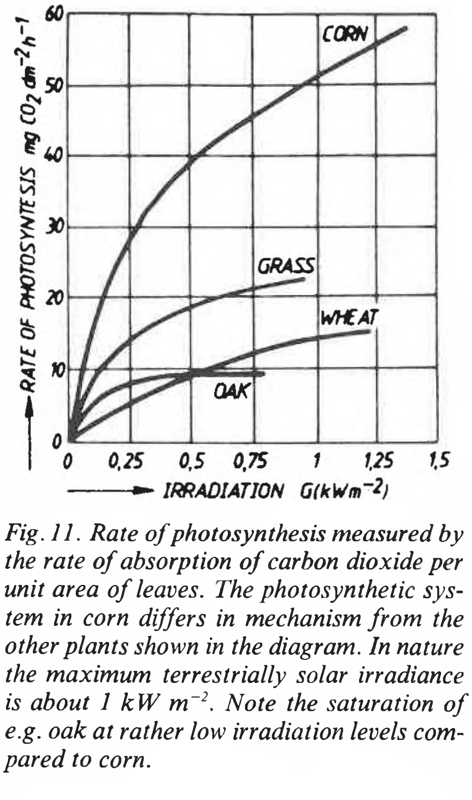


Fig. 11. Rate of photosynthesis measured by the rate of absorption of carbon dioxide per unit area of leaves. The photosynthetic system in corn differs in mechanism from the other plants shown in the diagram. In nature the maximum terrestrially solar irradiance is about 1 kW m^{-2}. Note the saturation of e.g. oak at rather low irradiation levels compared to corn.

9. Summary and Outlook

Solar driven chemical reactions are of importance for producing fuels and chemicals.

Solar fuels are reaction products which contain a high density (per mole, per weight, or per volume) of energy invested from solar radiation during their manufacture. The reaction pair hydrogen/oxygen produced in water splitting is a particular example of a solar fuel. The reaction can be driven purely thermally (in multi-stage cycles), purely electrochemically, or purely photochemically. Combinations such as thermo/electrochemical or photo/electrochemical are of advantage to match enthalpy and entropy requirements of the process at reaction parameters which are favorable for large-scale chemical engineering (cf. Fig. 12).

Solar chemicals are valuable substances which do not excel in high energy densities but in the need for high temperatures or high photon flux densities in their manufacturing, or where the reaction path is favorably influenced by photon assisted processes. Cement production is an example but also the manufacture of tensides by photo-sulfoxidation of alkanes. In the latter case the energy content of the reaction system is even lowered by the product formation.

Solar detoxification is a process, in which hazardous organic material becomes decomposed to less harmful small molecules. The combination of high temperatures simultaneous with high photon flux densities can here be favorable.

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