

Finding the criteria that reaction could be treated as well-mixed and transport free?

Which equation should be used to calculate t_{rl} ?

(1) from CH8: $t = [\text{SO}_2]_g / (R_{S(\text{IV})} * L)$;

(2) from CH9: $t = [S(\text{IV})]_{aq} / R_{S(\text{IV})}$;

Response:

You can answer your question below if you stop and think what the two criteria imply. You should do that while discussing it with your classmates. At the start you should recognize that the two criteria were presented for a specific reaction set and specific circumstances. Later on we will generalize this. Clearly, equation (2) provides you with the measure of characteristic reaction time in the liquid and you can compare that to characteristic time of diffusion via gas film (resistances in series) to determine which is dominant. You can also compare it to characteristic liquid diffusion time and reach a conclusion. Equation (1) includes the transport resistance from the gas phase and dissociation in liquid in the characteristic reaction time. So compute both and think what they mean. Play with the conditions and reach your own conclusion which one should you use. The purpose of HW 5 is to understand these things and not have me tell you which formula to use. I am convinced that you and your classmates can do it successfully.

The more subtle part that you should pay attention to is the fact that Ch 8N and all equations in Ch 9 are written as if the reaction is first order with respect to sulfur dioxide. But ozonation reaction of sulfur dioxide is second order: first order in ozone and first order in sulfur dioxide. (So is the reaction with hydrogen peroxide). So pseudo first order behavior is assumed with respect to the reactant that is present in smaller concentration. Dissolved ozone concentration is independent of pH but dissolved sulfur dioxide concentration is not. So I suggest that you find which reactant is the rate limiting first. Then calculate the pseudo – first order rate constant with respect to that reactant. (We had a similar HW problem where we had a second order constant and generated pseudo first order one or the other way around). The characteristic reaction time in the drop then without doubt is the reciprocal of that pseudo first order rate constant. Compare that with characteristic diffusion time of the limiting reactant.