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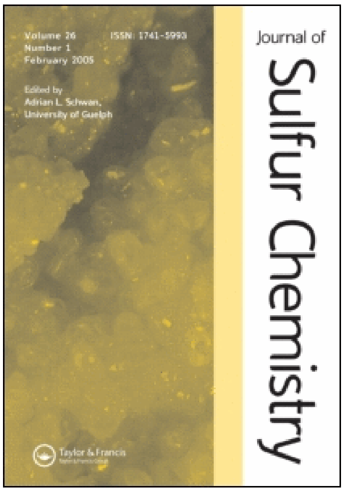

Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

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Online publication date: 13 May 2010

To cite this Article Clark, Peter D. and Dowling, Norman I.(2004) 'Capture of solar energy using elemental sulfur', Journal of Sulfur Chemistry, 25: 1, 7 — 11

To link to this Article: DOI: 10.1080/17415990410001661267

URL: http://dx.doi.org/10.1080/17415990410001661267

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J. Sulfur Chemistry, February 2004, Vol. 25, No. 1, pp. 7–11

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RESEARCH ARTICLE

CAPTURE OF SOLAR ENERGY USING ELEMENTAL SULFUR

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(Received 29 October 2003; In final form 12 December 2003)

Use of the equilibrium sulfur vapour system as the basis for a thermochemical solar energy conversion system is suggested. This chemical system is shown to be both thermodynamically and kinetically well suited, as well as possessing several other desirable features. A key advantage is provided by reliance on the proven mature Claus technology for materials handling and the heat recovery stage of the proposed scheme.

Keywords: Solar energy; Elemental sulfur

Thermochemical storage of solar energy has been proposed for numerous chemical systems since the late 1970s and early 1980s (Table I) [1–5]. In large part, these systems are simple thermal decomposition reactions that display the requisite reversible behaviour that allows storage and ultimately recovery of the solar energy. In general, these types of solar energy collection and storage systems rely on the use of endothermic bond-breaking and exothermic bond-making reversible chemical reactions as a means of solar energy storage. Thus, energy, in the form of heat, from the solar collector is supplied to enable the endothermic bond-breaking reaction to proceed, thereby storing the collected solar energy within the higher free energy of the product molecules. Recovery of this stored energy is then achieved by allowing the reverse exothermic reaction to occur in conjunction with some means of heat recovery coupled to electrical power generation.

In principle any chemical reaction that is capable of being driven thermodynamically to one or other extreme, within a suitably narrow temperature range up to 1000 °C, can function as a thermochemical solar energy storage or conversion system. However, in practice, issues relating to energy storage density, heat of reaction and equilibrium thermodynamics and kinetics of the system will determine the suitability of a given chemical reaction. The communication aims to show that the previously overlooked equilibrium sulfur vapour system possesses many of the required features for such a system, making it an ideal candidate for a high-temperature (500–1000 °C) thermochemical solar energy conversion system.

Sulfur is one of the few elements that can undergo concatenation to produce a wide variety of molecular forms. Thus, whereas the cycloocta-ring structure of S_8 is favoured in the solid,

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ISSN 1741-5993 print; ISSN 1741-6000 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/17415990410001661267

TABLE I Reversible chemical reactions proposed for thermochemical solar energy storage

Reaction	ΔH° *(kJmol^{-1})*	*Ref.*
$2NH_3 \leftrightarrows N_2 + 3H_2$	92.3	1
$SO_3 \leftrightarrows SO_2 + \frac{1}{2}O_2$	98.9	2
$CH_4 + H_2O \leftrightarrows CO + 3H_2$	206.2	3
$CH_4 + CO_2 \leftrightarrows 2CO + 2H_2$	247.4	4
$CaCO_3 \leftrightarrows CaO + CO_2$	178.3	5

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and at least initially within the liquid below the polymerization temperature of 160 °C, the vapor state is characterized instead by various molecular allotropes of the S_2–S_8 form [6]. These forms undergo rapid inter-conversion at the high temperatures in the vapour state to establish the equilibrium composition of sulfur vapour as a function of temperature shown in Figure 1. This diagram was calculated with the aid of a free energy minimization program using the JANAF thermodynamic database [7]. Figure 1 shows that the larger S_8 species is thermodynamically more favoured at lower temperatures closer to the normal boiling point of 444.6 °C, whereas the smaller S_2 molecule is favoured at higher temperatures, such that the composition of the vapour is almost entirely S_2 by 1000 °C. Equilibration between the various molecular S_x species within the vapour can therefore be characterized overall as the endothermic formation of S_2 at higher temperatures and the reverse exothermic re-formation of S_8 at lower temperatures.

$$S_8 \underset{-\Delta H}{\overset{+\Delta H}{\rightleftarrows}} 4S_2 \tag{1}$$

This unique property of sulfur vapour makes this chemical system well suited as a high temperature thermochemical solar energy conversion system for several reasons. A scheme based on this concept is illustrated in Figure 2. Such a system would be able to operate under normal pressures as shown from the calculated equilibrium at a total pressure of 1 atm in

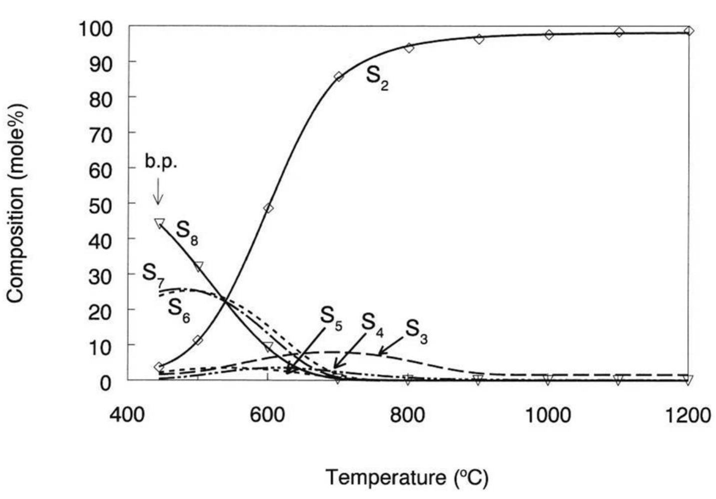

FIGURE 1 Equilibrium composition of sulfur vapour at a total pressure of 1 atm.

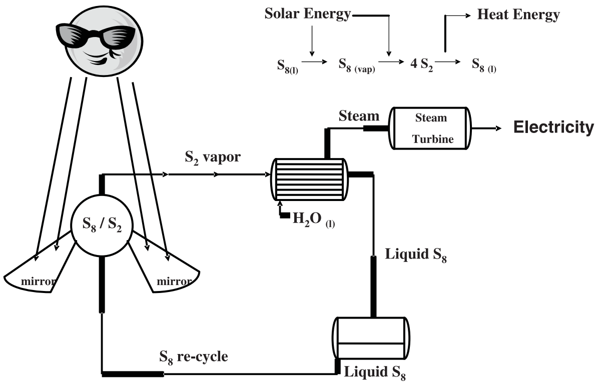

FIGURE 2 Scheme for use of elemental sulfur in solar energy collection.

Figure 1. This would avoid the costly need for specialized high-pressure storage vessels or solar reactor, as for some of the systems proposed [8]. Further, only a single storage vessel would be required for the liquid sulfur as no separation of reactants and products would be required or deemed desirable. Instead, direct conversion of the solar energy to electricity via high-pressure steam generated in a boiler is envisaged.

While the proposed scheme does not include the storage aspect of a typical thermochemical pipeline concept, it nonetheless represents a solar energy collection system based on thermochemical principles, which is ideally suited for the production of a high-temperature fluid from which energy can be harnessed. In principle, the use of thermochemical means, as opposed to sensible or latent heating, for solar energy applications is not restricted to the concept of a thermochemical pipeline. This concept relies on separation and storage or transportation of the products of the forward heat absorbing reaction prior to allowing the reverse exothermic reaction to occur (usually catalytically) for recovery of the stored energy. The present scheme, while relying on thermochemical principles of energy storage, is similar in other respects to more conventional sensible heating solar energy systems, but with the additional advantage provided by the thermochemical storage aspect.

Indeed, the heat recovery stage of the scheme illustrated in Figure 2 is already implemented as part of the proven technology used within every Claus sulfur recovery plant in refineries and natural gas processing facilities. In such plants the hot (typically up to 1200 °C) gases containing sulfur vapour leaving the reaction furnace pass through a waste heat boiler, where the sulfur is condensed to the liquid state and high pressure (600 psig) steam is generated [9]. This further means that all associated equipment and technical designs, such as liquid sulfur pumps, and refractory lining for flow pipes and tube sheet fabrication, are already well known.

For a given chemical system to be considered for thermochemical solar energy applications it must also possess certain other necessary features. These include rapid kinetics for both the forward, heat-absorbing, and reverse, heat-releasing, reactions within the perceived operating temperature range, along with the absence of any side reactions. The proposed equilibrium sulfur vapour system satisfies both of these criteria. Indeed, the very nature of the system, being inter-conversion between different allotropic forms, makes it difficult to conceive of side reactions. In practice it would be necessary to ensure exclusion of H_2O and O_2 from the system to prevent reaction with these species.

Although, to our knowledge, no direct study of the rates of sulfur vapour re-equilibration have been reported in the literature, there is ample evidence that the kinetics associated with the inter-conversion of these species is rapid. This again largely comes from the operation of

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Claus sulfur recovery units, where the quench time of the furnace gases within the waste heat boiler is typically on the order of 200 ms or less [10]. This time-scale is sufficient for both gas phase re-equilibration reactions and heat transfer to occur. This further highlights the fact that neither the endothermic solar collection reaction nor the reverse exothermic heat-releasing step requires the use of a catalyst, which simplifies the overall system.

A useful thermodynamic analysis to determine the suitability of chemical systems in thermochemical solar energy applications has been provided by Wentworth and Chen [5]. The focus of this analysis was on systems capable of producing high temperature (∼500 °C) heat suitable for generation of electrical power, which reflects the type of system envisaged in Figure 2 for capture of solar energy using elemental sulfur. These authors point out in their analysis that the chief thermodynamic criteria for a suitable reaction rests with being able to achieve a high yield for the forward (in this case $S_8 \rightarrow S_2$) reaction at $<\sim 1000\,^\circ\mathrm{C}$, and a correspondingly high yield for the reverse (in this case $S_2 \rightarrow S_8$) reaction at $>\sim 500\,^\circ\mathrm{C}$. In the terminology of their analysis this condition was specified as $773 < \Delta H^\circ/\Delta S^\circ < 1273$, where temperatures are noted in kelvin. The ratio of $\Delta H^\circ/\Delta S^\circ$ used by these authors provides an approximate value for the temperature at which the equilibrium constant for both the forward and reverse reactions is 1. This ratio is 858 K for Eq. (1), based on $\Delta H^\circ_{(298)} = 414\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^\circ_{(298)} = 482.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$ [7].

Restated, this condition requires that the equilibrium constant for the forward reaction be suitably large at a temperature on the order of 1000 °C and suitably small (*i.e.* large equilibrium constant for the reverse reaction) in the vicinity of 500 °C. This essential condition can be seen to be met by the equilibrium sulfur vapour system by examining the diagram in Figure 1, which shows that the percent S_2 in the system at 1000 °C is ∼98%, whereas only ∼4% S_2 exists at the normal boiling point of 444.6 °C. This means that both the heat-absorbing and heat-releasing reactions, within the solar collector and the boiler respectively, can be made to undergo near-quantitative conversion in the absence of any kinetic impediment.

It is also instructive to compare the standard reaction enthalpy, $\Delta H^\circ_{(298)}$, for the S_8 into S_2 conversion with that of other reactions already proposed for thermochemical solar energy applications (Table I). The $414\,\mathrm{kJ\,mol^{-1}}$ for Eq. (1) is far larger than for any of the other reactions. This in turn affords a relatively high energy storage density of $1617\,\mathrm{J\,g^{-1}}$, which is intermediate between the storage densities for the corresponding gaseous ammonia ($2714\,\mathrm{J\,g^{-1}}$) and SO_3 ($1236\,\mathrm{J\,g^{-1}}$) dissociation-based processes.

Finally, two of the other criteria mentioned by Wentworth and Chen for an ideal thermochemical solar energy system are also worth noting. These are the obvious preference for being able to adopt known technology in the handling of the compounds involved and for the materials to be readily available on a commercial scale. Both of these statements apply fully to elemental sulfur in terms of the mature Claus technology, which handles sulfur in both the liquid and gaseous states, and which is utilized worldwide for the production of recovered sulfur from hydrogen sulfide.

Global production of elemental sulfur is estimated to be 50–60 million metric tonnes on an annual basis, and is widely distributed on a regional basis, including North America, the Middle East, Europe and the former Soviet Union. This level of largely involuntary production has also traditionally resulted in significant inventorying, bringing yet a further advantage to the use of elemental sulfur in solar energy collection, namely, the low cost of this commodity, which is one of the perennial challenges faced within the sulfur industry. Overall, it is clear from this discussion that there is much to recommend the use of elemental sulfur as a thermochemical solar energy collection material. This includes both the salient properties of the material itself and the already well-developed technology that is in place for producing, handling and transporting this commodity.

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References

[1] Carden, P. O., *Solar Energy*, **19**, 365 (1977).
[2] Chubb, T. A., *Solar Energy*, **17**, 129 (1975).
[3] Hafele, W., *Science*, **84**, 360 (1974).
[4] Wyman, C., Castle, J. and Kreith, F., *Solar Energy*, **24**, 517 (1980).
[5] Wentworth, W. E. and Chen, E., *Solar Energy*, **18**, 205 (1976).
[6] Rau, H., Kutty, T. R. N. and Guedes de Carvalho, J. R. F., *J. Chem. Thermodynamics*, **5**, 833 (1973).
[7] Stull, D. R. and Prophet, H. (Eds.), *JANAF Thermochemical Tables* (National Bureau of Standards, Washington, DC, 1971), 2nd edn.
[8] Lovegrove, K., Luzzi, A. and Kreetz, H., A solar driven ammonia based thermochemical energy storage system, Paper presented at the *ISES 1999 Solar World Congress*, Jerusalem, Israel, 4–9 July (1999).
[9] Paskall, H. G., Capability of the Modified-Claus process, *Final Report* to the Department of Energy and Natural Resources, Province of Alberta, Western Research and Development, Calgary (1979).
[10] Nasato, L. V., Karan, K., Mehrotra, A. K. and Behie, L. A., *Ind. Eng. Chem. Res.*, **33**, 7 (1994).

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