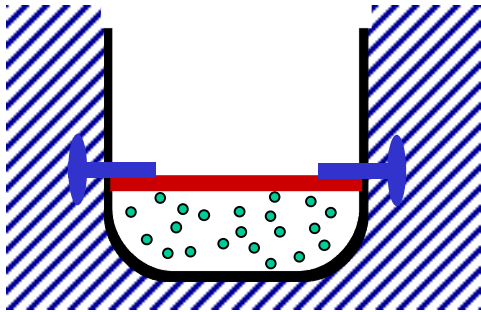
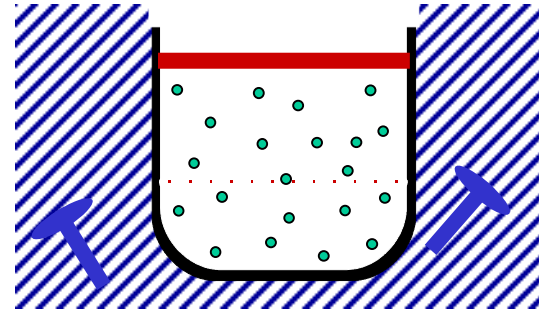


Consider work performed by a system in an isothermal expansion:



**Constant Temperature**

$$P_1 = 15 \text{ atm} \quad V_1 = 1 \text{ L}$$



$$P_2 = 1 \text{ atm} \quad V_2 = 15 \text{ L}$$

If the pins are removed what happens?

What is the change in internal energy?

$$\Delta U = U_1 - U_2 \propto \Delta T \quad \therefore \Delta U = 0$$

What is the change in enthalpy?

$$\Delta H = H_1 - H_2 = (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

$$\Delta H = 0$$

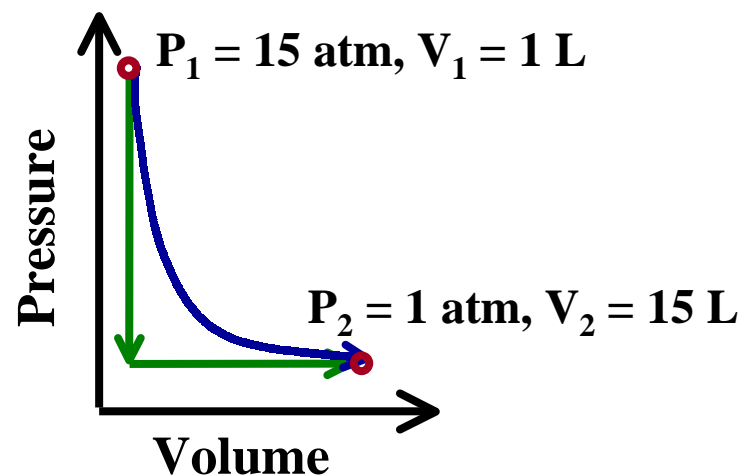
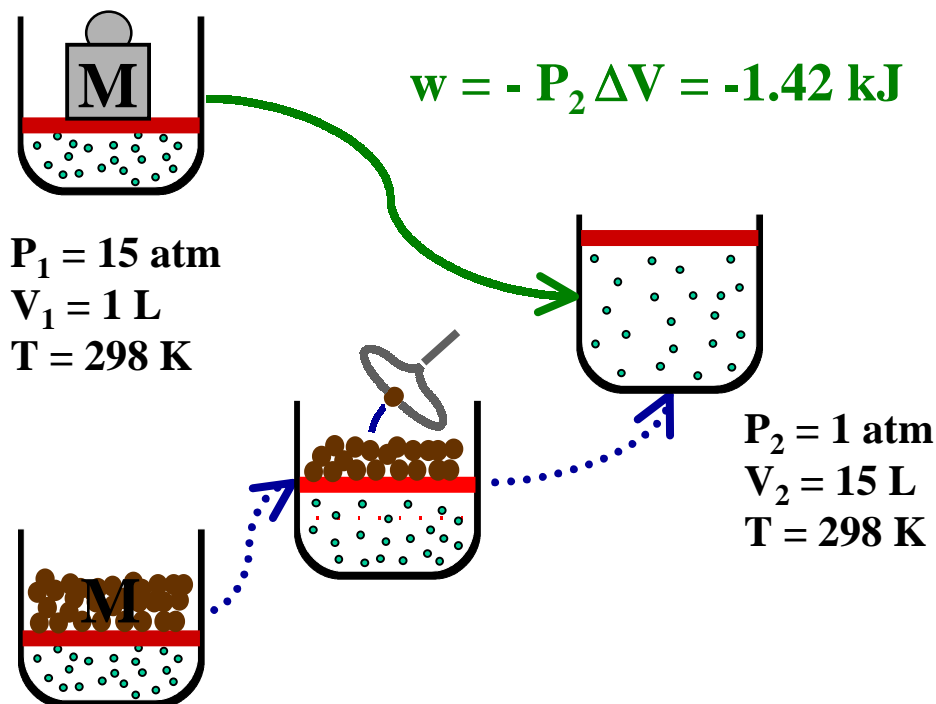
Note: this does not mean that  $q$  or  $w$  is 0, only that  $q = -w$ . In fact  $w = -P_{\text{ex}} \Delta V$ .

$$1 \text{ atm} = 101.325 \text{ kPa}$$

$$w = -101.325 \text{ kPa} (14 \text{ L}) (10^{-3} \text{ m}^3/\text{L})$$

$$w = -1.42 \text{ kJ} \quad q = 1.42 \text{ kJ}$$

The work performed in an isothermal expansion is pathway dependent:



$$w = - \int_{V_1}^{V_2} P \, dV = - nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w = - nRT \ln \left( \frac{V_2}{V_1} \right) = -4.12 \text{ kJ}$$

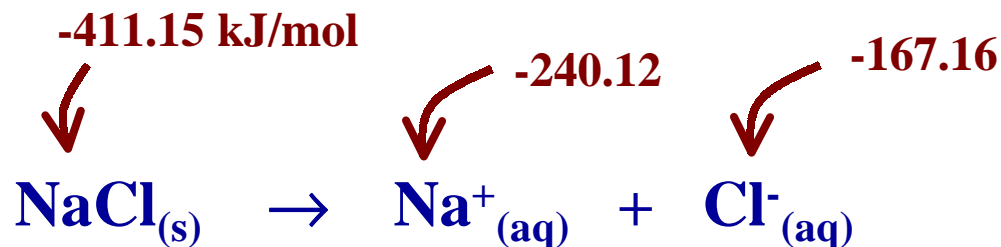
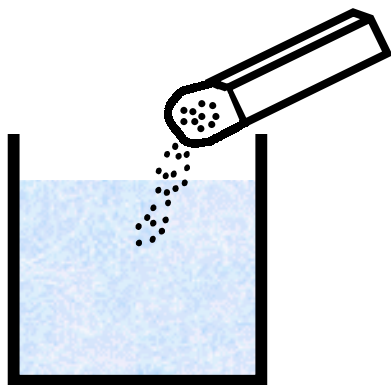
A reversible process represents the maximum possible PV work.

$$w = -(101.325 \text{ kPa/atm}) (15 \text{ L}) (10^{-3} \text{ m}^3/\text{L}) \ln(15)$$

A *reversible* process is in equilibrium at each step.

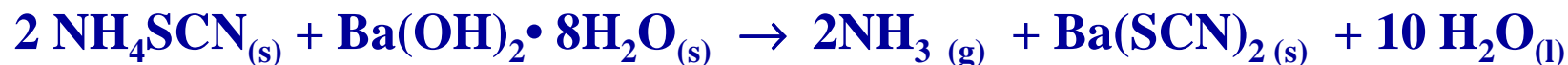
Consider:

Calculate  $\Delta H$  in kJ/mol



$$\Delta H = -167.16 - 240.12 - (-411.15) = 3.87 \text{ kJ/mol}$$

This is an endothermic reaction - but clearly **spontaneous**, as was the endothermic reaction demonstrated in class.



The reverse reactions are not **spontaneous**.

Qualitatively: **“Nature Prefers Disorder”**



# Entropy is the quantitative thermodynamic measure of disorder.

Consider a system with 3 balls



and 3 bowls:



A state of the system is 1 ball in each bowl.

1	2	3
A	B	C
A	C	B
B	A	C
B	C	A
C	A	B
C	B	A

6 Possibilities

$$\# = \frac{N!}{N_1! N_2! N_3!}$$

$$\# = \frac{3!}{1! 1! 1!}$$

Disordered State

Another state is 2 balls in bowl 1,  
1 ball in bowl 2.

1	2	3
AB	C	
AC	B	
BC	A	

3 Possibilities

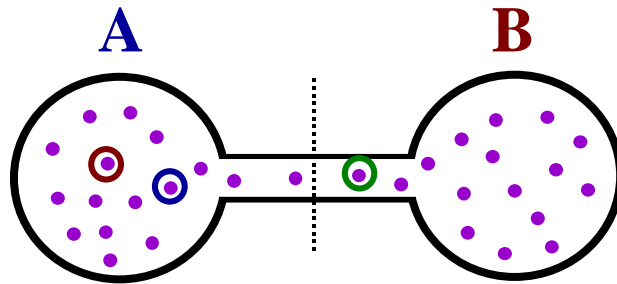
More ordered  
State

Or 3 balls in bowl 1.

1	2	3
ABC		

1 Possibility

Ordered State



Two gas bulbs of equal size

### Gas Molecules

The **probability** of any one molecule being in A is  $W = \frac{1}{2}$

Any two molecules in A is  $W = \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$

Any three molecules in A is  $W = \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{8}$



Probability of N molecules in A

$$W = \left(\frac{1}{2}\right)^N$$

### Coin Flips



$$\left(\frac{1}{2}\right)^1$$



$$\left(\frac{1}{2}\right)^2$$



$$\left(\frac{1}{2}\right)^3$$



N consecutive heads

$$W = \left(\frac{1}{2}\right)^N$$

# Entropy is the quantitative thermodynamic measure of disorder.

Consider a system with 3 balls



and 3 bowls:



A state of the system is 1 ball in each bowl.

1	2	3
A	B	C
A	C	B
B	A	C
B	C	A
C	A	B
C	B	A

6 Possibilities

$$\# = \frac{N!}{N_1! N_2! N_3!}$$

$$\# = \frac{3!}{1! 1! 1!}$$

$$W = \frac{6}{18} = \frac{1}{3}$$

Another state is 2 balls in bowl 1,  
1 ball in bowl 2.

1	2	3
AB	C	
AC	B	
BC	A	

3 Possibilities

$$W = \frac{3}{18} = \frac{1}{6}$$

Or 3 balls in bowl 1.

1	2	3
ABC		

1 Possibilities

$$W = \frac{1}{18}$$

# Statistical definition of entropy (**S**) for a state:

$$\mathbf{S} = k \ln W$$

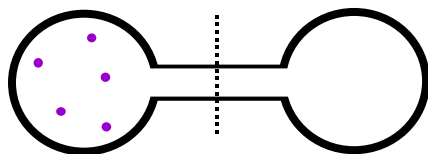
$W \propto$  probability of a state,  
degeneracy of a state, and/or  
number of microstates

Boltzmann Equation

$k$  = Boltzmann Constant  
 $1.3805 \times 10^{-23} \text{ J K}^{-1}$

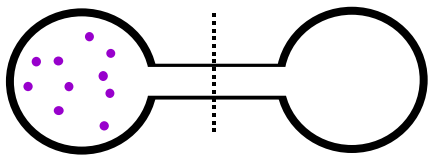
$\therefore \mathbf{S}$  has units of  $\text{J K}^{-1}$

**S** is an extensive function.



$$W = \left(\frac{1}{2}\right)^5 = \frac{1}{32}$$

$$\mathbf{S} = -3.47 k$$



$$W = \left(\frac{1}{2}\right)^{10} = \frac{1}{1024}$$

$$\mathbf{S} = -6.93 k$$

**S** is a state function.

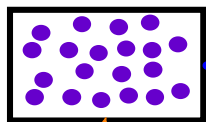
The value of **S** depends on the  
state, not on how the state was  
reached.

# Thermodynamic definition of entropy (**S**):

$$d\mathbf{S} = \frac{dq_{\text{rev}}}{T}$$

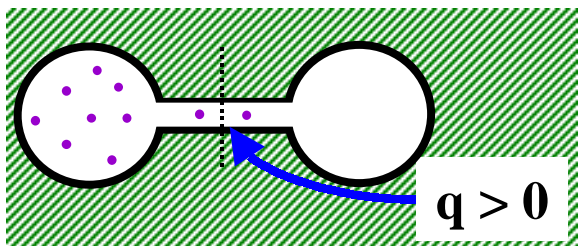
Heat that would be transferred in a reversible process

$$\Delta\mathbf{S} = S_B - S_A = \int_A^B \frac{dq_{\text{rev}}}{T}$$



$q > 0$

Adding heat increases the entropy of the system.



$q > 0$

The entropy of the system increases in an isothermal expansion.

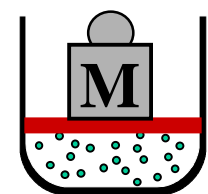


Entropy change in a system is calculated from reversible heat:

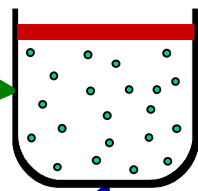
**Irreversible expansion**

$$q = -w = 1.42 \text{ kJ}$$

$$w = -P_2 \Delta V = -1.42 \text{ kJ}$$



$P_1 = 15 \text{ atm}$   
 $V_1 = 1 \text{ L}$   
 $T = 298 \text{ K}$

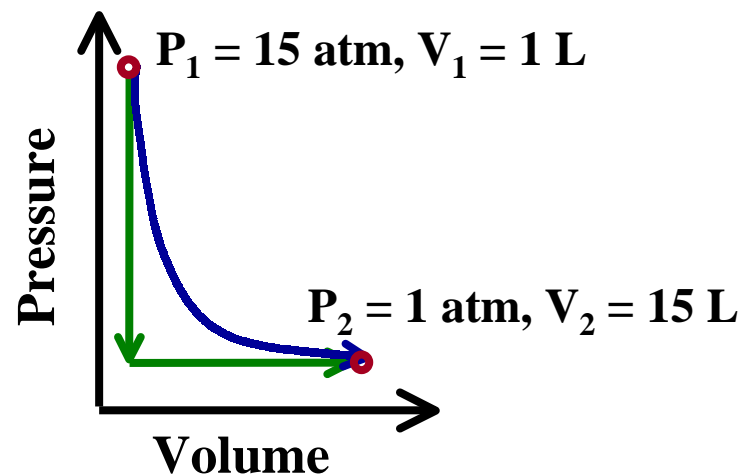


$P_2 = 1 \text{ atm}$   
 $V_2 = 15 \text{ L}$   
 $T = 298 \text{ K}$

**Reversible expansion**

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right) = -4.12 \text{ kJ}$$

$$q_{\text{rev}} = -w_{\text{rev}} = 4.12 \text{ kJ}$$



$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} = \frac{4.12 \text{ kJ}}{298 \text{ K}} = 13.8 \text{ J K}^{-1}$$

Consider the isothermal expansion of an ideal gas.

Thermodynamic definition:

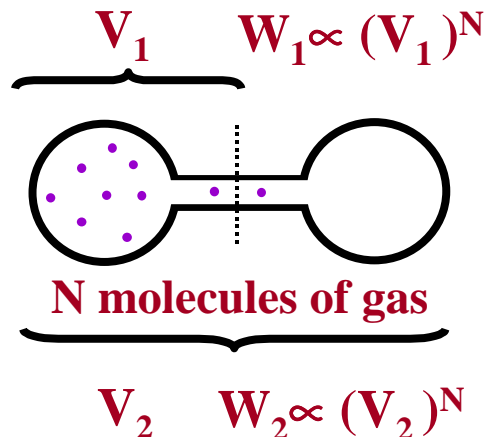
$$\Delta S = S_B - S_A = \int_A^B \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_A^B dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

isothermal  $\Rightarrow \Delta U = q + w = 0 \quad w_{\text{rev}} = -nRT \ln\left(\frac{V_2}{V_1}\right) \quad q_{\text{rev}} = nRT \ln\left(\frac{V_2}{V_1}\right)$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

entropy change in the isothermal expansion of an ideal gas.

Statistical definition (counting states):  $S = k \ln W$



$$\Delta S = k \ln (V_2)^N - k \ln (V_1)^N$$

$$\Delta S = k \ln \left( \frac{V_2}{V_1} \right)^N = N k \ln \left( \frac{V_2}{V_1} \right)$$

$$= \left( \frac{N}{N_A} \right) N_A k \ln \left( \frac{V_2}{V_1} \right)$$

$R$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$