

Chemistry 2710 Spring 2003 Test 2 Solutions

1. At equilibrium,

$$\begin{aligned}k_1[\text{HOBr}][\text{Br}^-][\text{H}^+] &= k_{-1}[\text{Br}_2]. \\ \therefore K &= \frac{[\text{Br}_2]}{[\text{HOBr}][\text{Br}^-][\text{H}^+]} = \frac{k_1}{k_{-1}} \\ &= \frac{1.6 \times 10^{10} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}}{110 \text{ s}^{-1}} = 1.5 \times 10^8 \text{ L}^2 / \text{mol}^2.\end{aligned}$$

This value is in reasonable agreement with the thermodynamic equilibrium constant, considering the number of significant figures in the calculation.

2. There are three possible solutions to this problem. All of them start with a consideration of the stoichiometry.

$$(\text{NO used}) = 2(\text{Cl}_2 \text{ used}) = (\text{NOCl produced}).$$

In mathematical form, we get

$$[\text{NO}]_0 - [\text{NO}] = 2([\text{Cl}_2]_0 - [\text{Cl}_2]) = [\text{NOCl}]. \quad (1)$$

What you do next depends on whether you want to work from the rate equation for NO, Cl₂ or NOCl.

Using [NO] as the variable. The rate of change of [NO] is

$$\frac{d[\text{NO}]}{dt} = -2k[\text{NO}]^2[\text{Cl}_2]. \quad (2)$$

Using equation 1, the concentration of Cl₂ is

$$[\text{Cl}_2] = [\text{Cl}_2]_0 - \frac{1}{2}([\text{NO}]_0 - [\text{NO}]).$$

We substitute this concentration into equation 2, and then carry out the separation of variables:

$$\begin{aligned}\frac{d[\text{NO}]}{dt} &= -2k[\text{NO}]^2 \left\{ [\text{Cl}_2]_0 - \frac{1}{2}([\text{NO}]_0 - [\text{NO}]) \right\}. \\ \therefore -2k dt &= \frac{d[\text{NO}]}{[\text{NO}]^2 \left\{ [\text{Cl}_2]_0 - \frac{1}{2}([\text{NO}]_0 - [\text{NO}]) \right\}}. \\ \therefore -2k \int_0^t dt' &= \int_{[\text{NO}]_0}^{[\text{NO}]} \frac{dx}{x^2 \left\{ [\text{Cl}_2]_0 - \frac{1}{2}([\text{NO}]_0 - x) \right\}}. \\ \therefore t &= \frac{-1}{2k} \int_{[\text{NO}]_0}^{[\text{NO}]} \frac{dx}{x^2 \left\{ [\text{Cl}_2]_0 - \frac{1}{2}([\text{NO}]_0 - x) \right\}}.\end{aligned}$$

Using $[\text{Cl}_2]$ as the variable. The rate of change of $[\text{Cl}_2]$ is

$$\frac{d[\text{Cl}_2]}{dt} = -k[\text{NO}]^2[\text{Cl}_2]. \quad (3)$$

Using equation 1, the concentration of NO is

$$[\text{NO}] = [\text{NO}]_0 - 2([\text{Cl}_2]_0 - [\text{Cl}_2]).$$

We substitute this concentration into equation 3, and then carry out the separation of variables:

$$\begin{aligned} \frac{d[\text{Cl}_2]}{dt} &= -k[\text{Cl}_2] \{[\text{NO}]_0 - 2([\text{Cl}_2]_0 - [\text{Cl}_2])\}^2. \\ \therefore -k dt &= \frac{d[\text{Cl}_2]}{[\text{Cl}_2] \{[\text{NO}]_0 - 2([\text{Cl}_2]_0 - [\text{Cl}_2])\}^2}. \\ \therefore -k \int_0^t dt' &= \int_{[\text{Cl}_2]_0}^{[\text{Cl}_2]} \frac{dx}{x \{[\text{NO}]_0 - 2([\text{Cl}_2]_0 - x)\}^2}. \\ \therefore t &= \frac{-1}{k} \int_{[\text{Cl}_2]_0}^{[\text{Cl}_2]} \frac{dx}{x \{[\text{NO}]_0 - 2([\text{Cl}_2]_0 - x)\}^2}. \end{aligned}$$

Using $[\text{NOCl}]$ as the variable. The rate of change of $[\text{NOCl}]$ is

$$\frac{d[\text{NOCl}]}{dt} = 2k[\text{NO}]^2[\text{Cl}_2]. \quad (4)$$

Using equation 1, the concentrations of NO and of Cl_2 expressed in terms of $[\text{NOCl}]$ are

$$\begin{aligned} [\text{NO}] &= [\text{NO}]_0 - [\text{NOCl}], \\ \text{and } [\text{Cl}_2] &= [\text{Cl}_2]_0 - \frac{1}{2}[\text{NOCl}]. \end{aligned}$$

We substitute this concentration into equation 4, and then carry out the separation of variables:

$$\begin{aligned} \frac{d[\text{NOCl}]}{dt} &= 2k([\text{NO}]_0 - [\text{NOCl}])^2 \left([\text{Cl}_2]_0 - \frac{1}{2}[\text{NOCl}] \right). \\ \therefore 2k dt &= \frac{d[\text{NOCl}]}{([\text{NO}]_0 - [\text{NOCl}])^2 \left([\text{Cl}_2]_0 - \frac{1}{2}[\text{NOCl}] \right)}. \\ \therefore 2k \int_0^t dt' &= \int_0^{[\text{NOCl}]} \frac{dx}{([\text{NO}]_0 - x)^2 \left([\text{Cl}_2]_0 - \frac{1}{2}x \right)}. \\ \therefore t &= \frac{1}{2k} \int_0^{[\text{NOCl}]} \frac{dx}{([\text{NO}]_0 - x)^2 \left([\text{Cl}_2]_0 - \frac{1}{2}x \right)}. \end{aligned}$$

3. (a)

$$\begin{aligned}\frac{da}{dt} &= -k_1a + k_{-1}b^2. \\ \frac{db}{dt} &= 2k_1a - 2k_{-1}b^2 - k_2b. \\ \frac{dc}{dt} &= k_2b.\end{aligned}$$

(b) $A \rightarrow 2C$

(c) If the second step is slow, we can use the EA for the (fast) first step:

$$\begin{aligned}k_1a &\approx k_{-1}b^2. \\ \therefore b &\approx \sqrt{\frac{k_1a}{k_{-1}}}.\end{aligned}$$

The rate of the reaction is

$$v = \frac{1}{2} \frac{dc}{dt} = \frac{1}{2} k_2 b.$$

Substituting in our approximate value for b , we get

$$v \approx \frac{k_2}{2} \sqrt{\frac{k_1}{k_{-1}}} a^{1/2}.$$

(d) $v = -\frac{da}{dt}$, so we have a simple rate law with an order of $\frac{1}{2}$ with respect to a . Substituting this order of reaction into the general integrated rate law, we get

$$a^{1/2} = a_0^{1/2} - \frac{1}{2}kt,$$

where

$$k = \frac{k_2}{2} \sqrt{\frac{k_1}{k_{-1}}}.$$

If we perform an experiment in which we follow a as a function of t , we can then plot \sqrt{a} vs t . We should get a straight line of slope $-k/2$. Note that we *can't* get any of the individual rate constants. We only get the combination named k above.

(e) We have the velocity vector

$$\mathbf{v} = (-k_1a + k_{-1}b^2, 2k_1a - 2k_{-1}b^2 - k_2b).$$

The a nullcline is the curve on which

$$\begin{aligned} -k_1 a + k_{-1} b^2 &= 0. \\ \therefore a &= k_{-1} b^2 / k_1. \end{aligned}$$

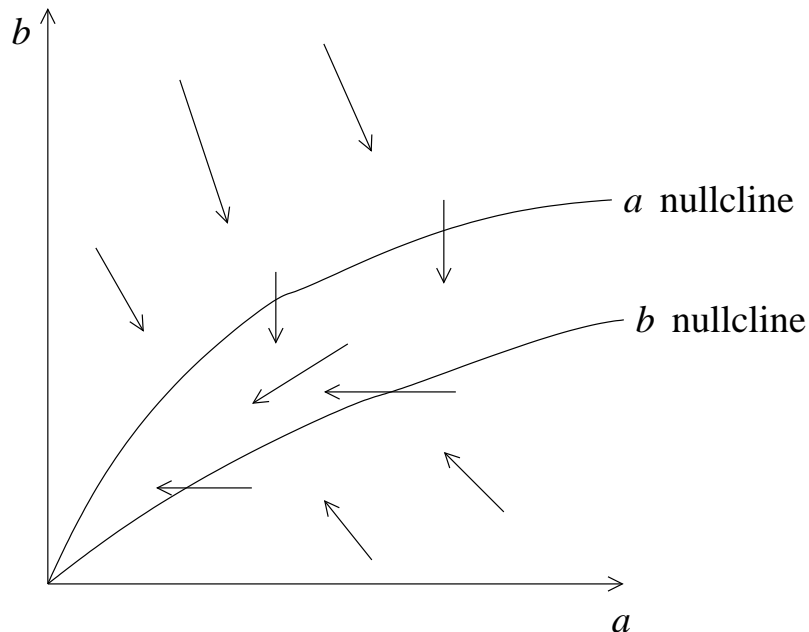
(You'll see in a minute why I'm solving for a rather than b .)

The b nullcline is the curve

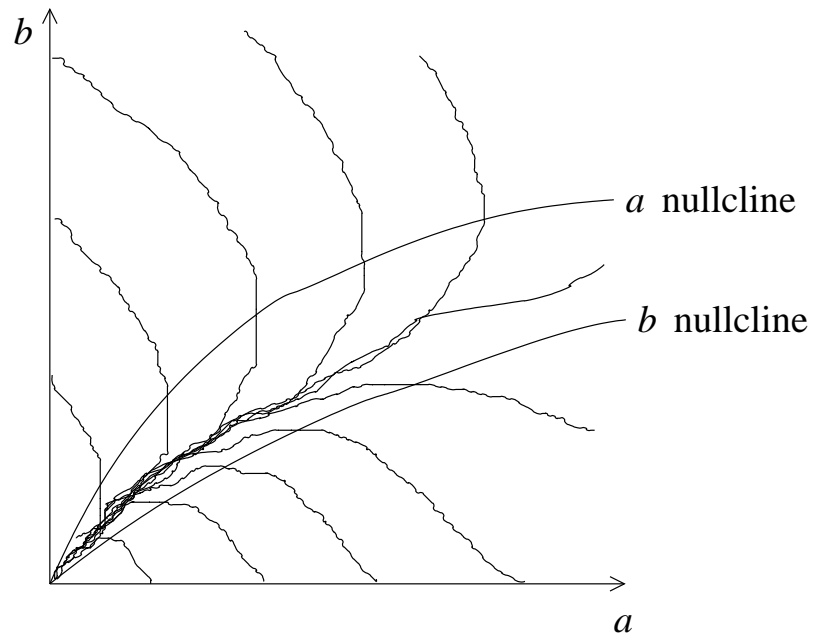
$$\begin{aligned} 2k_1 a - 2k_{-1} b^2 - k_2 b &= 0. \\ \therefore a &= \frac{b}{2k_1} (2k_{-1} b + k_2) = \frac{k_{-1}}{k_1} b^2 + \frac{k_2}{2k_1} b. \end{aligned}$$

The a and b nullclines are both parabolas in b passing through the origin. Comparing the formula for the b nullcline to the formula for the a nullcline, we see that at any given value of b , the b nullcline corresponds to a larger value of a . If a is on our horizontal axis, this means that the b nullcline is *below* the a nullcline.

At small values of b (near the a axis), $\mathbf{v} \rightarrow (-k_1 a, 2k_1 a) \sim (-, +)$. At small values of a (near the b axis), $\mathbf{v} \rightarrow (k_{-1} b^2, -2k_{-1} b^2 - k_2 b) \sim (+, -)$. Between the nullclines, the velocity vector has to point towards the equilibrium point, so it should be of the form $(-, -)$. This makes sense if we consider that (e.g.) we have to cross the b nullcline to get from the region where $\mathbf{v} \sim (-, +)$ to the space between the nullclines. The velocity field is shown below:



There's nothing to do now but to draw the trajectories:



We now know that there's a slow manifold between the two nullclines. The rate law derived in part c is consistent with our sketch provided the slow manifold is closer to the a nullcline than to the b nullcline.