Tarnishing of Metal Surfaces

CME 324: Transport Phenomena I

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Problem Statement Foundation (BSL 18B.13)

- We chose to study mass transport in the form of rust and other tarnishing!
- Oxidation reactions on most metals produce deposited oxide films that have greater volume than the metal consumed in the reaction.

- Our studies are based on BSL 18B.13
- The textbook problem is in Cartesian coordinates. Our studies will be around pipes, which are cylindrical coordinates.
- We will explore how mass transport in a pipe also affects heat and momentum transport.

18B.13. Tarnishing of metal surfaces. In the oxidation of most metals (excluding the alkali and alkaline-earth metals) the volume of oxide produced is greater than that of the metal consumed. This oxide thus tends to form a compact film, effectively insulating the oxygen and metal from each other. For the derivations that follow, it may be assumed that

(a) For oxidation to proceed, oxygen must diffuse through the oxide film and that this diffusion follows Fick's law.

(b) The free surface of the oxide film is saturated with oxygen from the surrounding air.

(c) Once the film of oxide has become reasonably thick, the oxidation becomes diffusion controlled; that is, the dissolved oxygen concentration is essentially zero at the oxide-metal surface.

(d) The rate of change of dissolved oxygen content of the film is small compared to the rate of reaction. That is, quasi-steady-state conditions may be assumed.

(e) The reaction involved is $\frac{1}{2}xO_2 + M \rightarrow MO_x$.

We wish to develop an expression for rate of tarnishing in terms of oxygen diffusivity through the oxide film, the densities of the metal and its oxide, and the stoichiometry of the reaction. Let c_0 be the solubility of O_2 in the film, c_f the molar density of the film, and z_f the thickness of the film. Show that the film thickness is

$$z_f = \sqrt{\frac{4\mathfrak{D}_{O_2-MO_x} t}{x} \frac{c_0}{c_f}} \qquad (18B.13\text{-}1)$$

This result, the so-called "quadratic law," gives a satisfactory empirical correlation for a number of oxidation and other tarnishing reactions.[10] Most of these are, however, much more complex than the mechanism given above.[11]

Solving BSL 18B.13 Part I: Assumptions

To solve this problem, we must first make some assumptions. Most of these assumptions are listed in 18B.13's problem statement.

- Steady State
- No Convection
- Diffusion obeys Fick's Law
- One-dimensional diffusion as a function of r
- Constant molar film density
- Constant diffusivity

All these assumptions are valid because after the first layer of film forms, diffusion is the only reasonable mechanism to cause further oxidation.

Solving BSL 18B.13 Part II: Boundary Conditions

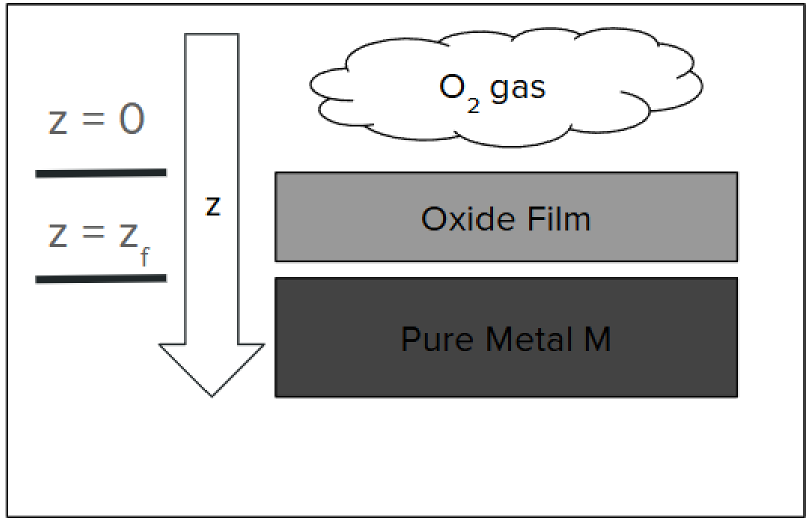
For Cartesian, Our coordinate system is set where z is the direction of oxygen gas diffusion.

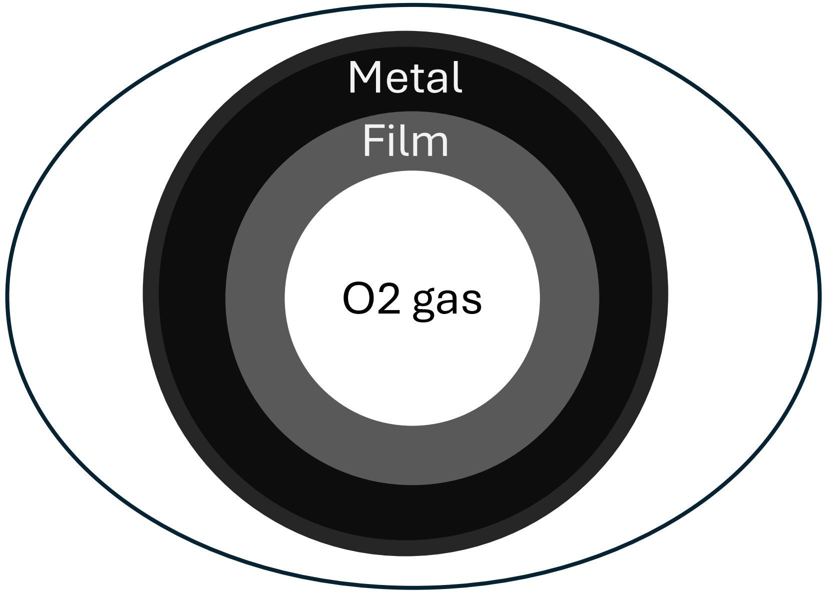
- At z = 0, $c_{O_2} = c_0$
- At z = z_f, $c_{O_2} = 0$

We assume that the dissolved concentration of oxygen gas is zero at the oxide-metal interface once the film is sufficiently thick.

For Cylindrical, our coordinate system is set where oxygen diffuses radially outward.

- At r = 0, $c_{O_2} = c_0$
- At r = r_f, $c_{O_2} = 0$





Solving BSL 18B.13 Part III: Combined Flux

Fick's Law for Cylindrical and Cartesian coordinates is the same for the r-direction! So, we can focus on just z for now.

When we apply Equation 18.0-1 from BSL to our system, we get:

- $N_{O_2,z} = -c\mathfrak{D}_{O_2-MO_x}\frac{\partial x_{O_2}}{\partial z} + x_{O_2}(N_{O_2,z} + N_{MO_x,z})$

However, we assumed no convection. We can simplify the concentration as well to get:

- $N_{O_2,z} = -\mathfrak{D}\frac{\partial c_{O_2}}{\partial z}$ (Letting $\mathfrak{D}$ = $\mathfrak{D}_{O_2-MO_x}$ for simplicity)

Our combined flux has simplified down into a Fick's Law relation.

In addition, we know the concentration gradient across the entire system from our boundary conditions!

Solving BSL 18B.13 Part IV: Finding the Gradient

- $N_{O_2,z} = -\mathfrak{D}\dfrac{\partial c_{O_2}}{\partial z}$

Our concentration gradient across the system, $\Delta\dfrac{c_{O_2}}{z}$, is already known because we have our boundary conditions. If we assume that gradient is constant, we can get:

- $\dfrac{\partial c_{O_2}}{\partial z} = \Delta\dfrac{c_{O_2}}{z} = \dfrac{0-c_0}{z_f-0} = -\dfrac{\boldsymbol{c_0}}{\boldsymbol{z_f}}$

Using the boundary conditions:

- At z = 0, $\mathrm{c}_{\mathrm{O}_2} = \mathrm{c}_0$
- At z = z_f, $\mathrm{c}_{\mathrm{O}_2} = 0$

Solving BSL 18B.13 Part V: Relating the Reaction to Diffusion

Here comes the hard part: We know the rate of oxygen diffusion, and we know the stoichiometry of the reaction:

- $\frac{1}{2}xO_2 + M \rightarrow MO_x$

So, for every $\frac{1}{2}$x mol of oxygen that diffuses, 1 mol of our metal reacts. In equation form, we can relate the reaction to our diffusion:

- $\frac{1}{2}xO_2 = MO_x$, so $O_2 = \frac{2MO_x}{x}$.
- Next step is relating oxide production to film thickness

Solving BSL 18B.13 Part VI: Relating the molar deposit to film thickness over time

From our previous equation, we can now say that:

- $MO_x = \frac{2\mathfrak{D}c_0}{xz_f}$. Now, assuming we know the molar density of the film deposit, we can divide both sides to get the thickness over time!
- $\frac{MO_x}{c_f} = \frac{2\mathfrak{D}c_0}{xz_f c_f}$. Measuring the differential change of our flux gives us:
- $\Delta\frac{MO_x}{c_f} = \Delta\frac{2\mathfrak{D}c_0}{xz_f c_f}$. The change of the film thickness is just z, so we can convert to differential form to get thickness over time:
- $d\frac{MO_x}{c_f} = \frac{dz}{dt} = \frac{2\mathfrak{D}c_0}{xzc_f}$. Now we can separate and integrate!

Solving BSL 18B.13 Part VII: Integration

- $\frac{dz}{dt} = \frac{2\mathfrak{D}c_0}{xzc_f} \rightarrow zdz = \frac{2\mathfrak{D}c_0}{xc_f}dt$ (Separate)

Our system ranges in the z direction from 0 to our film thickness z_f.

Our system ranges in time from 0 to some arbitrary time t.

Integrating in respect to these bounds gives us:

- $\int_0^{z_f} zdz = \int_0^t \frac{2\mathfrak{D}c_0}{xc_f}dt$
- $\frac{1}{2}z_f^2 = \frac{2\mathfrak{D}c_0 t}{xc_f}$

Solving BSL 18B.13 Part VIII: The Answer

Solving for z_f gives us:

- $z_f = \sqrt{\frac{4\mathfrak{D}_{O_2-MO_x}t}{x}\frac{c_0}{c_f}}$

This relationship is known as the “Quadratic Law”!

How can we interpret what this result tells us?

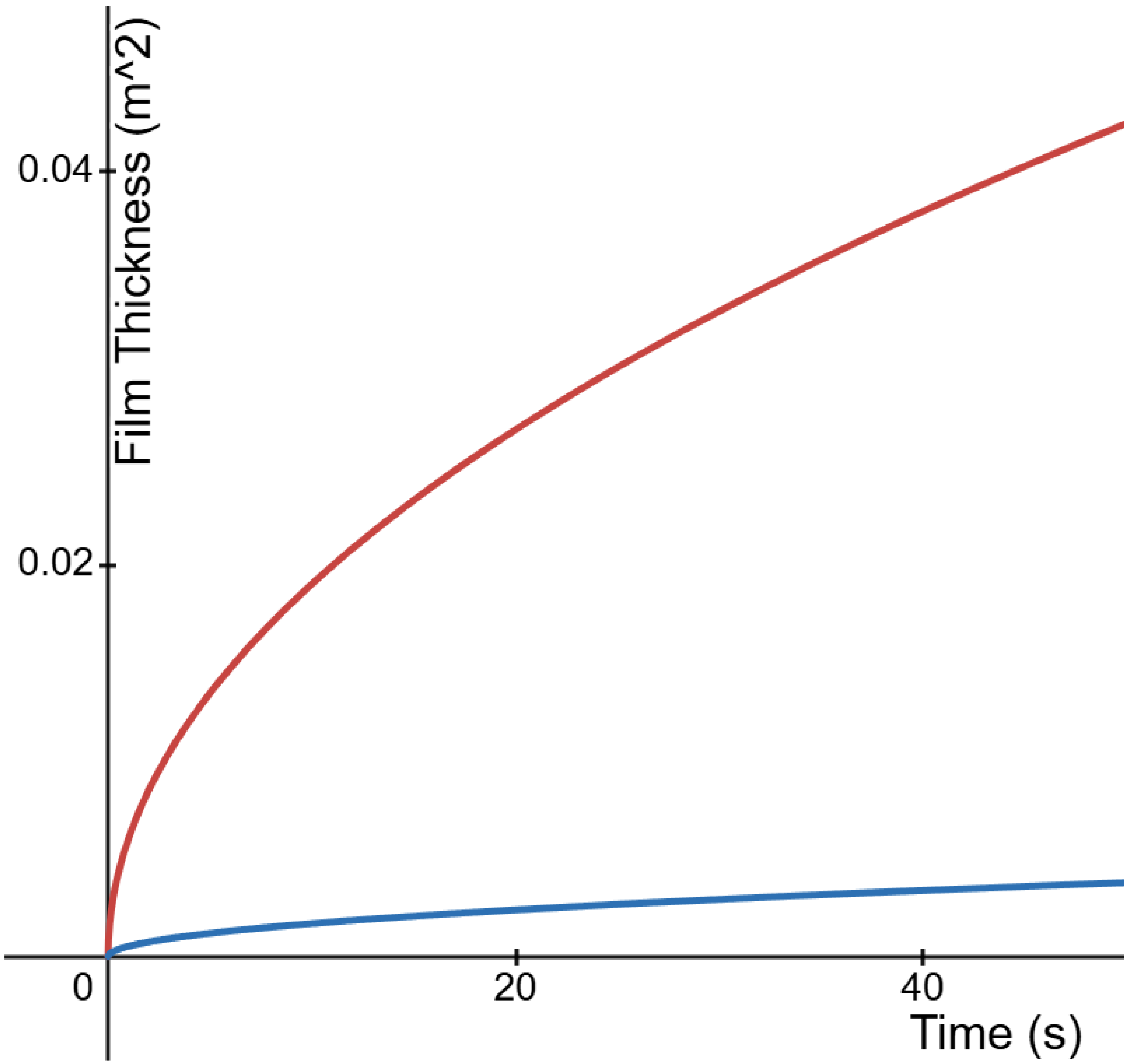
Fun fact: The unrevised 2nd edition of BSL incorrectly lists the coefficient as 2 instead of 4, likely indicating an integration error or a misunderstanding of the reaction stoichiometry.

Graphical Example: Two Different Metals

- X axis: Time, in seconds
- Y axis: Film thickness, in m^2
- Red Line: Aluminum (III) Oxide
  - $z_f \approx 6.002 * 10^{-3} * \sqrt{t}$
- Blue Line: Magnesium (I) Oxide
  - $z_f \approx 5.334 * 10^{-4} * \sqrt{t}$

Sources of constants: Journal of Applied Physics, 85 (1999) 7646.

- Other metals like titanium build up so slowly they would be a flat line at the bottom of this graph!



Modeling Layer Growth to Estimate Flow Rates

- Using transport equations, we can model how fast the oxide layer grows over time and the maximum thickness of the layer.
- As the oxide thickens, the pipe’s inner diameter shrinks.
- A smaller diameter increases flow resistance and lowers flow rate.
- By modeling growth, we can predict flow reduction without destructive measurements/testing.

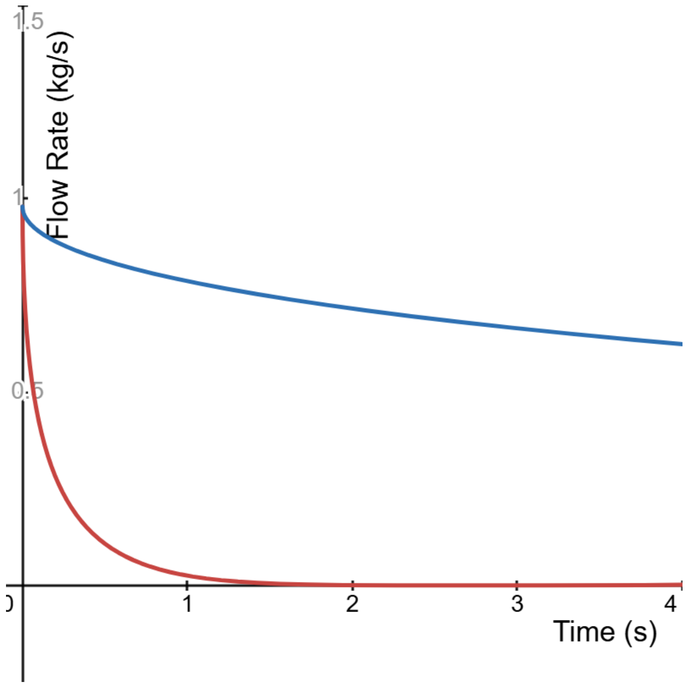
Determining Type of Rust Layer Based on Buildup Rate

- The diffusion coefficient ($\mathfrak{D}$) controls how fast ions or oxygen move through the oxide.
- Red rust is porous, so it has a higher $\mathfrak{D}$ and allows faster diffusion.
- Black rust is dense, leading to a lower $\mathfrak{D}$ and slower diffusion.
- A lower diffusion rate helps black rust protect the metal surface better.

$$z_f = \sqrt{\frac{4\mathfrak{D}_{O_2-MO_x} t}{x}\frac{c_o}{c_f}}$$

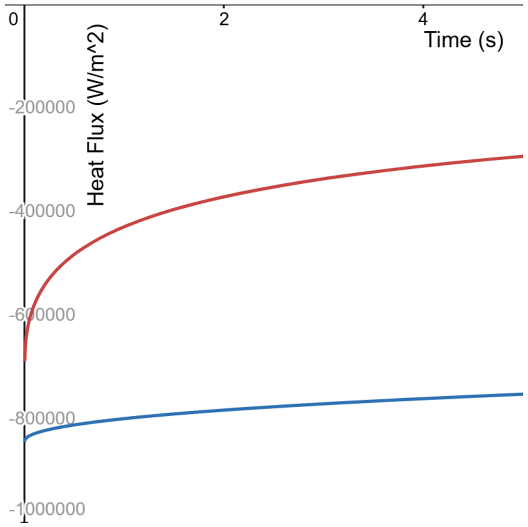
Mass Flow Rate Reduction in a Pipe

- Using our shell balance solutions and our film thickness equations, we can predict the mass flow rate drop.
- Hagen-Poiseuille Equation: $w = \frac{\pi(\wp_0 - \wp_L)R^4\rho}{8\mu L}$. Assume: Everything is constant except for the radii, where $R = R_0 - C\sqrt{t}$, where C depends on our metal.
- Here we can see the drastic difference again!
- In a 0.01m diameter pipe pumping water.
  - Aluminum (Red): Film blocks off pipe at 2.6 seconds.
  - Magnesium (Blue): After 5 seconds, pipe is operating at ~60% efficiency. Blocks off after over 5 minutes.
- A slight difference in material makes a huge difference in design!

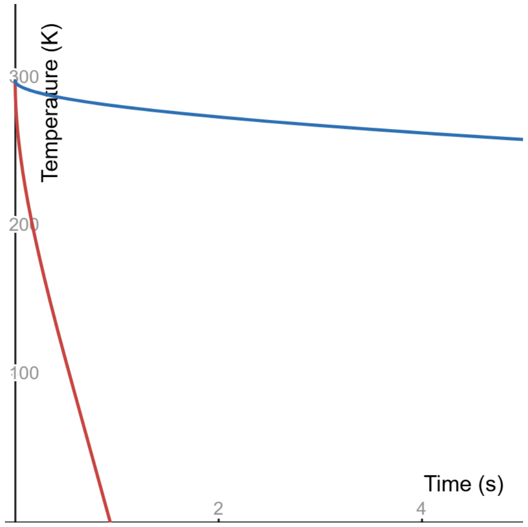


Heat Conduction Through a Pipe

- Similarly, we can predict a temperature and heat distribution change inside a pipe when the radius shrinks. From our heat in a Steam Pipe Notes:
- Heat Flux: $q = \frac{K(T_0 - T_S)}{r \ln K}$. Temperature: $\frac{T_r - T_0}{T_S - T_0} = \frac{\ln \frac{r}{R}}{\ln K}$



Heat Flux out of the pipe decreases by half for aluminum around 5 seconds. This happens because the heat flux is radially outward and has more material to travel through to escape.



The temperature at the outer surface of the pipe is even worse, with the aluminum pipe theoretically hitting absolute zero before a single second has passed.

Real World Applications

- In power production, the buildup of oxide layers can reduce thermal and mechanical output, reducing overall plant performance.
- In chemical production, monitoring and controlling corrosion levels limits the impurities found in final products.