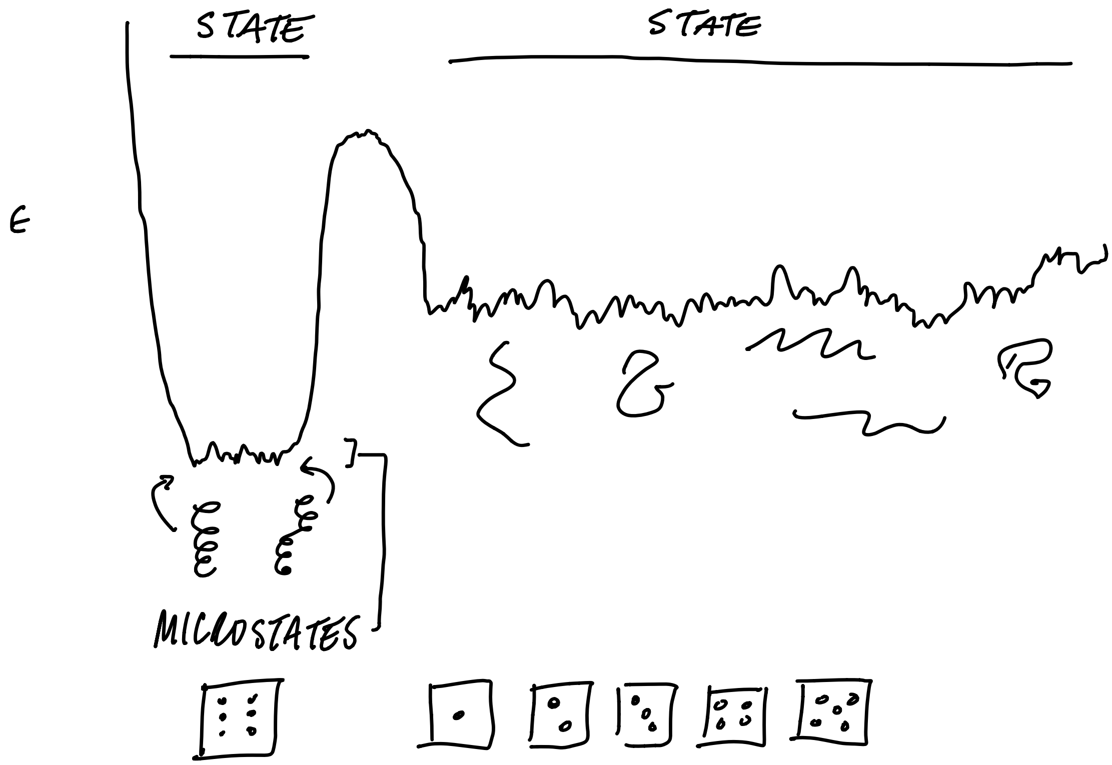
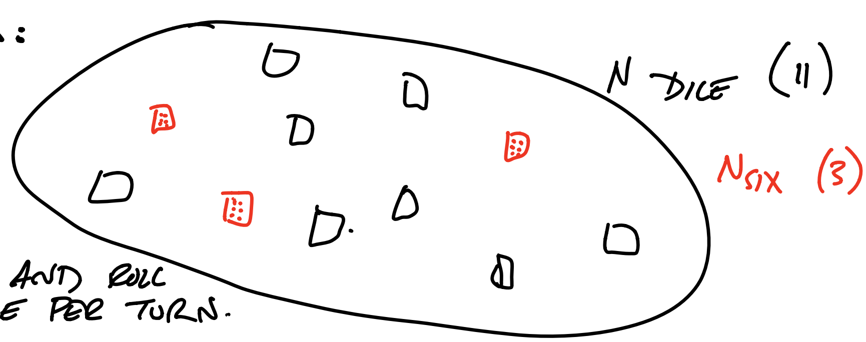


WHY DO REACTIONS CONVERGE TO PARTICULAR EQUILIBRIUM VALUE?

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 TOWARD EQUILIBRIUM.

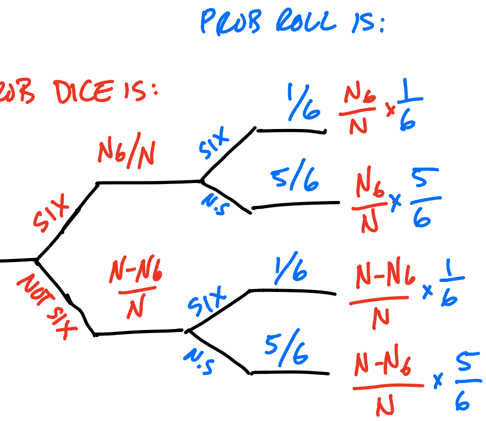
2. THERMODYNAMIC: EQUILIBRIUM VALUE BETWEEN TWO STATES IS DETERMINED BY THE NUMBER AND RELATIVE PROBABILITY OF THE MICROSTATES COMPATIBLE WITH EACH STATE.

REACTION:



PICK UP AND ROLL ONE DICE PER TURN.

PICK UP DICE



- You have N dice.
- Of these N dice, $N_{⚅}$ are currently showing ⚅.
- The probability of a dice coming up as ⚅ is $p = 1/6$.
- For each turn, you randomly pick up one dice and roll it.

1. What is the probability—in terms of N, $N_{⚅}$, and p—of a non-⚅ dice becoming a ⚅ over one turn?

$$(N-N_6)P \quad [\text{START AS NOT SIX}] \times P$$

2. What is the probability—in terms of N, $N_{⚅}$, and p—of a ⚅ dice becoming a non-⚅ over one turn?

$$N_6 \cdot (1-P) \qquad [\text{START AS SIX}] \times P_{\text{NOT SIX}}$$

3. What is the predicted overall change in $N_{⚅}$ —in terms of N, $N_{⚅}$, and p—over a turn?

$$\frac{\Delta N_6}{\text{TURN}} = (N-N_6)P - N_6(1-P)$$

4. Under what conditions will the predicted change in $N_{⚅}$ will be zero?

$$\frac{\Delta N_6}{\text{TURN}} = \emptyset = (N-N_6)P - N_6(1-P)$$

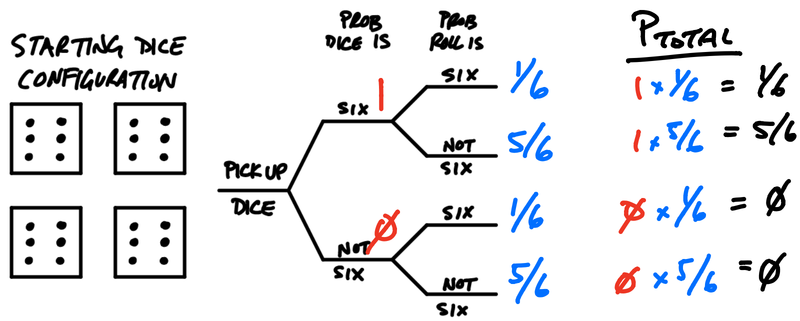
$$N_6(1-P) = (N-N_6)P$$

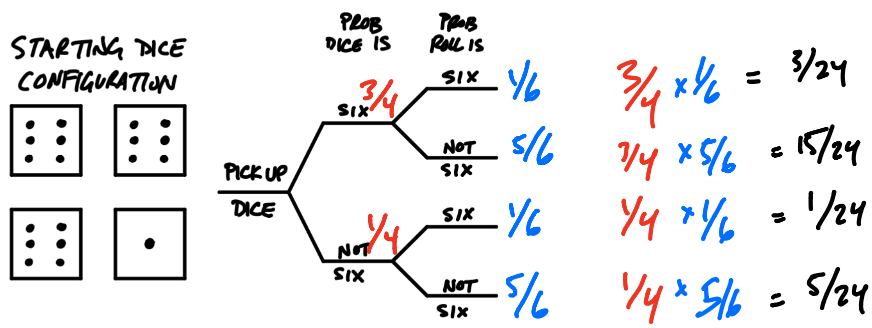
$$N_6 - \cancel{N_6 P} = NP - \cancel{N_6 P}$$

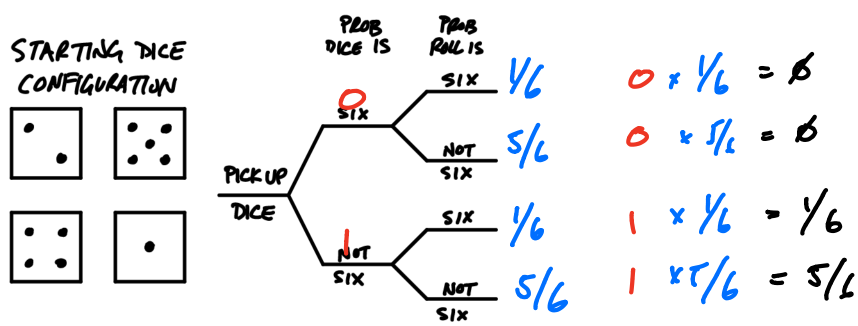
$$N_6 = N \cdot P$$

← AT THIS POINT, PROB OF LOSS OF SIX IS EXACTLY OFFSET BY PROB OF GAIN OF SIX.

You have a collection of four dice. You randomly pick up one dice and roll it. Assuming the dice are fair ($p = 1/6$ for all faces), fill out the contingency trees below and calculate the probability of each possible outcome.

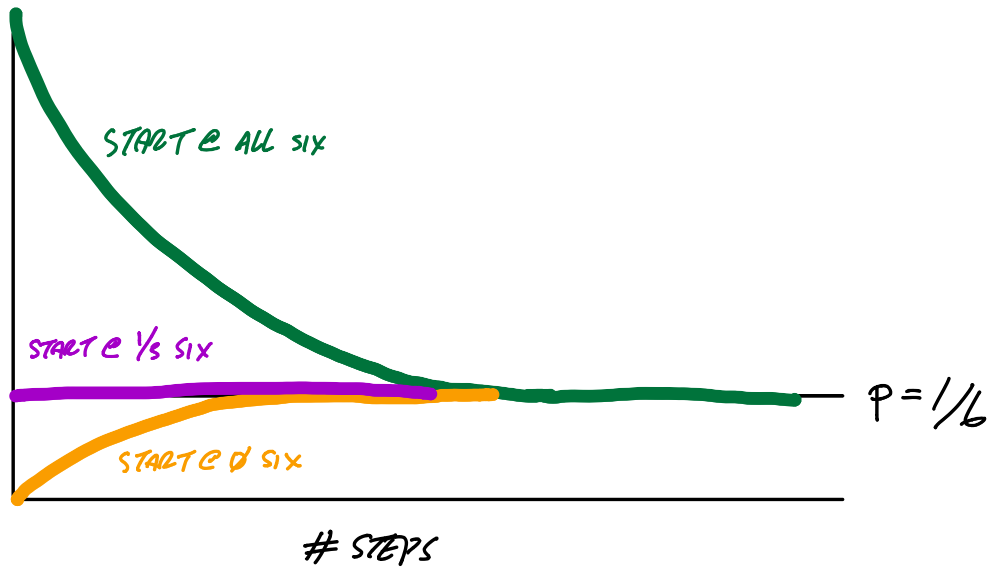






Based on this calculation, why does a dice reaction equilibrate away from configurations like the top configuration?

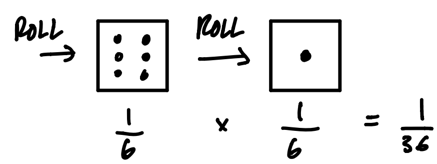
AT START, THE MOST LIKELY ROLL TAKES YOU AWAY FROM ALL SIX. NO ROLL INCREASES # OF SIXES. AFTER A SIX IS LOST, THE MOST PROBABLE OUTCOME IS STILL A LOSS OF SIX. AFTER EVERY SIX IS LOST, THERE IS A HIGHER PROB OF GAINING SIX (1/6) THAN LOSING (∅).



QUICK PROBABILITY REVIEW:

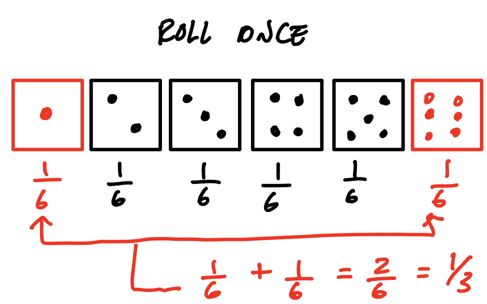
INDEPENDENT EVENTS MULTIPLY

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.

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

1_0	$n = 0$
$1_0 \quad 1_1$ (k)	$n = 1$
$1_0 \quad 2_1 \quad 1_2$	$n = 2$
$1_0 \quad 3_1 \quad 3_2 \quad 1_3$	$n = 3$
$1_0 \quad 4_1 \quad 6_2 \quad 4_3 \quad 1_4$	$n = 4$
$1_0 \quad 5_1 \quad 10_2 \quad 10_3 \quad 5_4 \quad 1_5$	$n = 5$
...	...

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

5 POSSIBILITIES
$$\begin{bmatrix} 1 & 1 & 1 & 1 & 0 \\ 1 & 1 & 1 & 0 & 1 \\ 1 & 1 & 0 & 1 & 1 \\ 1 & 0 & 1 & 1 & 1 \\ 0 & 1 & 1 & 1 & 1 \end{bmatrix} = \frac{n!}{k!(n-k)!} = \frac{5!}{4!(5-4)!} = \frac{5\times\cancel{4}\times\cancel{3}\times\cancel{2}\times\cancel{1}}{\cancel{4}\times\cancel{3}\times\cancel{2}\times\cancel{1}(\cancel{1})} = 5$$

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

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:

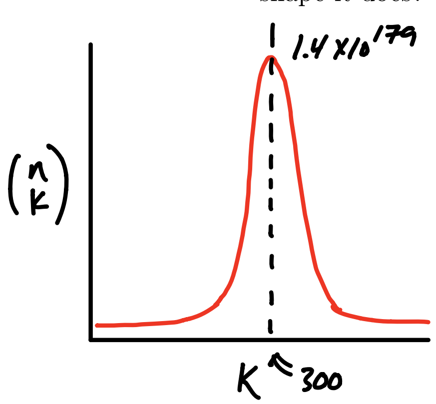
$$\binom{n}{k}$$

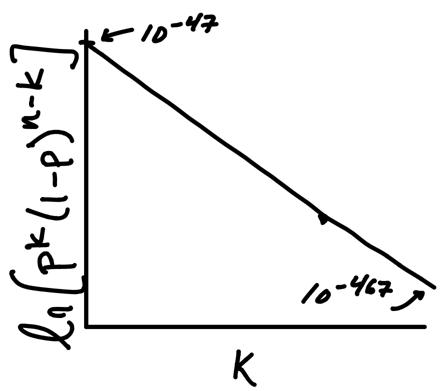
$$p^k(1-p)^{n-k}$$

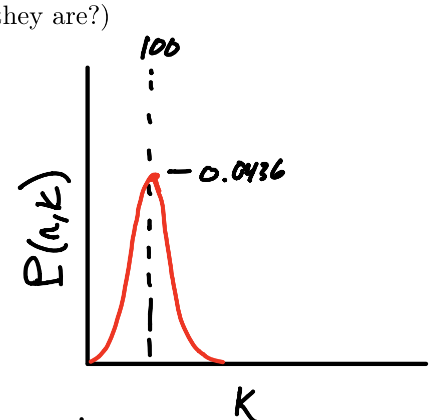
$$P(n,k) = \binom{n}{k} p^k (1-p)^{n-k}$$

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 $k=0 \rightarrow k=300$) AND $p^k(1-p)^{n-k}$ (DECREASES FROM $k=0 \rightarrow k=600$).

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

$$\frac{P(n,b)}{P(n,a)} \leftarrow \text{FOLD DIFFERENCE IN PROBABILITY} = \frac{P_b}{P_a}$$

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

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

$$\underbrace{-\ln(P_b/P_a)}_{\Delta\ \text{FREE ENERGY}} = \underbrace{-\ln(W_b/W_a)}_{\text{ENTROPY}} + \underbrace{-\ln\left(p^{b-a}(1-p)^{a-b}\right)}_{\text{ENTHALPY}}$$

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