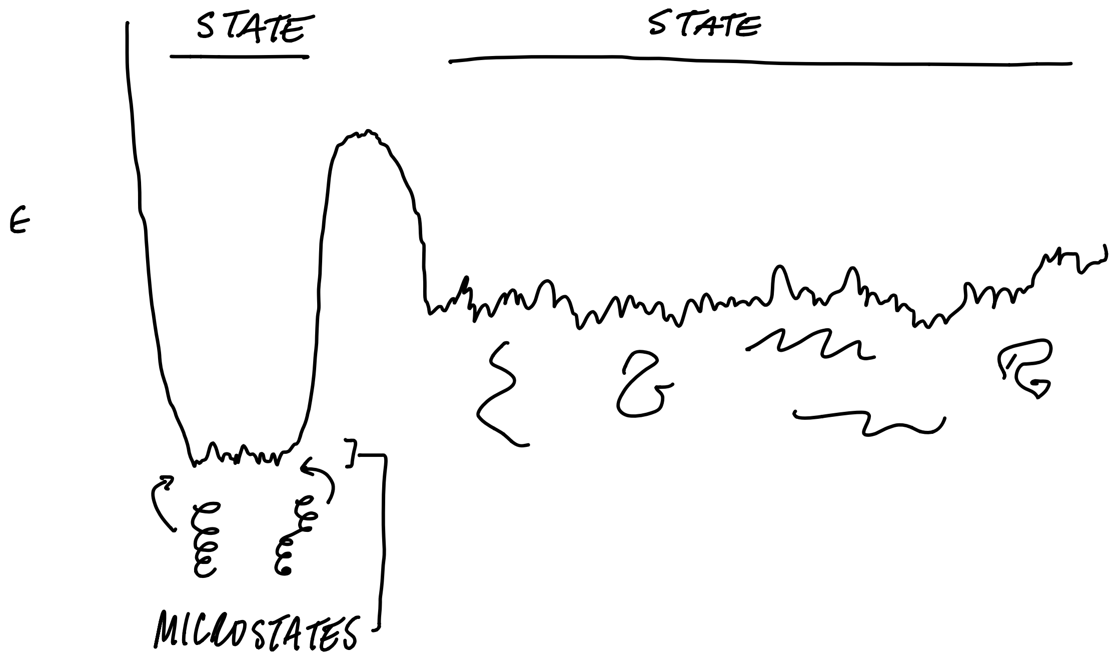
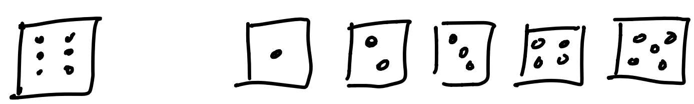


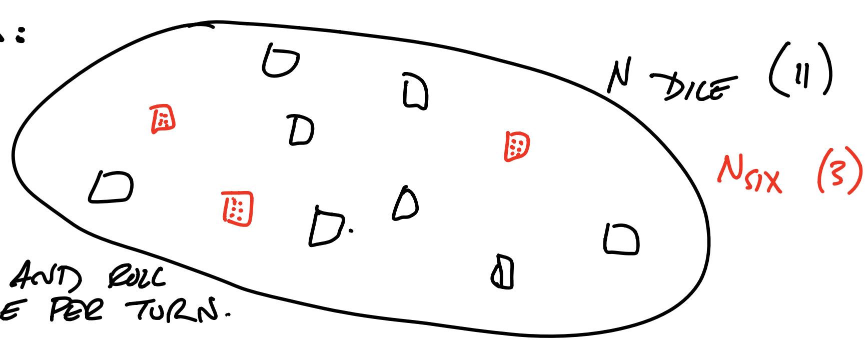


WHY DO REACTIONS CONVERGE TO PARTICULAR EQUILIBRIUM VALUE?

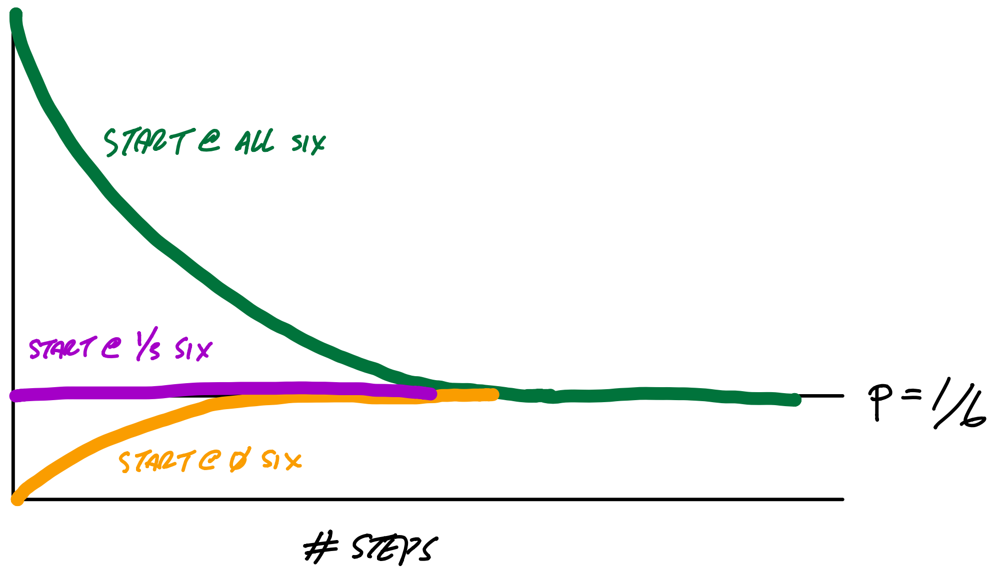
1. KINETIC: ENDS UP AT [SPECIES] WHERE RATES OF FORMATION AND LOSS EXACTLY OFFSET. AWAY FROM EQUILIBRIUM, RATES ARE DIFFERENT BY DEFINITION, LEADING TO CHANGES <u>TOWARD</u> EQUILIBRIUM.

2. THERMODYNAMIC: EQUILIBRIUM VALUE BETWEEN TWO STATES IS DETERMINED BY THE NUMBER AND RELATIVE PROBABILITY OF THE MICROSTATES COMPATIBLE WITH EACH STATE.

REACTION:



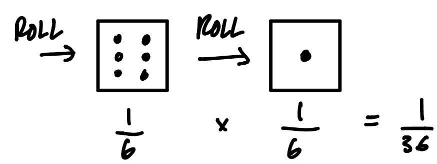
PICK UP AND ROLL ONE DICE PER TURN.



QUICK PROBABILITY REVIEW:

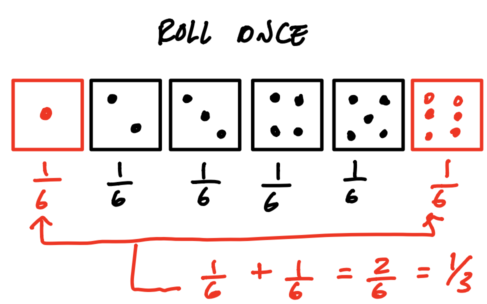
INDEPENDENT EVENTS MULTIPLY

P_6 AND P_1 $= P_6 \times P_1$



EXCLUSIVE EVENTS ADD:

P_6 OR P_1 $= (P_6 + P_1)$



1. You roll a dice 4 times and write down the observed sequence of faces you see (for example, ⚀, ⚃, ⚁, ⚅). How many different sequences of are possible?

$$6 \times 6 \times 6 \times 6 = 6^4 = 1296$$

2. What is the probability of seeing the following four rolls, in this order?

⚀ ⚅ ⚂ ⚅

INDEPENDENT EVENTS, SO:

$$\frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} = \frac{1}{1296}$$

3. What is the probability of seeing the following four rolls, in this order?

5/6 CHANCE {⚀, ⚁, ⚂, ⚃, ⚄} ⚅ {⚀, ⚁, ⚂, ⚃, ⚄} ⚅

1/6 CHANCE

{⚀, ⚁, ⚂, ⚃, ⚄} indicates that any of these faces come up. Hint: Try to come up with an approach that does not equire you to make all possible combinations of {⚀, ⚁, ⚂, ⚃, ⚄}.

$U = \{1,2,3,4,5\}$

$F = \{6\}$

$$P_{UFUF} = \left(\frac{5}{6}\right)\left(\frac{1}{6}\right)\left(\frac{5}{6}\right)\left(\frac{1}{6}\right) = \left(\frac{1}{6}\right)^2\left(\frac{5}{6}\right)^2 = \frac{25}{1296}$$

4. How many different ways are there to roll four dice and see the following come up in *any order*?

⚅, ⚅, {⚀, ⚁, ⚂, ⚃, ⚄}, {⚀, ⚁, ⚂, ⚃, ⚄}

F F U U

ORDERS:

FFUU	UFFU
FUFU	UFUF
FUUF	UUFF

6 POSSIBILITIES.

5. What is the probability of seeing the following four rolls, in *any order*? (Put another way, what is the probability of observing exactly two ⚅ in four rolls?)

⚅, ⚅, {⚀, ⚁, ⚂, ⚃, ⚄}, {⚀, ⚁, ⚂, ⚃, ⚄}

SIX MUTUALLY EXCLUSIVE POSSIBILITIES!

$$P_{TOTAL} = P_{FFUU} + P_{FUFU} + P_{FUUF} + P_{UFFU} + P_{UFUF} + P_{UUFF}$$

THESE ALL HAVE SAME PROBABILITY, SO:

$$P_{TOTAL} = 6 \times \left(\frac{1}{6}\right)^2 \times \left(\frac{5}{6}\right)^2 = \frac{150}{1296}$$

EXPRESSION GENERALIZES TO:

$$P(n,k) = \binom{n}{k} p^k \underline{(1-p)^{n-k}}$$

n : NUMBER OF SITES
k : NUMBER OF OCCUPIED SITES
p : PROB A SITE IS OCCUPIED

MULTIPLICITY. HOW MANY WAYS ARE THERE TO TAKE k SAMPLES FROM n SITES. (SEE #4 ABOVE)

PROB k DICE COMING UP 6s

PROB REMAINING $(n-k)$ DICE COME UP NOT 6.

$$\binom{n}{k} = \frac{n!}{k!(n-k)!} \Rightarrow$$

$$\begin{array}{ccccccccccccl}
 & & & & & 1_{\emptyset} & & & & & & & n=\emptyset \\
 & & & & 1_{\emptyset} & & 1_{1} & & & & & & n=1 \\
 & & & 1_{\emptyset} & & 2_{1} & & 1_{2} & & & & & n=2 \\
 & & 1_{\emptyset} & & 3_{1} & & 3_{2} & & 1_{3} & & & & n=3 \\
 & 1_{\emptyset} & & 4_{1} & & 6_{2} & & 4_{3} & & 1_{4} & & & n=4 \\
1_{\emptyset} & & 5_{1} & & 10_{2} & & 10_{3} & & 5_{4} & & 1_{5} & & n=5 \\
 & & & & & \cdots & & & & & & & \cdots
\end{array}$$

k

EXAMPLE : $\binom{5}{4} = 5$

$$\frac{n!}{k!(n-k)!} \downarrow = \frac{5!}{4!(5-4)!}$$

5 POSSIBILITIES
$$\begin{bmatrix} 1 & 1 & 1 & 1 & \emptyset \\ 1 & 1 & 1 & \emptyset & 1 \\ 1 & 1 & \emptyset & 1 & 1 \\ 1 & \emptyset & 1 & 1 & 1 \\ \emptyset & 1 & 1 & 1 & 1 \end{bmatrix} = \frac{5 \times \cancel{4} \times \cancel{3} \times \cancel{2} \times \cancel{1}}{\cancel{4} \times \cancel{3} \times \cancel{2} \times \cancel{1} (\cancel{1})}$$

$= 5$

$$P(n,k) = \binom{n}{k} p^k (1-p)^{n-k}$$

where n is the number of dice, k is the number of dice showing 6, p is the probability of obtaining 6 on a roll, and $\binom{n}{k}$ is the number of ways you can draw k dice out of n total.

F u

1. You have four dice. Enumerate all possible combinations of ⚅ vs. not-⚅ you can obtain for $k \in \{0, 1, 2, 3, 4\}$.

K = 0: UUUU] 1

K = 1: FUUU, UFUU, UUFU, UUUF] 4

K = 2: FFUU, FUFU, FUUF, UFFU, UFUF, UUFF] 6

K = 3: FFFU, FFUF, FUFF, UFFF] 4

K = 4: FFFF] 1

2. You have $n = 600$ fair dice ($p = 1/6$). In a plotting program of your choice, graph each of the following as a function of k:

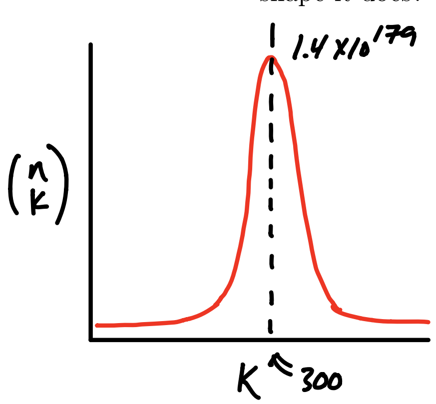
$$\binom{n}{k}$$

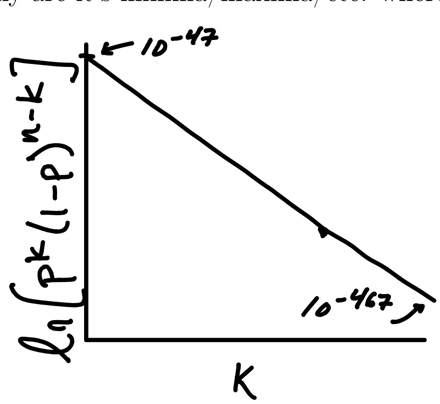
$$p^k (1-p)^{n-k}$$

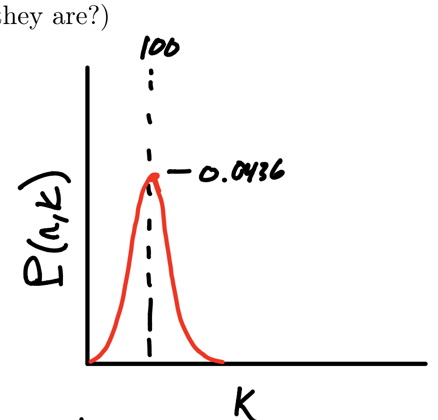
$$P(n,k) = \binom{n}{k} p^k (1-p)^{n-k}$$

You might want to put the y-axis on a log scale. (In Excel, the $\binom{n}{k}$ function is 'COMBIN'; in python it is 'scipy.special.comb'; in R it is 'choose').

3. Explain why each graph looks like it does. (Why does it have the overall shape it does? Why are it's minima/maxima/etc. where they are?)







FUNCTION PEAKS AT K=300; MOST WAYS TO ARRANGE DICE THERE. HUGE # OF POSSIBLE OUTCOMES. BINOMIAL DISTRIBUTION.

CONTINUOUSLY DECREASES (EXPONENTIAL). THIS IS BECAUSE 1-P IS MORE PROBABLE THAN P. ROLLS W/OUT SIX ALWAYS MORE PROBABLE.

PEAK AT 100. MAXIMIZES TRADEOFF BETWEEN $\binom{n}{k}$ (INCREASES FROM $K=0 \to K=300$) AND $p^k(1-p)^{n-k}$ (DECREASES FROM $K=0 \to K=600$).

$$P(n,k) = \binom{n}{k} p^k (1-p)^{n-k} \qquad \binom{n}{k} = W = \text{MULTIPLICITY}$$

$\dfrac{P(n,b)}{P(n,a)}$ ← FOLD DIFFERENCE IN PROBABILITY $= \dfrac{P_b}{P_a}$

$$\frac{P_b}{P_a} = \frac{W_b\, p^b (1-p)^{n-b}}{W_a\, p^a (1-p)^{n-a}}$$

$$-\ln(P_b/P_a) = -\ln\left(\frac{W_b}{W_a} \cdot \frac{p^b (1-p)^{n-b}}{p^a (1-p)^{n-a}}\right)$$

$$-\ln(P_b/P_a) = -\ln(W_b/W_a) + -\ln\left(p^{b-a} (1-p)^{a-b}\right)$$

↑ Δ FREE ENERGY

↑ ENTROPY

↑ ENTHALPY

$$[\Delta G = \Delta H - T\Delta S]$$