

## ENTROPY, STATISTICAL AND THERMODYNAMIC 10/1/19

SYSTEMS TEND TOWARDS EQUILIBRIUM  $\rightarrow$  WHICH IS THE STATE THAT MAXIMIZES THE NUMBER OF CONFIGURATIONS.

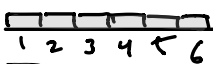
WE DEVELOPED AN IDEA OF THIS BEFORE FOR DICE USING A BINOMIAL DISTRIBUTION.

TODAY: A GENERAL DESCRIPTION OF ENTROPY:

$$S = -R \sum_i p_i \ln(p_i)$$

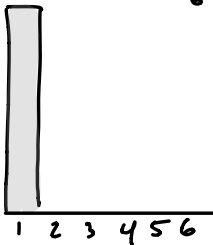
S

FAIR DICE: 6 BJS @  $p = 1/6$


$$-6 \times \frac{1}{6} \ln\left(\frac{1}{6}\right) = 1.8R$$

LOADED DICE: 1 BJS @  $p = 1$

$$-1 \ln(1) = 0 = 0R$$

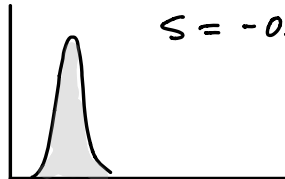


HOW MUCH INFORMATION DO I NEED TO COMMUNICATE THE POSSIBLE OUTCOMES GIVEN WHAT I ALREADY KNOW?

THE MORE EVEN A DISTRIBUTION, THE HIGHER THE ENTROPY AND THE MORE PROBABLE.

THINK ABOUT:

$n = 100$   
 $k \in [0, 100]$   
 $p = 1/6$



$$S = -0.0227 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

ALL SIXES:  $p = 1$

$$S = 0$$

$$\Delta S = -0.0227$$
$$T\Delta S = -6.8 \text{ kJ} \cdot \text{mol}^{-1}$$

ASIDE: YOU MAY HAVE SEEN

$$S = R \ln(W) \quad \text{WHERE } W \text{ IS \# STATES}$$

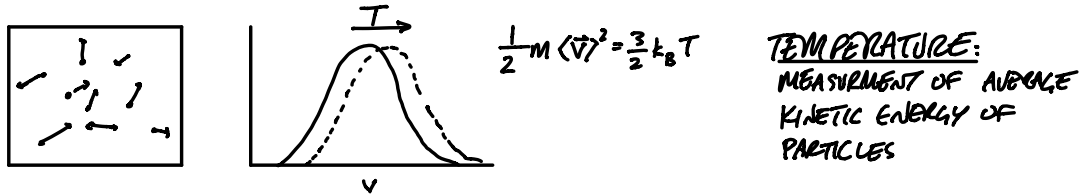
THIS IS A LIMITING CASE OF THE  $S = -R \sum p_i \ln(p_i)$  FORM OF ENTROPY

IF ALL  $p$  ARE SAME,  $p = 1/W$  WHERE  $W$  IS # OF STATES.

$$S = -R \sum_{i=1}^W \frac{1}{W} \ln\left(\frac{1}{W}\right) = -R \cdot W \cdot \frac{1}{W} \ln\left(\frac{1}{W}\right)$$
$$= -R \ln\left(\frac{1}{W}\right)$$
$$= R \ln(W)$$

SO WHAT DOES ANY OF THIS HAVE TO DO WITH HEAT?

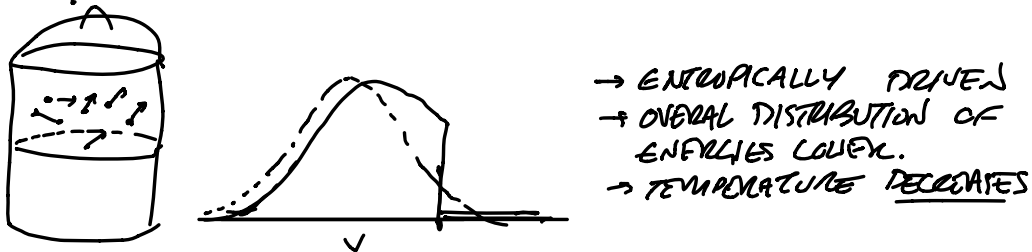
GOING TO HAVE TO MOVE AWAY FROM DICE TO ACTUAL PARTICLES.  
UNLIKE DICE: CONTINUALLY JOSTLING WITHOUT ADDING EXCESS ENERGY.



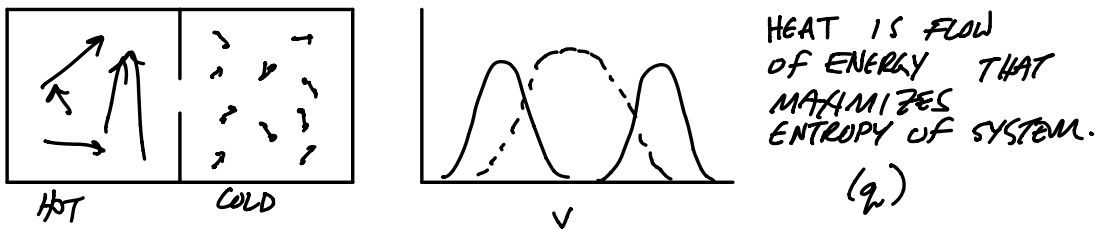
THINK ABOUT PROCESS OF INCREASING TEMPERATURE:



COOLING:



JUST LIKE DICE, IF YOU PERTURB DISTRIBUTION, EQUILIBRATES TO MAXIMALLY RANDOM STATE, FOR THE SAME REASON.



$$\Delta S = \frac{q_{\text{REV}}}{T} \quad \left[ \text{BOTH MEASURABLE.} \right]$$

## KEY IDEAS:

→ ENTROPY IS MEASURE OF DISORDER

$$S = -R \sum_i p_i \ln(p_i)$$

→ TEMPERATURE IS A MEASURE OF KINETIC ENERGY OF PARTICLES [MOL pp 254-255]

→ HEAT IS THE REDISTRIBUTION OF PARTICLE KINETIC ENERGIES TO MAXIMIZE ENTROPY.

→ THE CHANGE IN ENTROPY FOR A CLOSE-TO-REVERSIBLE REACTION IS

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

→ BECAUSE WE CAN MEASURE  $T$  AND  $q$ , WE CAN MEASURE ENTROPY.