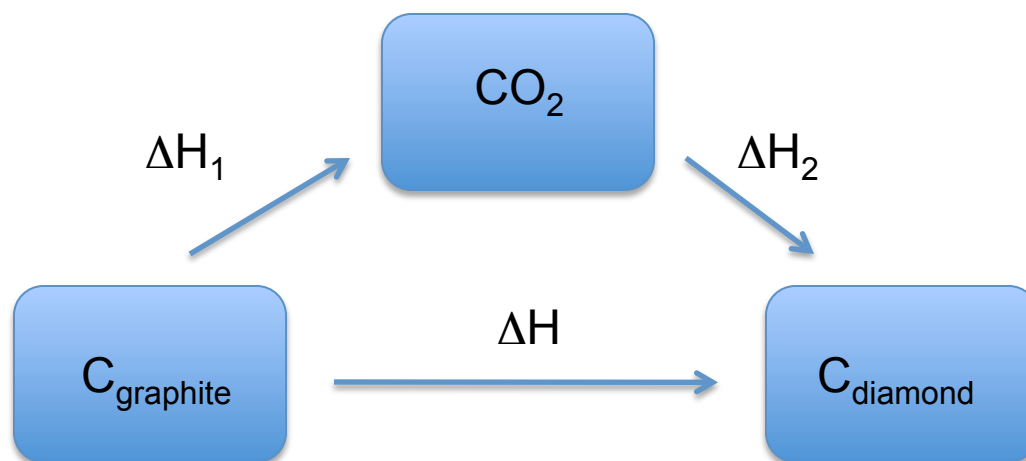


**Chem 123 (section 299)**  
**Lecture 5 (Jan. 14)**

## Hess's Law

Sum of  $\Delta H$  of all steps gives overall reaction enthalpy

H is a state function

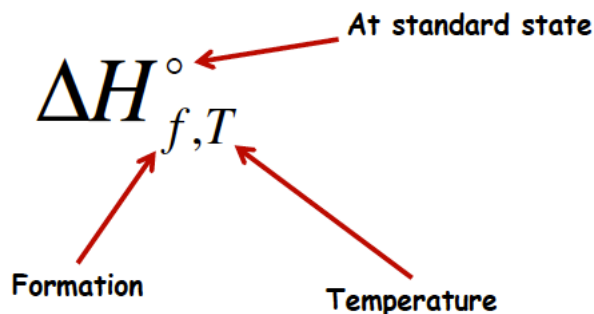


$$\Delta H = \Delta H_1 + \Delta H_2$$

## Standard enthalpy of formation

The **standard enthalpy of formation**,  $\Delta H_{f,T}^{\circ}$ , of a substance is the standard enthalpy for its formation from its elements in their standard state at a given temperature and pressure.

The standard enthalpy of formation of an element is equal to zero by definition.



## Standard state depends on state of aggregation

State of Aggregation	Standard State
Gas	Pressure of 1 atm, 298 K
Pure liquid or solid	Pure substance, 298 K
Solution	Solute: 1 M, 298 K Solvent: Pure liquid, 298K

1.  $\Delta H_f^0 = 0$  for elements in standard state.
2. Need to select one allotrope of element as reference form.  
 $C_{\text{graphite}}$  vs.  $C_{\text{diamond}}$  vs.  $C_{60}$   
 $S_{\text{rhombic}}$  vs.  $S_{\text{monoclinic}}$
3.  $\Delta H_f^0$  varies *slightly* with temperature...we use 298 K as default.

## Standard Enthalpy of Reaction $\Delta_r H^0$ :

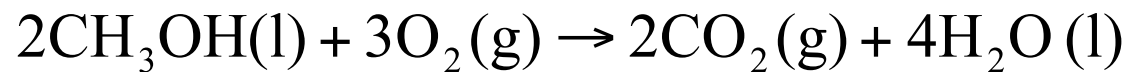
$$\Delta_r H^0 = \sum_i \nu_i \Delta H_{f,i}^0(\text{products}) - \sum_j \nu_j \Delta H_{f,j}^0(\text{reactants})$$

$\Delta H_f^0$  = Enthalpy of formation for each product / reactant

$\nu$  = Stoichiometric coefficient from reaction equation

## Examples

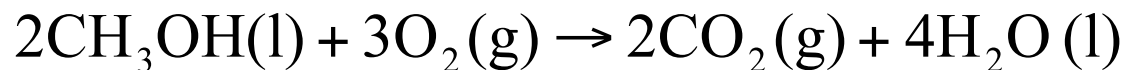
Calculate the standard enthalpy of reaction for the reaction:



Substance	$\Delta H_f^\circ / \text{kJmol}^{-1}$ (from the database)
$\text{CH}_3\text{OH}(\text{l})$	-238.86
$\text{O}_2(\text{g})$	
$\text{CO}_2(\text{g})$	-393.51
$\text{H}_2\text{O}(\text{l})$	-285.83

## Examples

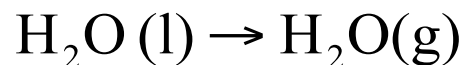
Calculate the standard enthalpy of reaction for the reaction:



Substance	$\Delta H_f^0 / \text{kJmol}^{-1}$ (from the database)	$\nu_j$
$\text{CH}_3\text{OH}(\text{l})$	-238.86	2
$\text{O}_2(\text{g})$	0	3
$\text{CO}_2(\text{g})$	-393.51	2
$\text{H}_2\text{O}(\text{l})$	-285.83	4

$$\begin{aligned}\Delta_r H^0 &= \sum_i \nu_i \Delta H_{f,i}^0(\text{products}) - \sum_j \nu_j \Delta H_{f,j}^0(\text{reactants}) \\ &= 4(-285.83) + 2(-393.51) - 3(0.00) - 2(-238.86) \\ &= -1452.62 \text{ kJ}\end{aligned}$$

b) Calculate the standard enthalpy of vaporization for water:

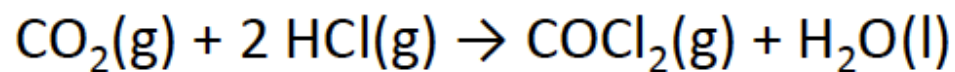


Substance	$\Delta H_f^0 / \text{kJmol}^{-1}$ (from the database at 298K)	$\nu_j$
H <sub>2</sub> O(l)	-285.83	1
H <sub>2</sub> O(g)	-241.82	1

$$\begin{aligned}\Delta H^0 &= \sum_i \nu_i \Delta H_{f,i}^0(\text{products}) - \sum_j \nu_j \Delta H_{f,j}^0(\text{reactants}) \\ &= -241.82 - (-285.83) = 44.01 \text{ kJ}\end{aligned}$$

## Clicker question

Determine  $\Delta H^\circ$  for the following reaction:



Molecule	$\Delta H_f^\circ$ (kJ / mol)
$\text{CO}_2(\text{g})$	-393.51
$\text{HCl}(\text{g})$	-92.30
$\text{CoCl}_2(\text{g})$	-223.01
$\text{H}_2\text{O}(\text{l})$	-285.85

- A) -994.67 kJ
- B) 23.05 kJ
- C) -23.05 kJ
- D) 69.25 kJ
- E) -69.25 kJ

# Chapter 6 and Chapter 7

(p83-96)

## Learning Objectives

By the end of this section, successful learners will be able to:

- Define entropy and recognize that entropy is a state variable
- Express the second law of thermodynamics for an isolated system
- Distinguish work in reversible versus irreversible changes in state

# The Second Law of Thermodynamics

Why do we need to know this?

The first law tells us how much energy is transferred in a reaction, but not the conditions necessary for the reaction to take place, nor why it goes in a particular direction. If the reaction takes place, the total energy of the reaction system and its surroundings remain unchanged, the first law says. But **why do some reactions have the tendency to occur whereas others don't?**

**Can the First Law of Thermodynamics tell us why?**



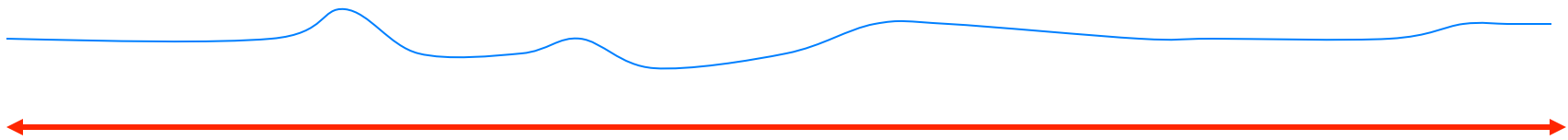
Ice melting at 5 °C  
Spontaneous



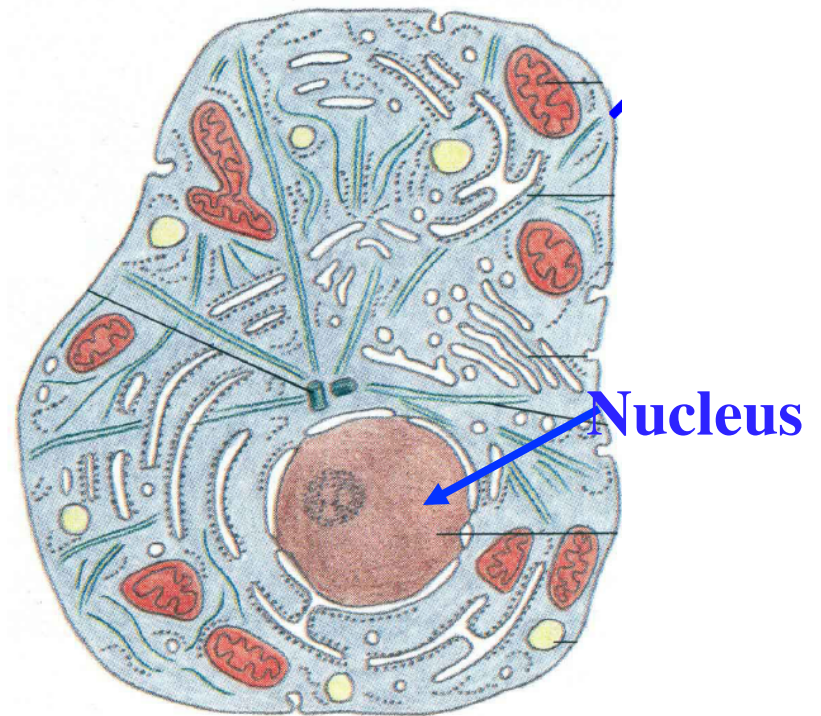
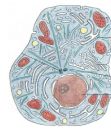
Mixing is spontaneous  
Desalination of sea water requires  
energy

Under normal conditions, DNA molecules are coiled, not straight! Why??

The contour length,  $L_c$ , of a single DNA double helix molecule from a human or an animal can be up to 0.1 meter long!

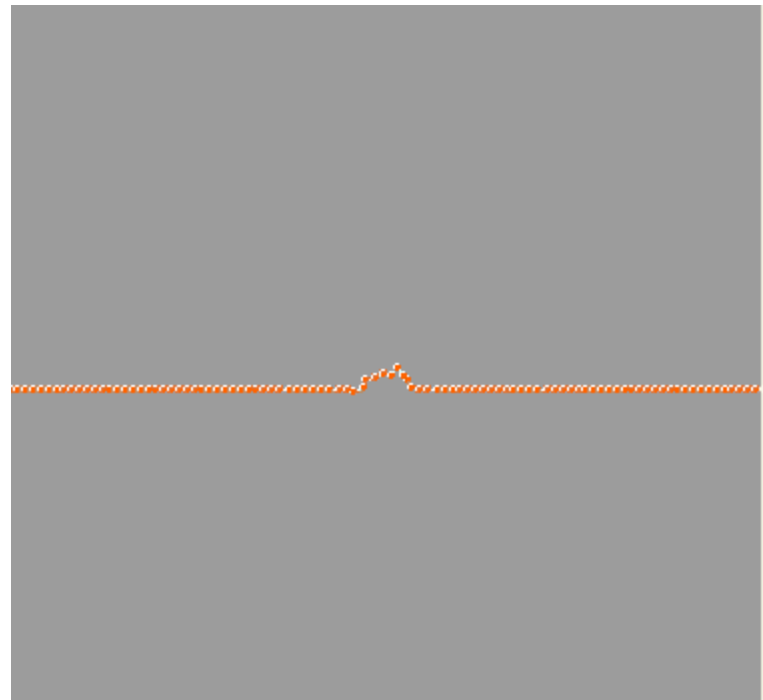


$L_c = 0.1$  meter



$$L_c = 0.1m$$

$$\sqrt{\langle R^2 \rangle} = 10^{-4}m = 100\mu m$$



Movie credit: Grosberg

## Spontaneity is not related to rate

It is important to note that a spontaneous change need not be fast (see later kinetics). A mixture of  $H_2$  and  $O_2$  can be stored for centuries, if a spark is not provided. diamonds have a natural tendency to turn into graphite,

Spontaneous!!!

*Diamond*  $\rightarrow$  *Graphite*



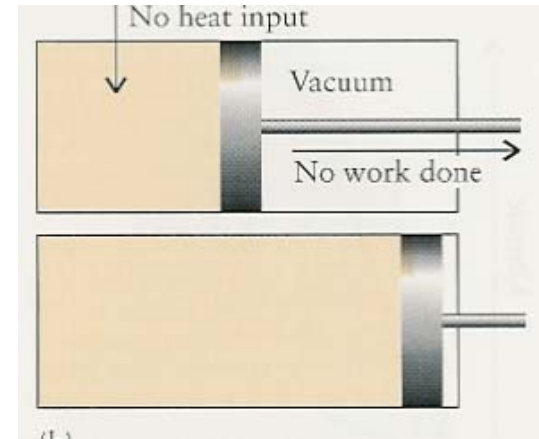
why do some reactions have the tendency to occur  
whereas others don't?

Can the First Law of Thermodynamics tell us why?

Consider the following ideal gas process:

$$p_{ex} = 0, w = 0, q = 0,$$

Thus  $\Delta E = 0, \Delta T = 0,$  and  $\Delta H = 0$



We have no change in any property the 1<sup>st</sup> law deals with.

Can the First Law of Thermodynamics tell us why?

NO.

But the process is indeed spontaneous. Therefore, we need a new state function to tell us when a process will be spontaneous.

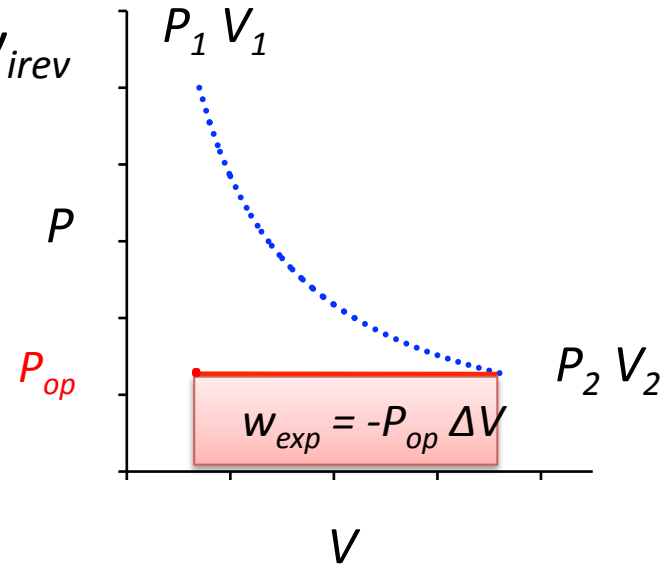
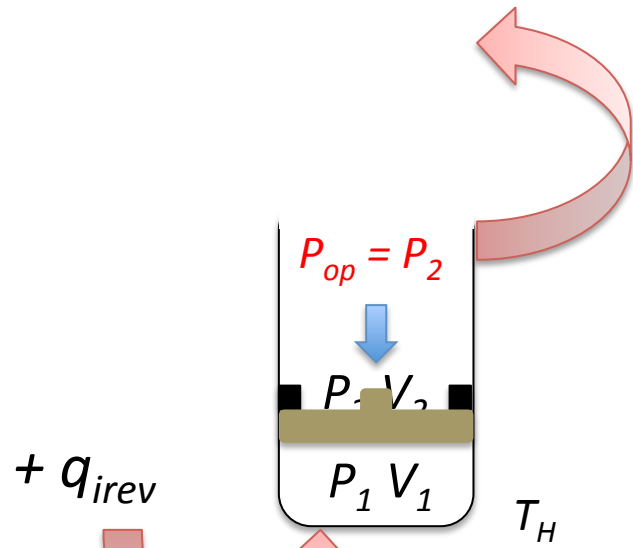
Clausius statement (about The Second Law of Thermodynamics):

*Heat cannot spontaneously flow from cold regions to hot regions without external work being performed on the system*

The perpetual engine of the second type  
Impossible!!!



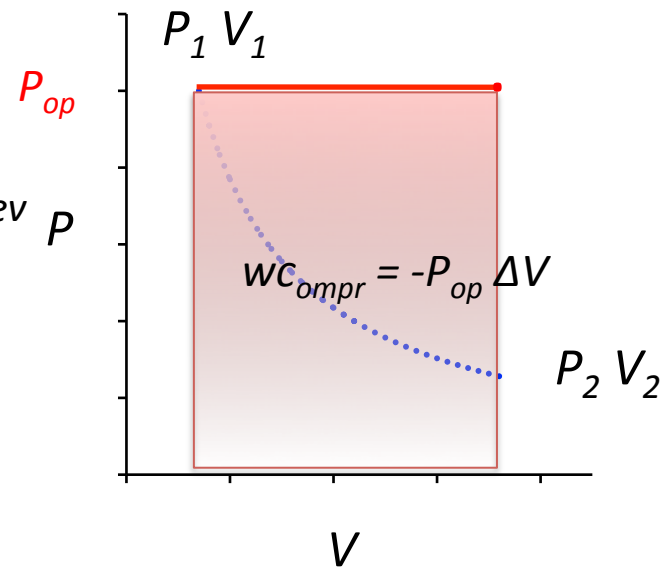
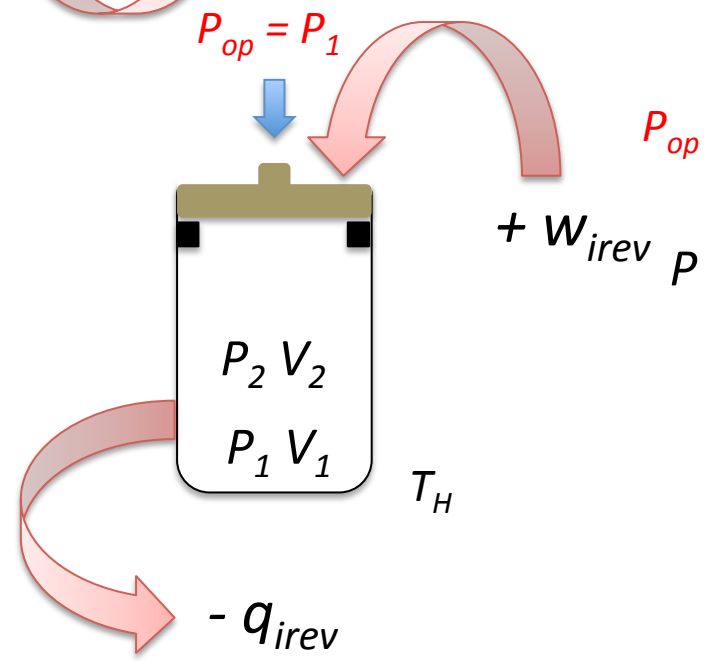
# Irreversible versus reversible work



What is the work produced?

What is the sign of this work?

-



What is the work consumed?

What is the sign of this work?

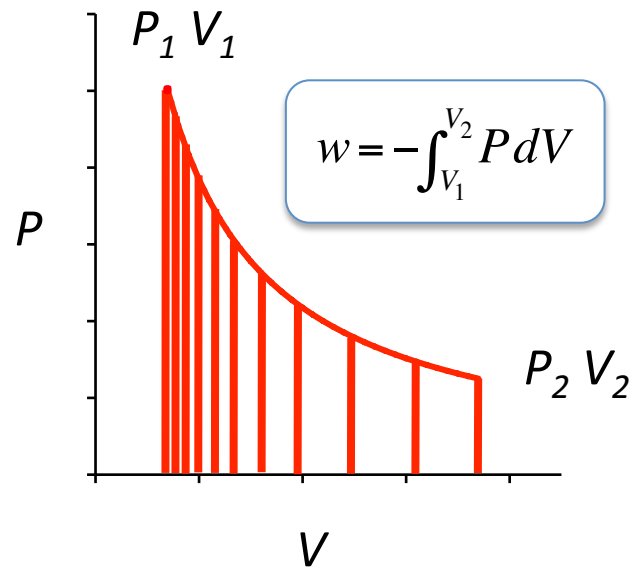
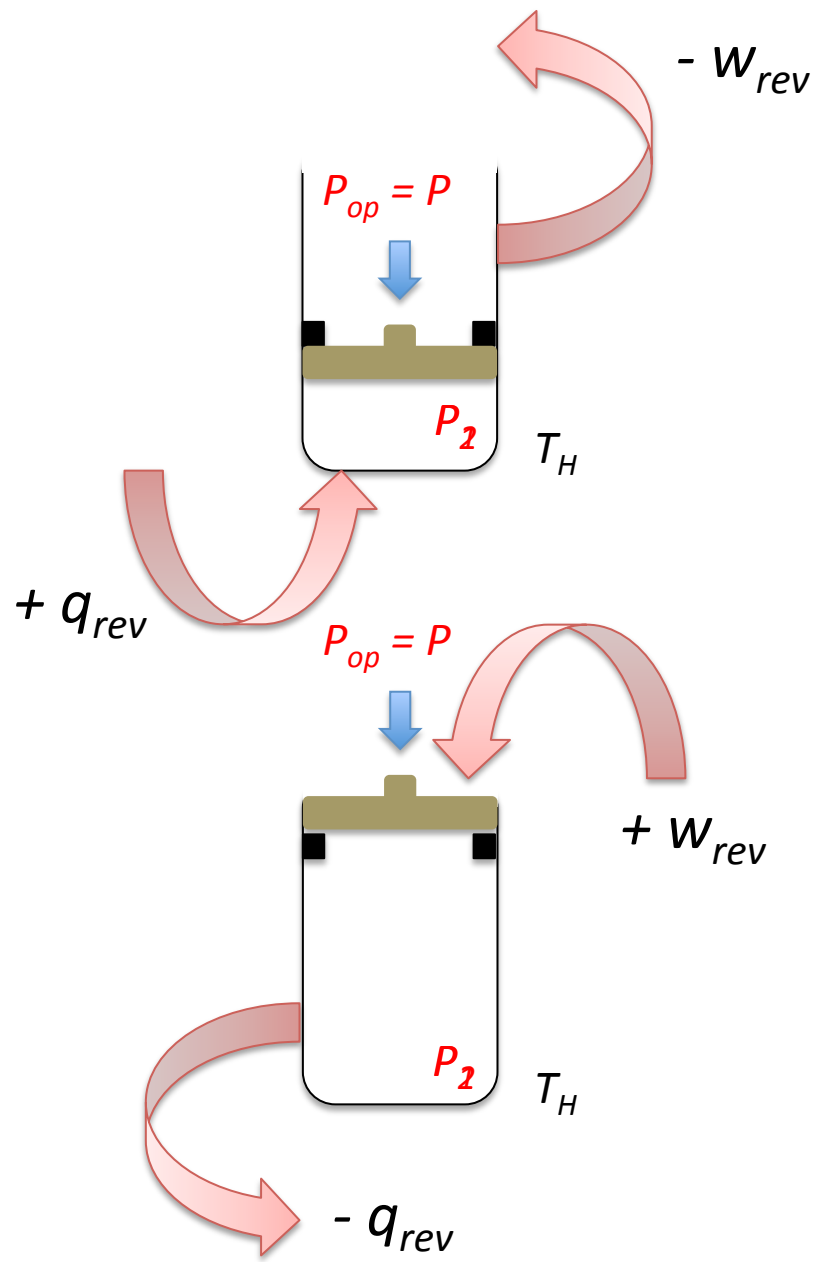
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Irreversible expansion and compression

## Reversible expansion and compression

If we take an infinitely large number of steps, at each step, the system is always in equilibrium with the surroundings,

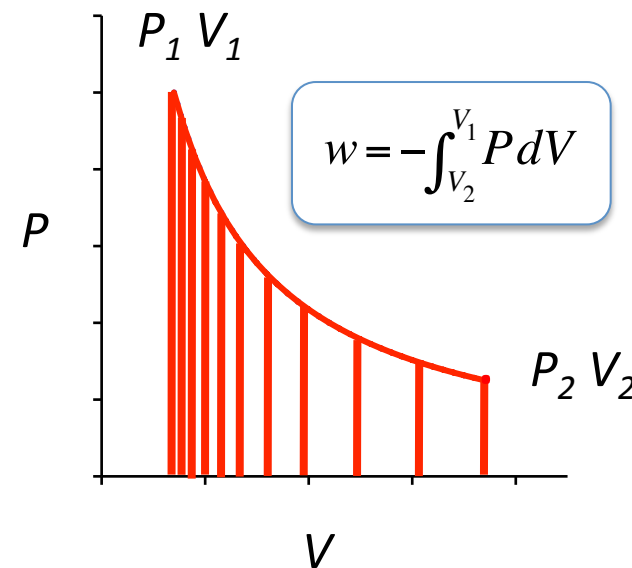
$$P_{\text{op}} = P$$



What is the work produced?

What is the sign of this work?

-



What is the work consumed?

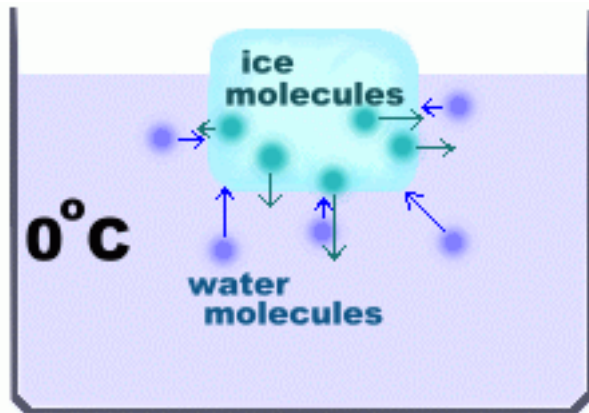
What is the sign of this work?

+

Reversible expansion and compression

## In real life...

- Reversible processes are very very difficult to achieve since they require an infinite number of steps.
- Most processes around us are irreversible, leading to the loss of usable work.



Reversible processes

Ice melting at 1 atm  $0^{\circ}\text{C}$   
(water freezing)

Water boiling at 1 atm and  $100^{\circ}\text{C}$

# Thermodynamic definition of Entropy

a) For every system a state function exists called **Entropy  $S$** .

$$\Delta S = S_2 - S_1 = \frac{q_{rev}}{T}$$

Entropy:  $[S]=[J/K]$  (**Extensive property**)

Molar entropy:  $S_m = S/n$  ;  $[S_m] = [J / (K \cdot mol)]$

Entropy is a measure of disorder

A change in entropy can be calculated by the energy transferred as heat in a **reversible process** divided by the temperature at which the reversible process occurred.

# The Second Law of Thermodynamics

a) For reversible processes holds:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

b) For spontaneous processes holds:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

**For an isolated system (the system does not exchange energy with the surroundings)**

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = \Delta S_{system}$$

a) For reversible processes holds:

$$\Delta S_{system} = 0$$

b) For spontaneous processes holds:

$$\Delta S_{system} > 0$$

$$\Delta S_{system} \geq 0$$