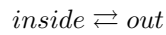


- **Set up:** What is the “equilibrium constant” for the “reaction” we’re studying?



- **Predict:** what is the ratio of the time the robot spends inside versus outside the circle ( $t_{inside}/t_{outside}$ )? The circle’s radius is 20 *in* and the square’s sides are 200 *in*. Once you have an answer, raise your hand and one of us will check it.

$$\frac{t_{inside}}{t_{outside}} =$$

- **Interpret:** Circle an answer and be prepared to defend it. We think  $t_{inside}/t_{outside}$  is determined by:  
ENTROPY    or    ENTHALPY

- **Predict:** What do you predict would happen if we introduced a “hole” of depth  $d$  inside the circle?

- **Observation.** Plot  $t_{in}/t_{out}$  against  $d$  in a spreadsheet program. Fit a trend line to the data, choosing the model that best fits the data.

$d$	$t_{in}/t_{out}$

- Combine the fit you just did with the equation you found in the top part. What do you think each of the terms of your fit mean?

- Circle an answer and be prepared to defend it. We think the hole adds:

ENTROPY   or   ENTHALPY

to the robot system.

- Imagine, instead of a robot exploring a plane, we have a peptide chain exploring arrangements of bonds (conformations). (See the video on the screen). Draw a plane with a hole below. Can you label different conformations from the video on the drawing? What is the *in* state? What is the *out* state?

Our final relationship is:

$$\frac{t_{inside}}{t_{outside}} = \frac{A_{inside}}{A_{outside}} \cdot e^{d/C}$$

- $A_{\text{inside}}/A_{\text{outside}}$  is \_\_\_\_\_ : the amount of time a robot spends in a region depends on the region's area. *The amount of time a molecule spends in a "state" (region) depends on the number of microstates (area) within that state.*
- $d$  is \_\_\_\_\_ : a region is more favorable for the robot, so it will spend more time there. *The amount of time a molecule spends in a state depends on how favorable interactions are in that state (the depth of the hole).*
- $C$  is \_\_\_\_\_ : at higher  $C$ , the robot is less likely to get stuck. If  $C$  is large, the robot can always climb out (as  $C \rightarrow \infty$ ,  $e^{d/C} \rightarrow 1$ ). If  $C$  is small, the robot is stuck (as  $C \rightarrow 0$ ,  $e^{d/C} \rightarrow \infty$ ). *A molecule can break favorable interactions if the temperature is high enough.*

Using simple algebra, we can turn our equation into  $\Delta G = \Delta H - T\Delta S$ .

1. Take the natural log of both sides:

$$\ln\left(\frac{t_{inside}}{t_{outside}}\right) = \ln\left(\frac{A_{inside}}{A_{outside}} \cdot e^{d/C}\right)$$

2. Use the log rule  $\log(A \cdot B) = \log(A) + \log(B)$ :

$$\ln \left( \frac{t_{inside}}{t_{outside}} \right) = \ln \left( \frac{A_{inside}}{A_{outside}} \right) + \ln \left( e^{d/C} \right)$$

3. Simplify using the log rule  $\ln(e^x) = x$ :

$$\ln\left(\frac{t_{inside}}{t_{outside}}\right) = \ln\left(\frac{A_{inside}}{A_{outside}}\right) + \frac{d}{C}$$

4. Multiply both sides by  $-C$ :

$$-C \cdot \ln\left(\frac{t_{inside}}{t_{outside}}\right) = -C \cdot \ln\left(\frac{A_{inside}}{A_{outside}}\right) - d$$

5. From above,  $C = RT$ . Substitute this in:

$$-RT \cdot \ln \left( \frac{t_{inside}}{t_{outside}} \right) = -RT \cdot \ln \left( \frac{A_{inside}}{A_{outside}} \right) - d$$

6. Now we just give all of the terms in our equation special names:

$$\Delta G \equiv -RT \ln \left( \frac{t_{inside}}{t_{outside}} \right)$$

$$\Delta S \equiv R \ln \left( \frac{A_{inside}}{A_{outside}} \right)$$

$$\Delta H \equiv -d$$

7. Finally, we're left with:

$$\Delta G = -T\Delta S + \Delta H$$