

APPENDIX 2

THE THERMAL OXIDATION OF GRAPHITE

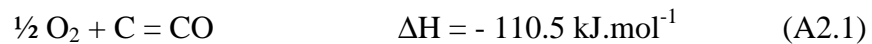
A. Blanchard

A2.1. General

Graphite is used in a variety of nuclear reactor types; principally for moderator, reflector, fuel sleeve and fuel tube material. Since it is a form of carbon, like coal and charcoal, its oxidation behaviour might be expected to be of concern to the graphite chemist. The oxidising environments of particular interest are air (oxygen), carbon dioxide and steam (water).

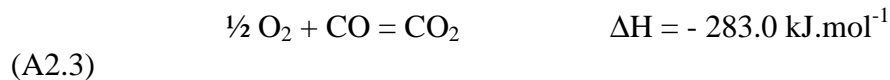
A2.2. Reactions and Thermodynamics

A2.2.1. Reaction with Oxygen



where ΔH is the standard enthalpy of formation at 298 °C.

Reaction (A2.1) maximises the amount of carbon which may be removed by a given mass of oxygen (as carbon monoxide). Reaction (A2.2) maximises the amount of heat produced by oxidising a given mass of carbon (to carbon dioxide). Reaction (A2.2) may also be regarded as proceeding in stages, with reaction (A2.1) followed by



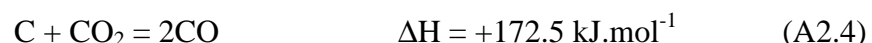
(obtained by difference - Hess's law)

Reaction (A2.3) can take place wholly in the gas phase.

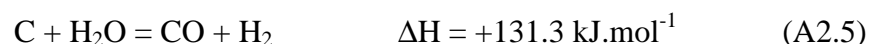
The above reactions are exothermic and favoured thermodynamically. Despite this fact, pure dense nuclear graphites do not readily react with air, so kinetic factors are obviously of importance.

A2.2.2. Reaction with Carbon Dioxide

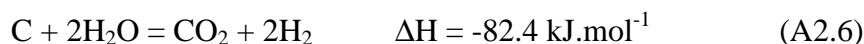
This can be readily inferred by multiplying reaction (A2.1) by 2, including the ΔH term. The result is then added to reaction (A2.2) reversed. Overall, the (Boudouard) reaction is



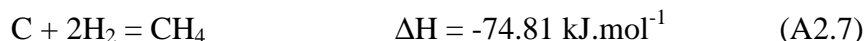
A2.2.3. Reaction with Water (water gas reaction)



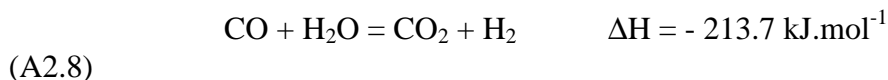
also



The hydrogen produced can then react with carbon:



Subtracting (A2.5) from (A2.6) gives



This is the water gas shift reaction which takes place in the gas phase.

In many practical cases, products from the above reactions are free to escape, such that thermodynamic equilibrium is not reached. The enthalpy changes are of importance, however, since they give a measure of the heat produced in exothermic reactions.

A2.3. Mechanisms, Regimes and Kinetics

A2.3.1. Mechanisms

The oxidation mechanisms consist of a series of physical and chemical steps. Non-catalysed oxidation typically follows the route:

- (i) Transport of oxidant to the graphite surface.
- (ii) Adsorption of oxidant onto the graphite surface (physisorption).
- (iii) Formation of carbon-oxygen bonds (chemisorption).
- (iv) Formation of carbon-hydrogen bonds in reaction (A2.7) (reduction).
- (v) Breaking of the carbon-carbon bonds.
- (vi) Desorption of carbon monoxide, or other product.
- (vii) Transport of reaction product from the graphite surface.

Any of the above steps may be rate controlling, i.e. develop the major reactant concentration gradient.

A2.3.2. Controlling Factors

Factors controlling the rate of oxidation may include the following:

- (viii) The rate at which the oxidant is supplied to the surface.
- (ix) The partial pressure of the oxidant.
- (x) The reactive surface area available to the oxidant at the surface.

- (xi) The amount and distribution of catalytic impurities in the graphite.
- (xii) The temperature.
- (xiii) The rate at which reaction products are removed.
- (xiv) The fast neutron damage to the graphite.
- (xv) The amount of pre-oxidation (radiolytic or thermal burn-off).
- (xvi) The quantity of in-pore deposits.
- (xvii) The effective diffusion coefficient.

A2.3.3. Oxidation Regimes and Kinetics

Regime 1

At low oxidation rates (generally at relatively low temperatures for the particular oxidation reaction) the oxidant may be at essentially the same concentration throughout the transport pores of the graphite. This ‘chemical’ regime is characterised by the fact that the reaction rate is largely determined by the intrinsic reactivity of the graphite (steps (ii) to (vi), above). Different parts of the structure may react at different rates; the binder being more reactive than the graphite particles and edge atoms being more reactive than basal plane atoms, for example. It may also be the case that the gas composition varies in non-transport pores and that the effect of a given gas composition varies with pore shape (because of gas phase reactions).

Reaction between air and pure nuclear graphites is generally not measurable below about 350 °C and only becomes significant in the region of 400 °C. The rate of reaction is typically of the order of $3-8 \times 10^{-10} \text{ kg.kg}^{-1}.\text{s}^{-1}$ at this temperature (historically expressed in $\mu\text{g/gh}$; $1\mu\text{g/gh}$ being $2.78 \times 10^{-10} \text{ kg.kg}^{-1}.\text{s}^{-1}$). The chemical regime then extends typically up to 550-600 °C.

The units for oxidation rate imply a rate law of the form

$$\frac{dm}{dt} = k m \quad (\text{A2.9})$$

where

- m = graphite mass (kg)
- t = time (s)
- k = a (rate) constant (s^{-1})

However, for a solid reacting body, rate laws of the form shown below would be expected for reaction at the superficial surface (with some simple assumptions):

$$\text{Slabs} \quad \frac{dm}{dt} = k \quad (\text{A2.10})$$

$$\text{Cylinders} \quad \frac{dm}{dt} = k m^{1/2} \quad (\text{A2.11})$$

$$\text{Spheres} \quad \frac{dm}{dt} = k m^{2/3} \quad (\text{A2.12})$$

The reaction is, of course, taking place within the porous body of the graphite. It cannot, however, be related to the initial open pore volume (which might be expected to be proportional to graphite mass) since the reaction must take place at the surface of the pores. The rate law is thus only superficially similar to a homogeneous first order gas phase expression and care must be taken in its use, particularly in describing the time dependence of graphite burn off.

The variation of reaction rate with temperature is of importance:

$$k = A e^{-\frac{E}{RT}} \quad (\text{A2.13})$$

where

A is a pre-exponential factor (s^{-1})

E is the apparent temperature coefficient of reaction ('activation energy') ($\text{J}\cdot\text{mol}^{-1}$)

R is the gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

E has a typical value of $170 \text{ kJ}\cdot\text{mol}^{-1}$.

Similar considerations apply to reaction with carbon dioxide and water vapour (H_2O). The reaction with CO_2 is of less importance, however, since it is negligible at $625 \text{ }^\circ\text{C}$ (Thurlbeck, 1962) and does not pose a problem even at the highest AGR inner sleeve temperatures of $675 \text{ }^\circ\text{C}$ (Prince, 1976). The reaction is also endothermic (equation (A2.4)) and so does not have the same safety implications as the reaction with air.

The reaction with H_2O is of particular importance in HTR reactors, because of the (generally small) inleakage from the steam side into the gas circuit, where it can react with hot graphite fuel tubes. Since the partial pressure of the water vapour is a variable in this system, rate equations of the form

$$r = A P^n \quad (\text{A2.14})$$

are applied, where

r = the specific reaction rate ($\text{kg}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)

A = a (rate) constant ($\text{s}^{-1}\cdot(\text{N}\cdot\text{m}^{-2})^{-1}$)

P = partial pressure of water vapour ($\text{N}\cdot\text{m}^{-2}$)

The reaction with water vapour is generally insignificant below $800 \text{ }^\circ\text{C}$ and approximately obeys equation (A2.14) with $n=0.5$ over the temperature range $1000\text{-}1200 \text{ }^\circ\text{C}$. The kinetics can also be described by a Langmuir-Hinshelwood scheme (Walker *et al*, 1959; Atkins, 1987; Stairmand, 1990).

Regime 2

In this regime, the reaction rate becomes high enough for access of the gas to the in-pore

structure to be significantly limited by diffusion control (steps (i) and (vii), above). This can also arise from a particularly restrictive structure. For the air-graphite system, this occurs approximately in the range 600-900 °C. The ‘activation energy’ is halved in this regime and the kinetic expressions involve the effective diffusion coefficient for the graphite (Walker *et al*, 1959; Giberson and Walker, 1965).

Regime 3

This is the mass transfer regime (Burnette *et al*, 1979; Raeder and Gulden, 1989), where reaction at the superficial surface of the graphite is so high that most of the oxidant is consumed there, the oxidant concentration gradient generally developing across the laminar sub-layer. The reaction rate is now expressed in terms of the superficial surface area of the graphite ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) together with any oxidant partial pressure dependence. The change from one regime to another may be progressive and mode 2 may appear to be missing in some cases.

Two other ‘regimes’ appear trivial, but can usefully be distinguished:

Regime 4

If there is a fixed rate of ingress of oxidant to the system, for example as a known quantity of impurity in the make-up gas, the rate of oxidation cannot exceed the rate of supply of oxidant (rate balance). The preferred site of any resulting oxidation may not be known, however.

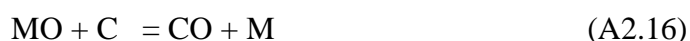
Regime 5

If the system contains a fixed amount of oxidant, for example that remaining after blowing down and recharging the coolant gas, the extent of oxidation is limited by the amount of oxidant available (mass balance). Neither the location, nor the rate of reaction, may be known in this case.

A2.3.4. Catalysis

The kinetics in the chemical regime may be further complicated by catalysis (McKee, 1981). The catalyst (impurity) particles act to increase the reaction rate by offering an alternative reaction pathway. This lowers the activation energy. Reaction rates are particularly increased at lower temperatures (this leads to a ‘compensation’ effect).

A simple catalytic model involves the oxidation of metal atoms (M) by oxygen, followed by reduction of the oxide by carbon:



The reaction may proceed by a ‘tunnelling’ mechanism.

Reaction inhibitors are also known (McKee, 1991) and some substances are able to act to either promote or inhibit reaction, perhaps by competing for active sites (e.g. water/oxygen). Boron (with phosphorus) is known as an inhibitor for thermal oxidation, but when intercalated into the graphite structure will promote oxidation (Karra *et al*, 1995)

(perhaps by mimicking fast neutron damage).

A2.4. Requirements for the Information

Early designs of graphite moderated reactor operated with air as the coolant and there was a requirement to understand both the likely ongoing oxidation behaviour of the graphite and its behaviour during a temperature excursion. As these reactors were superseded by carbon dioxide cooled designs, an understanding of the reaction of graphite with air remained important for the following reasons:

- (i) Safety case information relevant to both major and minor ingresses of air to the system under fault or other conditions (Dodson, 1960; Nairn and Wilkinson, 1960; Blanchard and Fitzgerald, 1978).
- (ii) The possible requirements to carry out deliberate oxidations to
 - (a) Remove deposits from fuel.
 - (b) Open up the structure of low diffusivity graphite to improve inhibitor (e.g. methane) access.
 - (c) Remove deposits from fuel pin and heat exchanger surfaces to improve heat transfer.
 - (d) Estimate the amount of deposit in graphite moderator and fuel sleeves by differential thermal oxidation (Welch, 1972; Oxley and Dymond, 1972; Baguley and Livesey, 1972) (so as to be able to correct the weight loss).
 - (e) Alter the structure of experimental graphites in controlled ways to improve theoretical knowledge of the interaction between reactivity and structure.

A2.5. Essential Measurements and Knowledge

The complexity of graphite oxidation behaviour is such that the following are generally required:

- (i) Good statistical data on the relevant oxidation rates for a range of blocks and heats.
- (ii) An awareness of the relevant oxidation regime and the rate laws which are likely to apply.
- (iii) Information on the temperature coefficient of reaction.
- (iv) Information or measurement on the heat change on reaction.
- (v) Theoretical or experimental information on factors affecting the oxidation rate, such as fast neutron damage, burn-up, deposition of potential catalysts, etc.
- (vi) Modelling knowledge to extrapolate from small scale samples, or full scale tests.

As some graphite reactors are coming to the end of their lives, there is an increasing requirement to carry out assessments for long term storage or disposal (Wickham *et al*, 1996). The potential oxidation behaviour is also of concern in this context.

A2.6. Acknowledgements

In compiling this account, the author has been particularly grateful for reviews by John Stairmand (Stairmand, 1990) and Tony Wickham *et al* (Wickham *et al*, 1996) who in turn cite the pioneering work of P.L. Walker (Walker *et al*, 1959) and Dubinin (Dubinin, 1966). Any important omissions are the author's own, however.

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