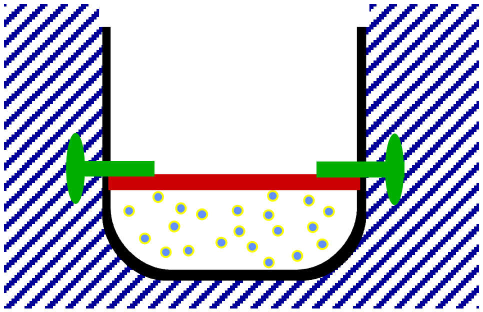
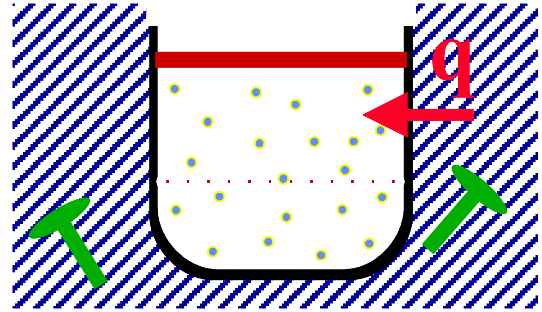
Isothermal expansion of a perfect gas



n, R, T constant
$\Rightarrow p_1V_1 = p_2V_2$
(for a perfect gas)



constant temperature (isothermal)

$n = 1$ mol; $p_1 = 15$ atm; $V_1 = 1$ L

$\Rightarrow p_2 = 1$ atm; $V_2 = 15$ L

If the pins are removed what happens?

What is the change in internal energy?

$\Delta U = U_2 - U_1 \propto \Delta T \qquad \Rightarrow \Delta U = 0$

What is the change in enthalpy?

0 0

$\Delta H = H_2 - H_1 = (U_2 + p_2V_2) - (U_1 + p_1V_1)$

$\Rightarrow \Delta H = 0$

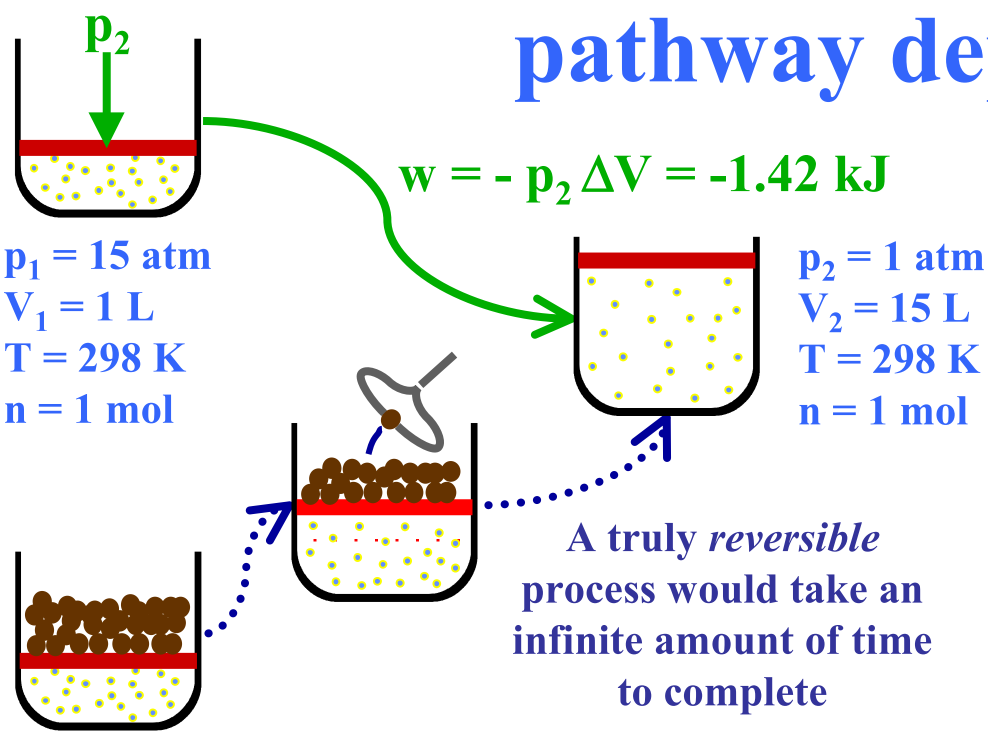
Note: $\Delta U = 0$ does not mean that q or w is 0, only that $q = -w$; in fact, $w = - p_2\Delta V$

e.g., $p_2 = 1$ atm $= 101{,}325$ Pa

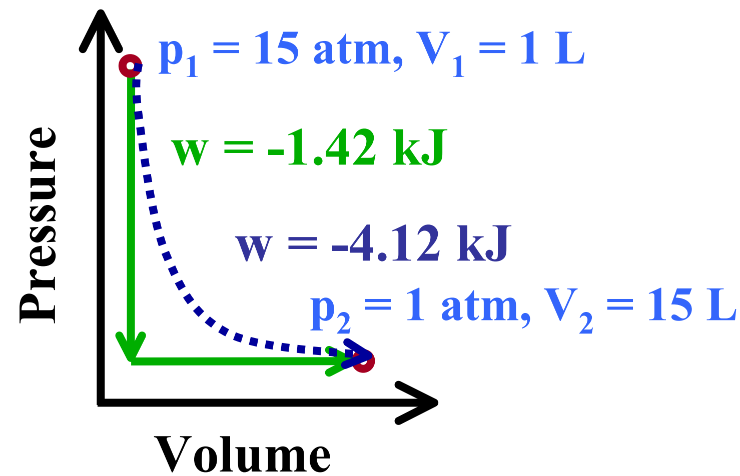
$w = -101{,}325$ Pa $(14$ L$)$ $(10^{-3}$ m^3/L$)$

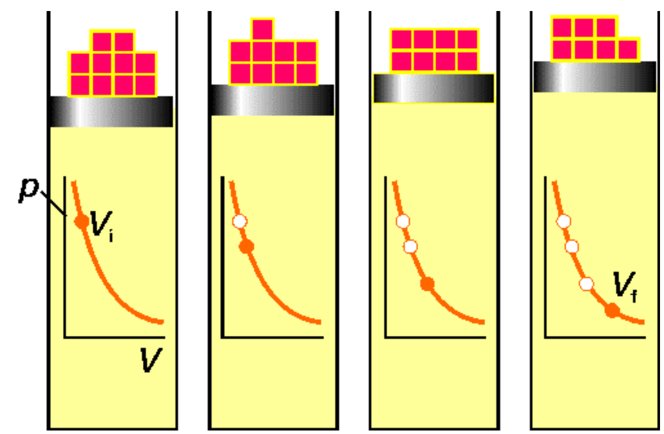
$\Rightarrow w = -1.42$ kJ $\qquad q = 1.42$ kJ

Work in an isothermal expansion is pathway dependent



A truly *reversible* process would take an infinite amount of time to complete





A *reversible* process is in equilibrium at all times

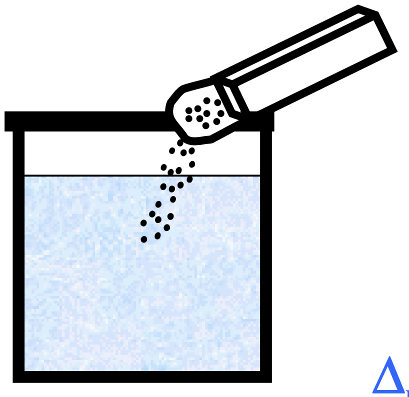
perfect gas

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

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

A reversible process represents the maximum possible pV work

But there's more: Disorder



-411.15 kJ/mol -240.12 kJ/mol -167.16 kJ/mol

$$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

Hess: $\Delta_r H^\ominus = \sum \nu \Delta_f H^\ominus(\text{Prod.}) - \sum \nu \Delta_f H^\ominus(\text{React.})$

$$\Delta_r H = [-167.16 - 240.12 - (-411.15)]\ \text{kJ/mol} = +3.87\ \text{kJ/mol}$$

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

$$2\ NH_4SCN_{(s)} + Ba(OH)_2 \bullet 8H_2O_{(s)} \rightarrow 2NH_{3\ (g)} + Ba(SCN)_{2\ (s)} + 10\ H_2O_{(l)}$$

The reverse reactions are not spontaneous

Qualitatively: "Nature Prefers Disorder"

$NaCl_{(s)}$ "Ordered" $\rightarrow$ $Na^+_{(aq)} + Cl^-_{(aq)}$ "Disordered"

Measuring disorder in thermodynamics: Statistical thermodynamics

Consider a system with 3 balls --- and 3 bowls:

A B C

1 2 3

A possible 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 possible state is 2 balls in bowl 1, 1 ball in bowl 2

1	2	3
AB	C	
AC	B	
BC	A	

3 Possibilities

$$\# = \frac{3!}{2!\,1!\,0!}$$

More ordered State

Or 3 balls in bowl 1

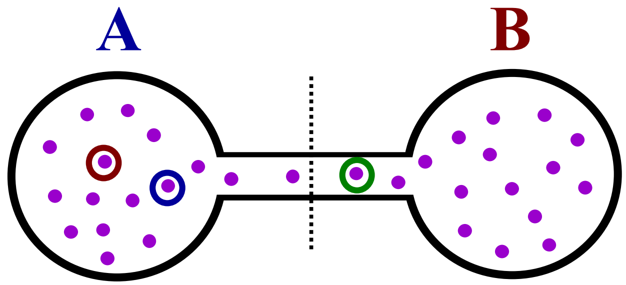
1	2	3
ABC		

1 Possibility

$$\# = \frac{3!}{3!\,0!\,0!}$$

Ordered State

What the h… does this have to do with a gas?



Gas molecules in two gas bulbs of equal size

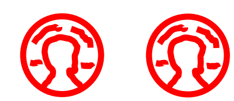
Coin Flips

The probability of

any one molecule being in A is $P = \frac{1}{2}$

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

any two molecules in A is $P = \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$



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

any three molecules in A is $P = \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{8}$

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

⋮

Probability of N molecules in A

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

N consecutive heads

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

Measuring disorder in thermodynamics: Statistical thermodynamics

Consider a system with 3 balls --- and 3 bowls:

A possible 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

$$W = 6$$

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

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

1	2	3
AB	C	
AC	B	
BC	A	

3 Possibilities

$$W = 3$$

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

Or 3 balls in bowl 1

1	2	3
ABC		

1 Possibility

$$W = 1$$

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

Che

The statistical definition of disorder = entropy S

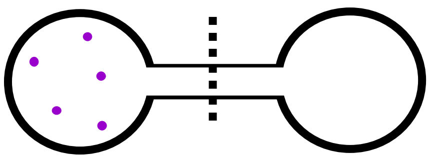
Boltzmann Equation

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

W = number of microstates or degeneracy of a macrostate

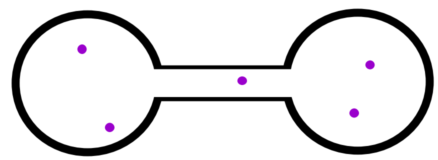
k = Boltzmann Constant 1.3805×10^{-23} J K^{-1}

$\Rightarrow$ S has units of J K^{-1}



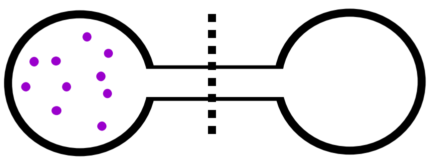
W = 5 $\boxed{S = 1.61\ k}$

S accounts for the **disorder**



W = 10 $\boxed{S = 2.30\ k}$

S is an **extensive** function



W = 10 $\boxed{S = 2.30\ k}$

S is a <u>state function</u>, i.e., the value of S depends on the state, not on how the state was reached