Kinetic and Thermodynamic Study of the Wet Desulfurization Reaction of ZnO Sorbents at High Temperatures

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Supplementary material: spherical geometry model of rate constant and diffusion coefficient.

To study diffusion phenomena, it has been considering Fick's second law in spherical coordinates.

$$\frac{\dot{n}_2}{V} = \frac{dc_{p2}}{dt} = \bar{k}_0 \cdot c_p \tag{S1}$$

$$\dot{n}_2 = \bar{k}_0 \cdot c_p \cdot 4\pi r^2 dr \tag{S2}$$

Where Eq. S2 means the decrease of the moles within the particle volume.

$$\frac{dn_1}{dt} = \dot{n}_1 = \left(\frac{(J_{r+dr} \cdot A_{r+dr}) - J_r \cdot A_r}{4\pi r^2 dr}\right) \cdot 4\pi r^2 dr \tag{S3}$$

The term of Eq. S3 corresponds to the increasing of moles within the particle volume, while the flux rises with respect to *r*, but it goes towards the center of the particle.

$$\frac{dc_{p1}}{dt} = \frac{1}{4\pi r^2}\frac{d}{dr}(J \cdot A) \tag{S4}$$

The flux has the opposite sign to the gradient, and considering Eq. S4, it is:

$$J = -D\frac{dc_p}{dr} \tag{S5}$$

$$\frac{dc_{p1}}{dt} = -\frac{1}{4\pi r^2}\frac{d}{dr}\left(D\frac{dc_p}{dr} \cdot 4\pi r^2\right) \tag{S6}$$

$$\frac{dc_{p1}}{dt} = -D\frac{1}{r^2}\frac{d}{dr}\left(\frac{dc_p}{dr} \cdot r^2\right) \tag{S7}$$

$$\frac{dc_p}{dt} = -D\frac{1}{r^2}\frac{d}{dr}\left(\frac{dc_p}{dr} \cdot r^2\right) - \bar{k}_0 c_p \tag{S8}$$

Where D is the diffusion coefficient, c_p is the gas concentration within the particle, r is the spherical coordinate and t is the time.

Taking into account non-steady conditions, a suitable solution for the partial differential equation (Eq. S8) could be $c_p(r,t) = X(t) \cdot Y(r)$, that is, the variable c_p is decomposed into two variables in function of t or r.

So,

$$\frac{\partial X}{\partial t} Y = -D \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Y}{\partial r}) X - \bar{k}_0 X \cdot Y \tag{S9}$$

And following:

$$\frac{\partial X}{\partial t} Y = X \cdot \left[-D \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Y}{\partial r}) - \bar{k}_0 \cdot Y \right] \tag{S10}$$

$$\frac{\partial X}{\partial t} \cdot \frac{1}{X} = \left[-\frac{1}{Y} \cdot \frac{D}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Y}{\partial r}) - \bar{k}_0 \right] \tag{S11}$$

It is noted that the left-hand side of these equations (Eq.S9-S11) is only a function of t and the right-hand side only dependences on r. Given these equations, a constant K is necessary set to balance both sides.

Let's solve the right member first:

$$K = \left[-\frac{1}{Y} \cdot \frac{D}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Y}{\partial r}) - \bar{k}_0 \right] \tag{S12}$$

$$\left[\frac{1}{Y} \cdot \frac{D}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Y}{\partial r}) + (\bar{k}_0 + K) \right] = 0 \tag{S13}$$

$$\left[\frac{D}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Y}{\partial r}) + Y \cdot (\bar{k}_0 + K) \right] = 0 \tag{S14}$$

Taking Y= $\frac{Z}{r}$; $\frac{\partial Y}{\partial r} = \frac{1}{r} \frac{\partial Z}{\partial r} - \frac{Z}{r^2}$;

$$\frac{\partial}{\partial r} \left[\frac{\partial Z}{\partial r} \cdot r - Z \right] = r \frac{\partial^2 Z}{\partial r^2} \tag{S15}$$

And replacing in Eq. S14 we will have Eq. S16:

$$\frac{D}{r} \cdot \frac{\partial^2 Z}{\partial r^2} + \frac{Z}{r} (\bar{k}_0 + K) = 0 \tag{S16}$$

Then, it can be written:

$$Z'' + \frac{\bar{k}_0 + K}{D} Z = 0 \tag{S17}$$

while for Eq. S14 you can write immediately:

$$K = \frac{\partial X}{\partial t}\frac{1}{X} \tag{S18}$$

Eq. S18 can be then presented like,

$$X = C_1 e^{Kt} \tag{S19}$$

for$t \rightarrow \infty$, X does not diverge and follows that K <0

$$X = C_1 e^{-|K|t} \tag{S20}$$

Indicating explicitly the sing for K,

$$Z'' + \frac{\bar{k}_0 - |K|}{D} Z = 0 \tag{S21}$$

Suggesting $\bar{k}_0 - |K| = \bar{K}$, it is a second order differential equation with constant coefficients whose characteristic polynomial is in which we have assumed $\bar{k}_0 > |K|$, making the term $\bar{K}$positive, which will then be verified.The following characteristic polynomial is obtained, replacing Eq. S21.

$$\alpha^2 + \frac{\bar{K}}{D} = 0 \tag{S22}$$

With

$$\alpha = \pm i\sqrt{\frac{\bar{K}}{D}} \tag{S23}$$

The solution of the differential equation is:

$$Z = Ae^{i\sqrt{\frac{\bar{K}}{D}}r} + Be^{-i\sqrt{\frac{\bar{K}}{D}}r} \tag{S24}$$

And

$$Y = \frac{Ae^{i\sqrt{\frac{\bar{K}}{D}}r} + Be^{-i\sqrt{\frac{\bar{K}}{D}}r}}{r} \tag{S25}$$

$$c_p = C_1 e^{-Kt} \frac{Ae^{i\sqrt{\frac{\bar{K}}{D}}r} + Be^{-i\sqrt{\frac{\bar{K}}{D}}r}}{r} \tag{S26}$$

In fact, Eq. S26 can be also written by adding a constant

$$c_p = K_1 + C_1 e^{-Kt} \frac{Ae^{i\sqrt{\frac{\bar{K}}{D}}r} + Be^{-i\sqrt{\frac{\bar{K}}{D}}r}}{r} \tag{S27}$$

Since this equation must also be respected for r = 0, we set A = -B and therefore:

$$c_p = K_1 + K_2 e^{-Kt} \frac{(e^{i\sqrt{\frac{\bar{K}}{D}}r} - e^{-i\sqrt{\frac{\bar{K}}{D}}r})}{r} \tag{S28}$$

Taking $C_2 = \frac{K_2}{2i}$and using$e^{x+iy} = e^x[cos(y) + isen(y)]$

It is possible to have:

$$c_p = K_1 + K_2 e^{-Kt} \frac{sen(\sqrt{\frac{\bar{K}}{D}}r)}{r} \tag{S29}$$

Considering that

$\sqrt{\frac{\bar{K}}{D}}R = \lambda\pi$for$\lambda = 1$;$\bar{K} = \frac{\pi^2 D}{R^2}$;$|K| = \left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right|$

The relationship could be expressed like

$$|K| = \frac{\pi^2 D}{R^2} - \bar{k}_0 \text{if} \frac{\pi^2 D}{R^2} > \bar{k}_0 \tag{S30}$$

Or

$$|K| = \bar{k}_0 - \frac{\pi^2 D}{R^2} \text{if} \frac{\pi^2 D}{R^2} < \bar{k}_0 \tag{S31}$$

Let's assume$|K| = \frac{\pi^2 D}{R^2} - \bar{k}_0$, and $\frac{\pi^2 D}{R^2} > \bar{k}_0$, to then verify this assumption.

$$c_p = K_1 + K_2 e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right|t} \frac{sen(\frac{\pi}{R}r)}{r} \tag{S32}$$

The boundary conditions are established to be

$t \to 0$; r =R ; $c_p = c_g \Rightarrow K_1 = c_g$

$$c_p = c_g + K_2 e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \frac{sen(\frac{\pi}{R} r)}{r} \tag{S33}$$

$t \to 0$; r =0 ; $c_p = 0 \Rightarrow K_2 = -\frac{c_g R}{\pi}$ and c_p can be represented like:

$$c_p = c_g - \frac{c_g R}{\pi} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \frac{sen(\frac{\pi}{R} r)}{r} \tag{S34}$$

The expression from Eq. S35 can be re-written as

$$c_p = c_g \left[1 - \frac{R}{\pi} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \frac{sen(\frac{\pi}{R} r)}{r}\right] \tag{S35}$$

The equation also satisfies the following condition:
$t \to \infty$; r = r ; $c_p = c_g$

Now, knowing the function $c_p = c_p(r, t)$, it is possible to determine the flux per surface unit for the particle. By matching both the Fick's second law and the total enteringfluxinto the particle, let's have

$$J(r,t) = -D \frac{\partial c}{\partial r} \text{ and } \bar{J}(R,t) = -D \left[\frac{\partial c}{\partial r}\right]_R \cdot 4\pi R^2 \tag{S36}$$

$$\bar{J}(r,t) = -D \frac{\partial c}{\partial r} 4\pi r^2 = -D \cdot 4\pi r^2 \cdot c_g \frac{\partial}{\partial r}\left[1 - \frac{R}{\pi} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \frac{sen(\frac{\pi}{R} r)}{r}\right] \tag{S37}$$

$$\bar{J}(r,t) = 4\pi r^2 D c_g \frac{R}{\pi} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \left[\frac{cos\left(\frac{\pi \cdot r}{R}\right)\frac{\pi}{R}}{r} - \frac{sen\left(\frac{\pi \cdot r}{R}\right)}{r^2}\right] \tag{S38}$$

$$\bar{J}(r,t) = 4RDc_g e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \left[cos\left(\frac{\pi \cdot r}{R}\right)\frac{\pi}{R} r - sen\left(\frac{\pi \cdot r}{R}\right)\right] \tag{S39}$$

Considering that the flux moves with respect to the opposite direction of *r*, let's have for one particle that

$$\bar{J}(t)_R = -4RDc_g \pi e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \tag{S40}$$

$$|\bar{J}(t)|_R = 4RDc_g \pi e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \tag{S41}$$

If we consider all the particles,

$$|\bar{J}(t)|_R = \frac{4RDc_g\pi}{4\pi R^2} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \cdot S \tag{S42}$$

Where *S* is the total surface for particle in the bed

$$|\bar{J}(t)|_R = \frac{Dc_g}{R} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \cdot S \tag{S43}$$

The infinitesimal flux relative to the infinitesimal surface of the bed is equal to:

$$d\bar{J}_R = \frac{Dc_g}{R} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \cdot dS \tag{S44}$$

By defining a specific surface *s* as the surface offered by the particles per unit volume of the bed, we have that$dS = s \cdot dV$

$$dJ_R = \frac{Dc_g}{R} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \cdot sdV \tag{S45}$$

Once a portion of the volume of the bed *dV* is fixed, this flow is linked to the variation of the moles in the gas that serves this infinitesimal portion of the bed, over time, matching Eq. S44 and S45.

$\frac{Dc_g}{R} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \cdot sdV = -\frac{d\Delta c_g}{dt} dV$ This variation decreases over time until it is zero.

$\Delta c_g = c_{in\_g} - c_{out\_g}$ where $c_{in\_g} = cos\,t$ and $c_{out\_g} = c_g$

So,

$\frac{Dc_g}{R} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \cdot s = \frac{dc_g}{dt}$ or also (S46)

$\frac{dc_g}{c_g} = \frac{sD}{R} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \cdot dt$,giving as a result Eq. S47

$$\int_{c_t}^{c_0} \frac{dc_g}{c_g} = \frac{sD}{R} \int_t^{\infty} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \cdot dt \tag{S47}$$

After integrating with respect to concentration and time,

$$ln\frac{c_0}{c_{g\_t}} = \frac{RDs}{\left(\pi^2 D - \bar{k}_0 R^2\right)} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \tag{S48}$$

$$ln\frac{c_0}{c_{g\_t}} = \frac{RDs}{\left(\pi^2 D - \bar{k}_0 R^2\right)} e^{-\left|\frac{\pi^2 D}{R^2} - \bar{k}_0\right| t} \tag{S49}$$

$$ln\left(ln\frac{c_0}{c_{g\_t}}\right) = ln\left(\frac{RDs}{\left(\pi^2 D - \bar{k}_0 R^2\right)}\right) - \frac{\pi^2 D - \bar{k}_0 R^2}{R^2} t \tag{S50}$$

Comparing the Eq. S40 with the relative deactivation model equation (Eq. S51), it is observed

$$ln\left(ln\frac{c_0}{c_{g\_t}}\right) = ln\left(\frac{k_s W}{Q}\right) - k_a t \tag{S51}$$

$$\frac{k_s W}{Q} = \frac{RDs}{\left(\pi^2 D - \bar{k}_0 R^2\right)} \quad \text{(S52)}$$

$$k_d = \frac{\left(\pi^2 D - \bar{k}_0 R^2\right)}{R^2} \quad \text{(S53)}$$

Then,

$$k_{s0} = \frac{sDQ}{WRk_d} \quad \text{(S54)}$$

By using $s = \frac{S}{V}$ as the surface per volume unit from the bed:

$S = s_p \cdot n_p = 4\pi R^2 \cdot n_p$ while

$$V = \frac{V_p \cdot n_p}{(1-\varepsilon)} = \frac{\frac{4}{3}\pi R^3 \cdot n_p}{(1-\varepsilon)} \quad \text{(S55)}$$

The total volumeis equal to:

$$V = V_{particle} + V_{vaccium} \quad \text{(S56)}$$

Defying ε as the vacuum fraction:

$$\varepsilon = \frac{V_{vaccium}}{V} \quad \text{(S57)}$$

and then a similar analysis for the particle fraction corresponds to Eq. S57.

$$(1-\varepsilon) = \frac{V_{particle}}{V} \quad \text{(S58)}$$

Now, matching Eq. S58 with previous analysis

$V = \frac{V_{particle}}{(1-\varepsilon)} = \frac{\frac{4}{3}\pi R^3 \cdot n_p}{(1-\varepsilon)}$, and $s = \frac{S}{V} = \frac{3\cdot(1-\varepsilon)}{R}$

(S59)

Now, taking $k_s = \frac{3DQ(1-\varepsilon)}{WR^2 k_d}$

$D = \frac{k_s k_d W R^2}{3Q(1-\varepsilon)}$ on the right side, we have all known quantities.

Now known the value of D, it is possible to determine the value of $\bar{k}_0$,

$$\bar{k}_0 = \frac{\pi^2 D}{R^2} - k_d \quad \text{(S60)}$$