

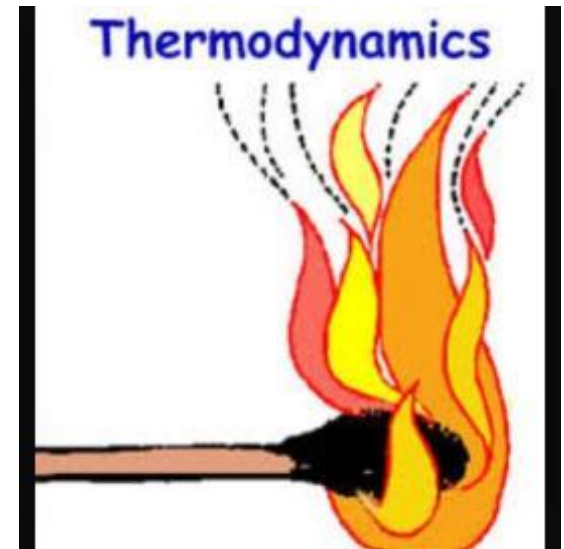
Thermodynamics

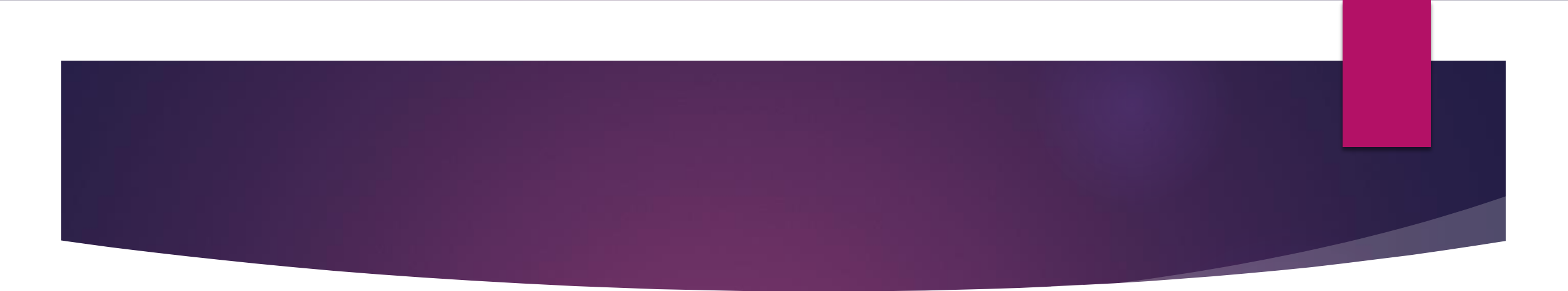
BY

AQEEL A. KHUDHAIR

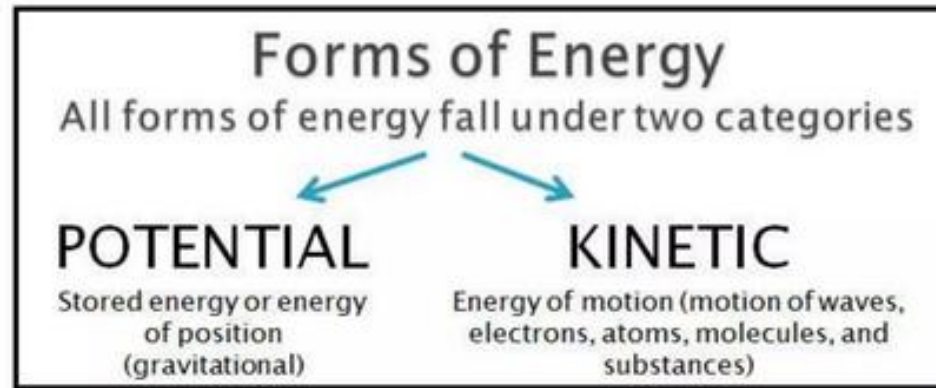
Thermodynamics

- ▶ Thermodynamics is the study of the effects of work, heat, and energy on a system
- ▶ Thermodynamics is only concerned with macroscopic (large-scale) changes and observations.



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- ▶ All of thermodynamics can be expressed in terms of four quantities
 - ▶ Temperature (T)
 - ▶ Internal Energy (U)
 - ▶ Entropy (S)
 - ▶ Heat (Q)

Forms of energy

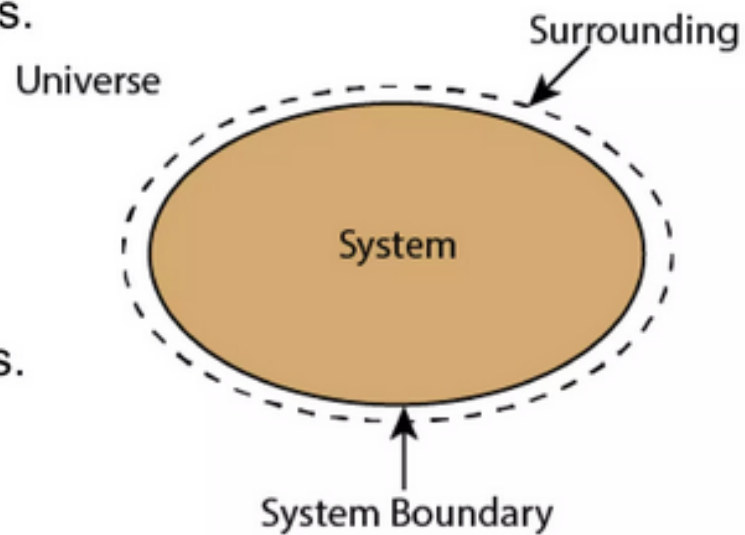


The **INTERNAL ENERGY, E** of a system is the sum of the kinetic and potential energies of all the particles that compose the system or the **total energy of a system**.

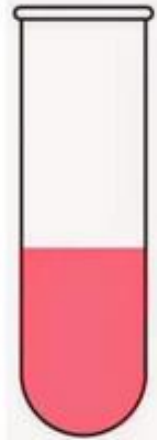


Definitions

- ▶ **System:** A region of the universe that we direct our attention to.
- ▶ **Surroundings:** Everything outside a system is called surroundings.
- ▶ **Boundary:** The boundary or wall separates a system from its surroundings.



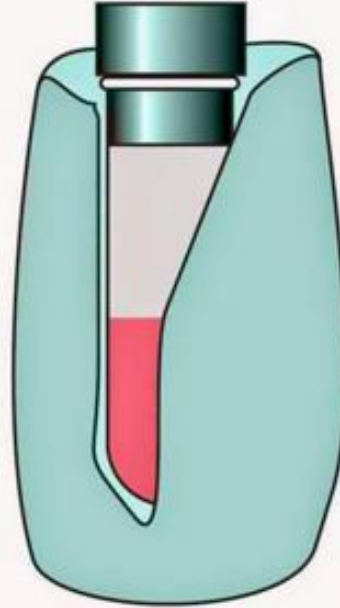
Thermodynamic systems



Open

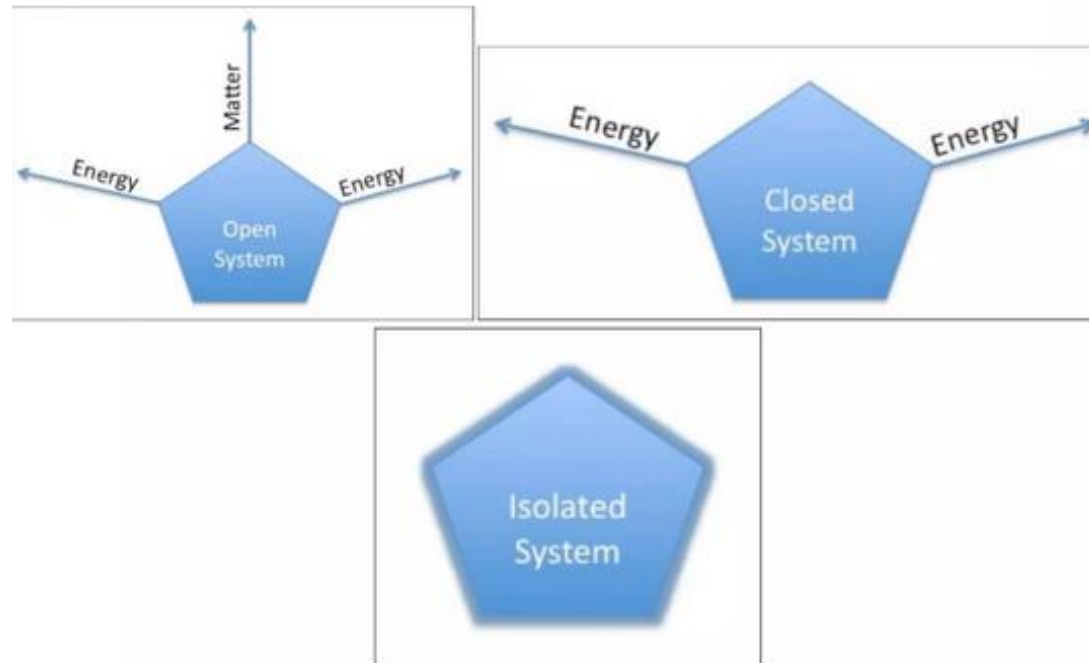


Closed



Isolated

Thermodynamic systems

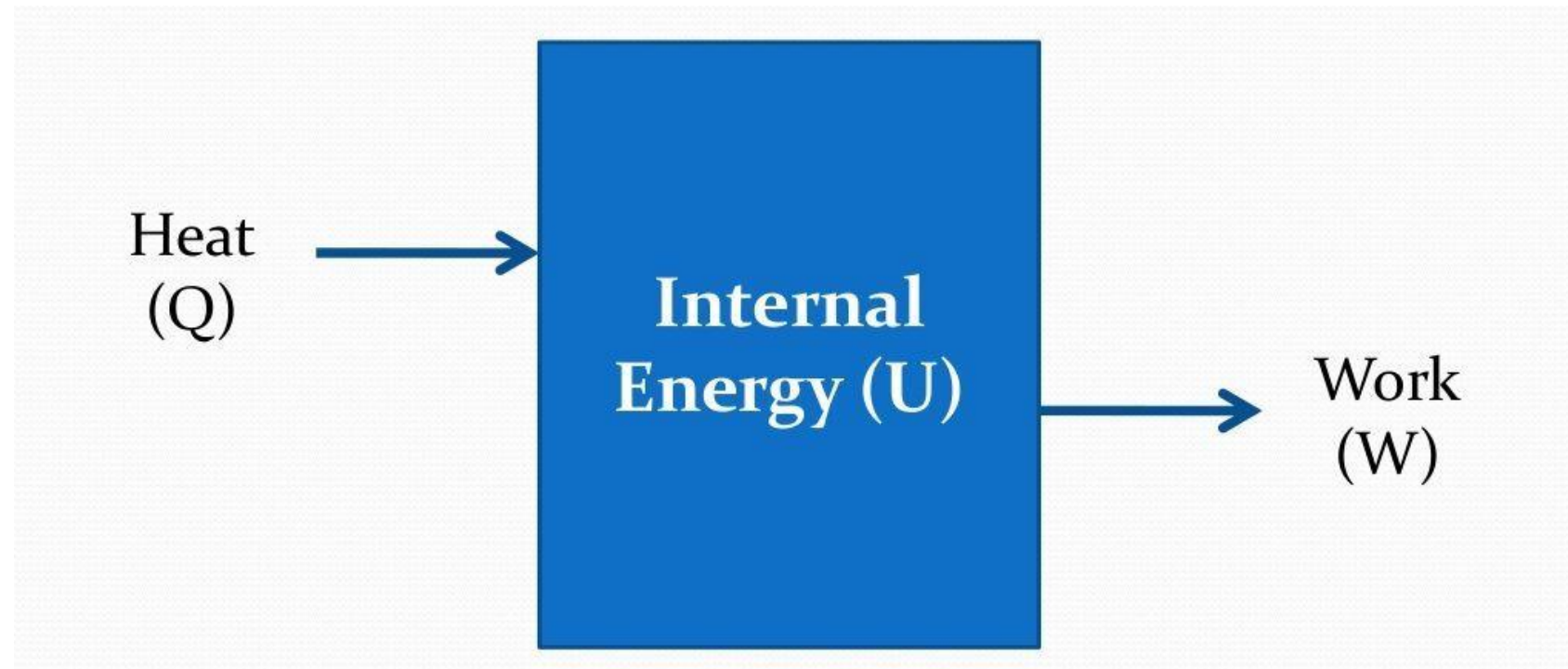


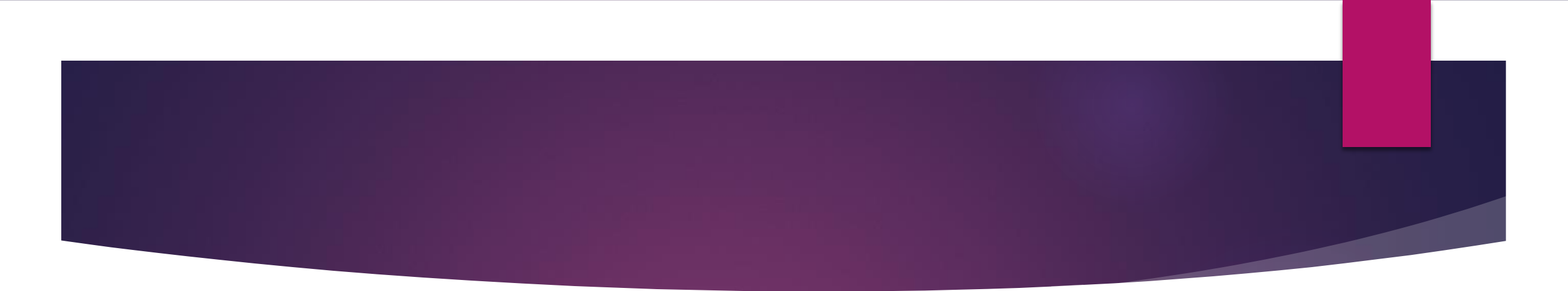
You can't win (1st law of Thermodynamics)

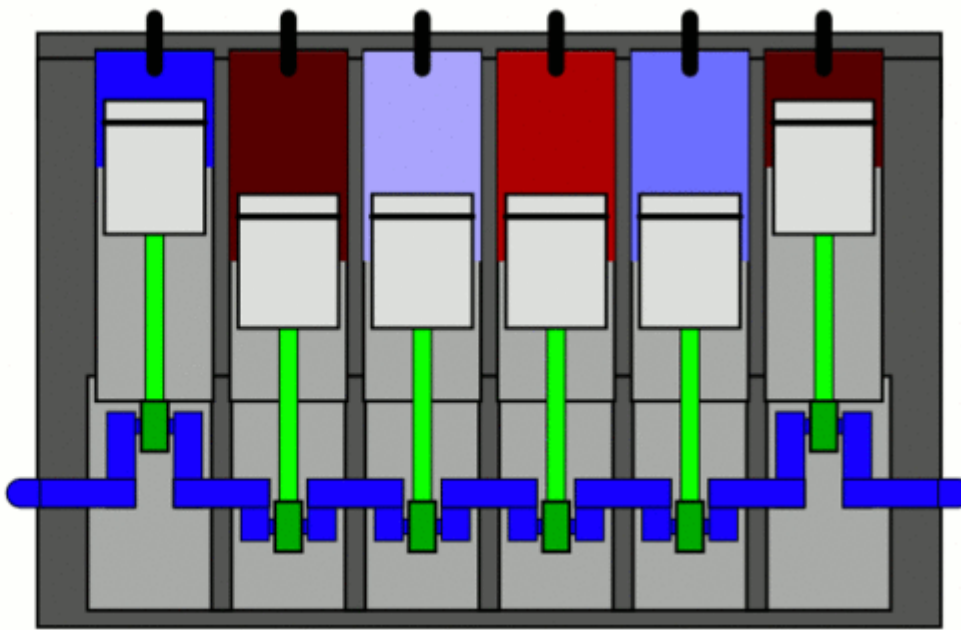
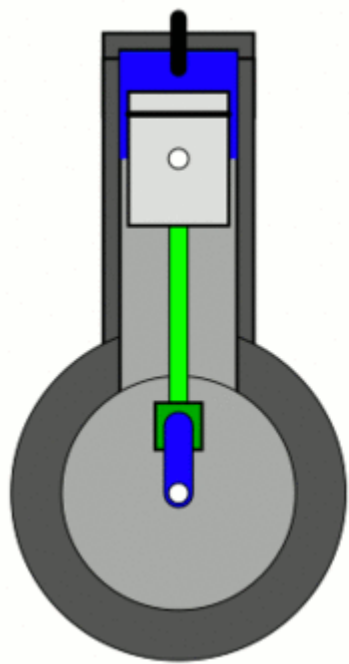
- ▶ The first law of thermodynamics is an extension of the law of conservation of energy
- ▶ The change in internal energy of a system is equal to the heat added to the system minus the work done by the system

<https://www.youtube.com/watch?v=dHdIH3l8FkM>

The first law of thermodynamics



- 
- ▶ $\Delta E = Q - W$
 - ▶ E is the enternal energy
 - ▶ Q is the heat
 - ▶ W is work





Process Terminology

- ▶ Adiabatic – no heat transferred
- ▶ Isothermal – constant temperature

Adiabatic Process

- ▶ An **adiabatic process** transfers no heat
 - ▶ therefore $Q = 0$
- ▶ $\Delta E = Q - W$
- ▶ When a system expands adiabatically, W is positive (the system does work) so ΔE is negative.
- ▶ When a system compresses adiabatically, W is negative (work is done on the system) so ΔE is positive.

Isothermal Process

- ▶ An **isothermal process** is a constant temperature process. Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium
- ▶ For ideal gases, if ΔT is zero, $\Delta E = 0$
- ▶ Therefore, $Q = W$
 - ▶ Any energy entering the system (Q) must leave as work (W)

Maximum work



$$w = - \int_{V_1}^{V_2} P dV \quad \text{----- (i)}$$

By ideal gas equation

$$PV = nRT$$
$$P = \frac{nRT}{V}$$

Substitute in (i), we get.

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

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

$$w = - nRT [nV]_{V_1}^{V_2} \quad \left[\because \int \frac{dx}{x} = \ln x \right]$$

$$w = - nRT [\ln V_2 - \ln V_1]$$

$$w = - nRT \ln \frac{V_2}{V_1}$$

$$w = -2.303 nRT \log \frac{V_2}{V_1}$$

[$\ln x = 2.303 \log x$]

Since $P_1 V_1 = P_2 V_2$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$w = -2.303 nRT \log \frac{P_1}{P_2}$$

Example 3–2. One mole of water in equilibrium with its vapor is converted into steam at 100° C and 1 atm. The heat absorbed in the process (i.e., the heat of vaporization of water at 100° C) is about 9720 cal/mole. What are the values of the three first-law terms, Q , W , and ΔE ?

The amount of heat absorbed is the heat of vaporization, given as 9720 cal/mole. Therefore,

$$Q = 9720 \text{ cal/mole}$$

The work W performed against the constant atmospheric pressure is obtained by using equation (3–8), $W = P(V_2 - V_1)$. Now V_1 is the volume of 1 mole of liquid water at 100° C, or about 0.018 liter. The volume V_2 of 1 mole of steam at 100° C and 1 atm is given by the gas law, assuming that the vapor behaves ideally:

$$V_2 = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.6 \text{ liters}$$

It is now possible to obtain the work,

$$W = P(V_2 - V_1) = 1 \times (30.6 - 0.018) =$$

$$30.6 \text{ liters atm/mole} = 741 \text{ cal/mole}$$

The internal energy change ΔE is obtained from the first-law expression

$$\Delta E = Q - W = 9720 - 741 = 8979 \text{ cal/mole}$$

Example 3-4

What is the maximum work done in the isothermal reversible expansion of 1 mole of an ideal gas from 1 to 1.5 liters at 25°C?

The conditions of this problem are similar to those of *Example 3–2*, except that equation (3-10) can now be used to obtain the (maximum) work involved in expanding reversibly this gas by 0.5 liters; thus,

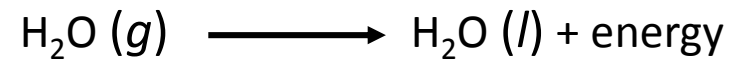
$$W = -(1 \text{ mole})(8.3143 \text{ joules/K mole})(298.15 \text{ K}) \ln (1.5/1.0)$$

$$W = -1005.3 \text{ joules}$$

Thermochemistry

- Thermochemical equation: a chemical equation that includes the enthalpy change
- Heat of reaction: the enthalpy change for a chemical equation exactly as it is written
- Heat of combustion: the heat of reaction for the complete burning of one mole of a substance

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.



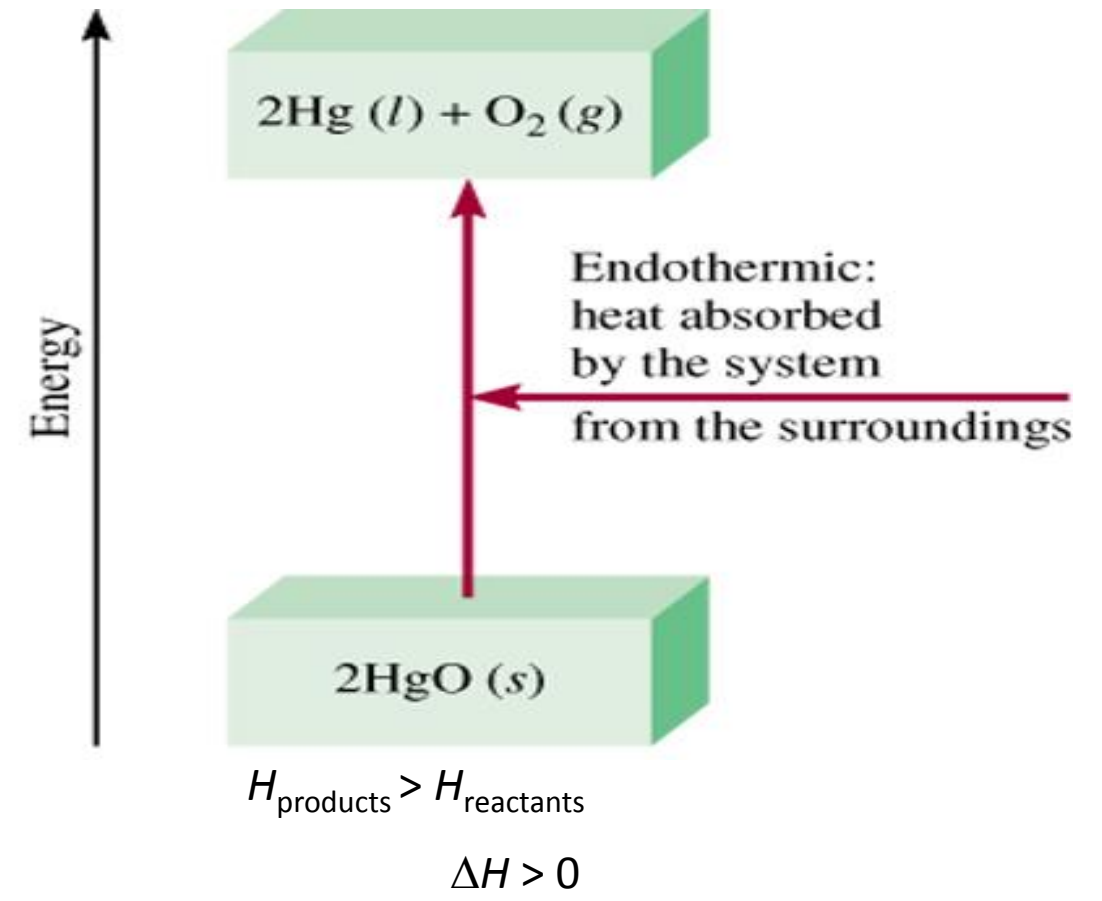
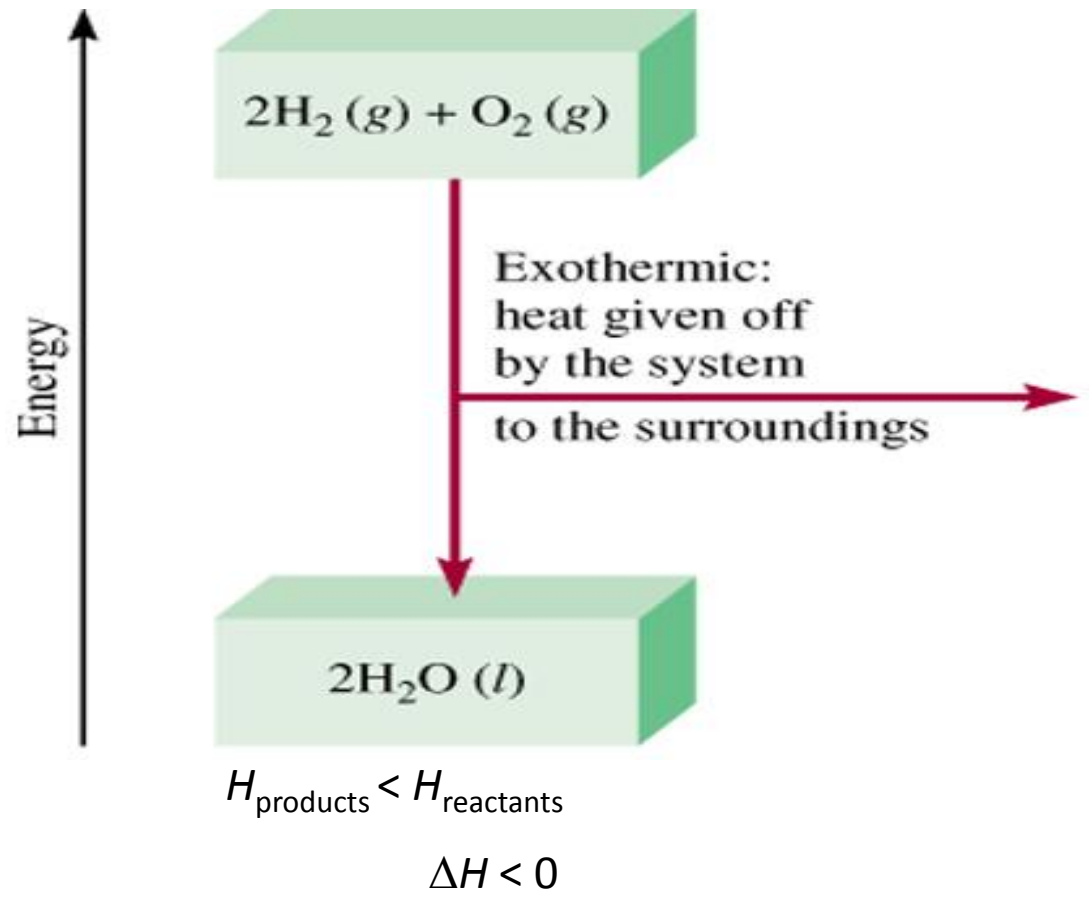
Endothermic process is any process in which heat has to be supplied to the system from the surroundings.



Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

$$\Delta H = H (\text{products}) - H (\text{reactants})$$

ΔH = heat given off or absorbed during a reaction



Thermochemical Equations

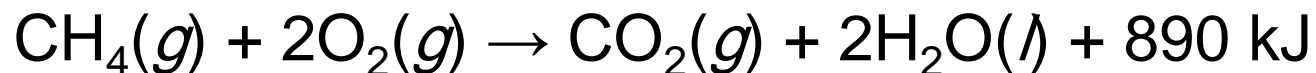
Heats of Combustion

The **heat of combustion** is the heat of reaction for the complete burning of one mole of a substance.

Thermochemical Equations

▶ Heats of Combustion

Small amounts of natural gas within crude oil are burned off at oil refineries.

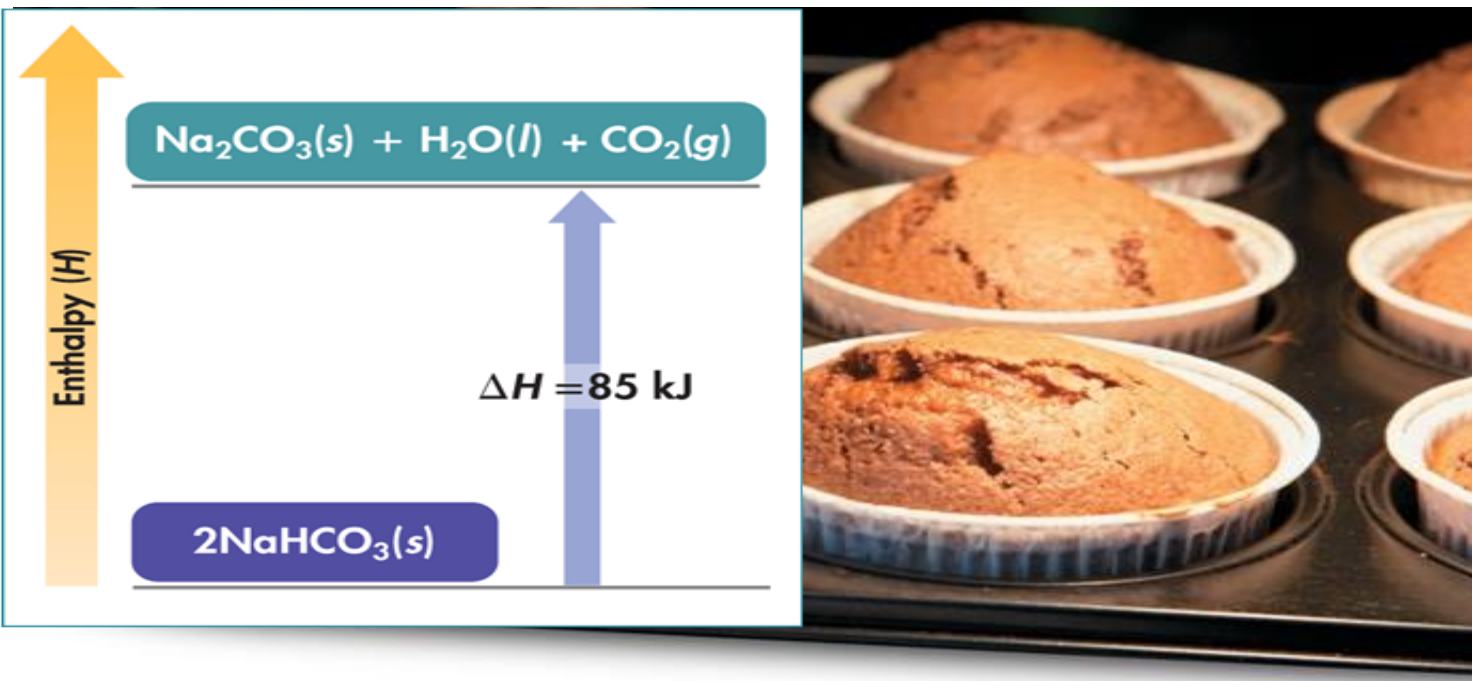
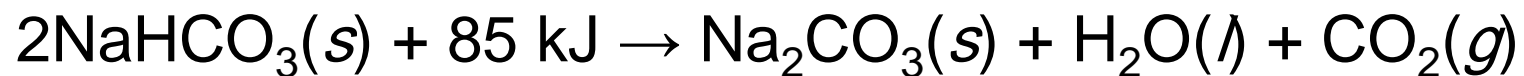


- This is an exothermic reaction.
- Burning 1 mole of methane releases 890 kJ of heat.
- The heat of combustion (ΔH) for this reaction is -890 kJ per mole of methane burned.

Thermochemical Equations

▶ Heats of Reaction

Baking soda (sodium bicarbonate) decomposes when it is heated. This process is endothermic.



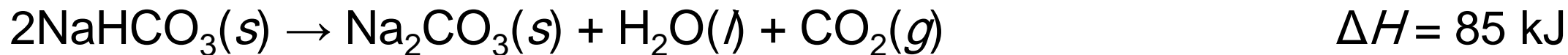
The carbon dioxide released in the reaction causes muffins to rise while baking.

Thermochemical Equations

► Heats of Reaction



Remember that ΔH is positive for endothermic reactions.
Therefore, you can write the reaction as follows:



Thermochemical Equations

Heats of Reaction

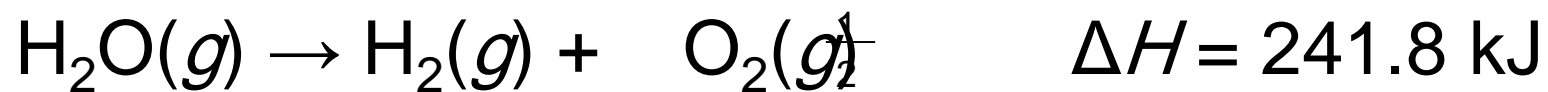
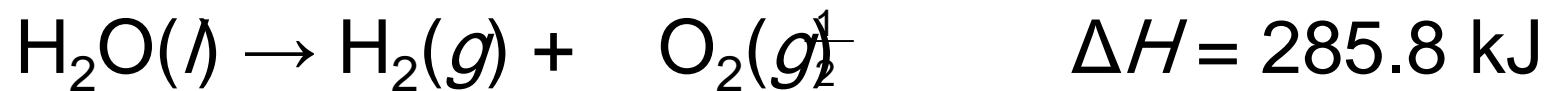
The amount of heat released or absorbed during a reaction depends on the number of moles of the reactant involved.

- The decomposition of 2 moles of sodium bicarbonate requires 85 kJ of heat.
- Therefore, the decomposition of 4 moles of the same substance would require twice as much heat, or 170 kJ.

Thermochemical Equations

► Heats of Reaction

To see why the physical state of the reactants and products must be stated, compare the following two equations.



difference = 44.0 kJ

You can't break even (2nd Law of Thermodynamics)

- ▶ Second law of thermodynamics is about spontaneity of processes.
- ▶ Heat does not go from a colder body to a hotter body.
- ▶ The 2nd Law can also be stated that heat flows spontaneously from a hot object to a cold object (spontaneously means without the assistance of external work)

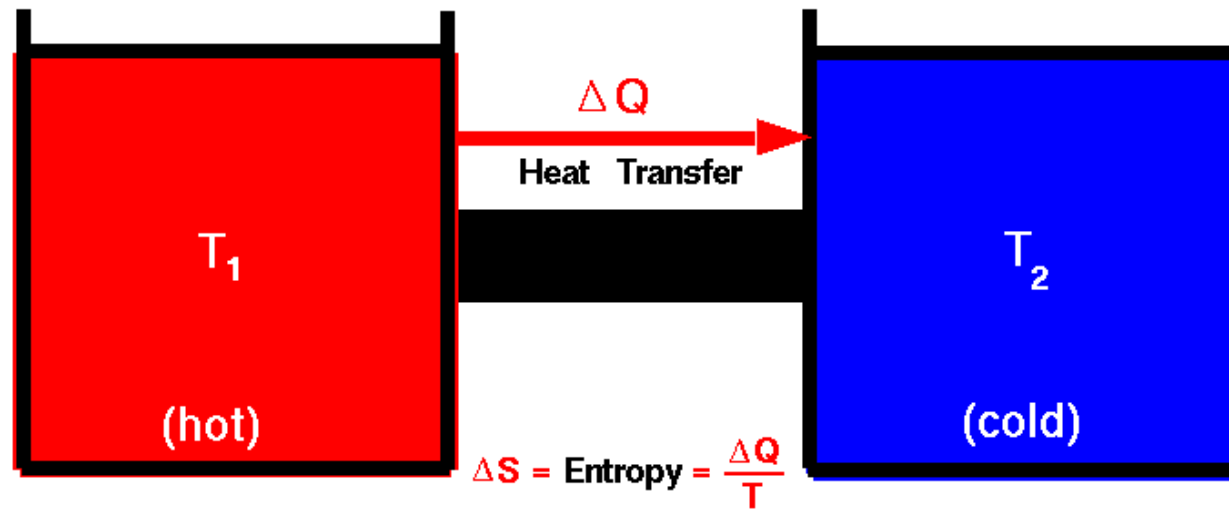


The Second Law of Thermodynamics says that processes that involve the transfer or conversion of heat energy are irreversible



Second Law of Thermodynamics

Glenn
Research
Center



There exists a useful thermodynamic variable called entropy (S). A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus the environment to increase for an irreversible process and to remain constant for a reversible process.

$$S_f = S_i \text{ (reversible)}$$

$$S_f > S_i \text{ (irreversible)}$$

Concerning the 2nd Law

- ▶ The second law of thermodynamics introduces the notion of entropy (S), a measure of system disorder (messiness)
- ▶ U is the quantity of a system's energy, S is the quality of a system's energy.

Implications of the 2nd Law

- ▶ Time marches on
 - ▶ If you watch a movie, how do you know that you are seeing events in the order they occurred?
 - ▶ If I drop a raw egg on the floor, it becomes extremely “disordered” (greater Entropy) – playing the movie in reverse would show pieces coming together to form a whole egg (decreasing Entropy) – highly unlikely!

Direction of a Process

- ▶ The 2nd Law helps determine the preferred direction of a process
- ▶ A reversible process is one which can change state and then return to the original state
- ▶ This is an idealized condition – all real processes are irreversible

Example 3-8

What is the entropy change accompanying the vaporization of 1 mole of water in equilibrium with its vapor at 25°C? In this reversible isothermal process, the heat of vaporization ΔH_v required to convert the liquid to the vapor state is 10,500 cal/mole.

The process is carried out at a constant pressure, so that $Q_p = \Delta H_v$, and because it is a reversible process, the entropy change can be written as

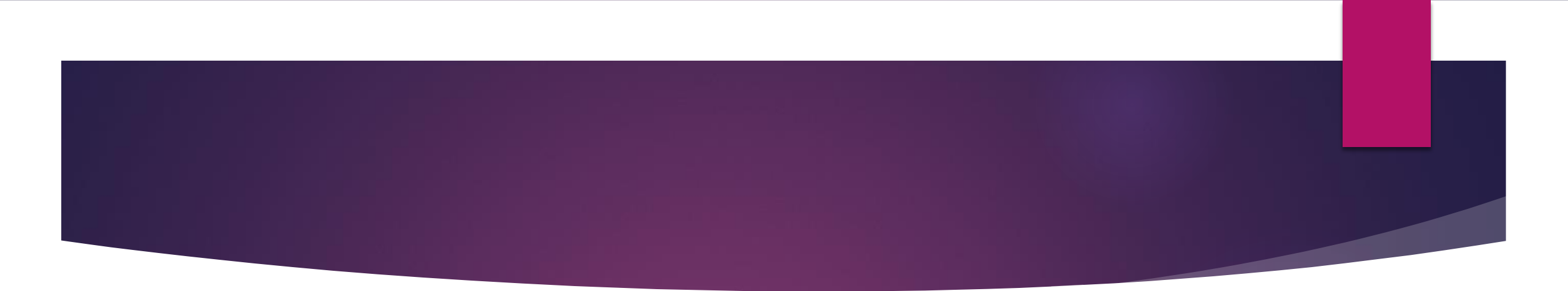
$$\Delta S = \frac{\Delta H_v}{T} = \frac{10,500}{298} = 35.2 \text{ cal/mole deg}$$

- In case of irreversible processes, change in entropy can be carried out as below:

$$\Delta S = C_p \ln \frac{T_2}{T_1} = 2.303 C_p \log \frac{T_2}{T_1}$$

Free energy

- ▶ $\Delta G = \Delta H - T\Delta S$
- ▶ ΔH refers to the heat change for a reaction. A positive ΔH means that heat is taken from the environment (endothermic). A negative ΔH means that heat is emitted or given to the environment (exothermic).
- ▶ ΔG is a measure for the change of a system's free energy.

- 
- ▶ If $\Delta G < 0$, the process occurs spontaneously.
 - ▶ If $\Delta G = 0$, the system is at equilibrium.
 - ▶ If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

$$\Delta G = \Delta H - T\Delta S$$

Case	ΔH	ΔS	ΔG	Reaction
1. high temperature	-	+	-	Spontaneous
2. low temperature	-	+	-	Spontaneous
3. high temperature	-	-	+	Nonspontaneous
4. low temperature	-	-	-	Spontaneous
5. high temperature	+	+	-	Spontaneous
6. low temperature	+	+	+	Nonspontaneous
7. high temperature	+	-	+	Nonspontaneous
8. low temperature	+	-	+	Nonspontaneous

Example 3-10

ΔH and ΔS for the transition from liquid water to ice at -10°C and at 1 atm pressure are -1343 cal/mole and -4.91 cal/mole deg, respectively. Compute ΔG for the phase change at this temperature ($-10^{\circ}\text{C} = 263.2$ K) and indicate whether the process is spontaneous. Write

$$\Delta G = -1343 - [263.2 \times (-4.91)] = -51 \text{ cal/mole}$$
$$= -213 \text{ joules}$$

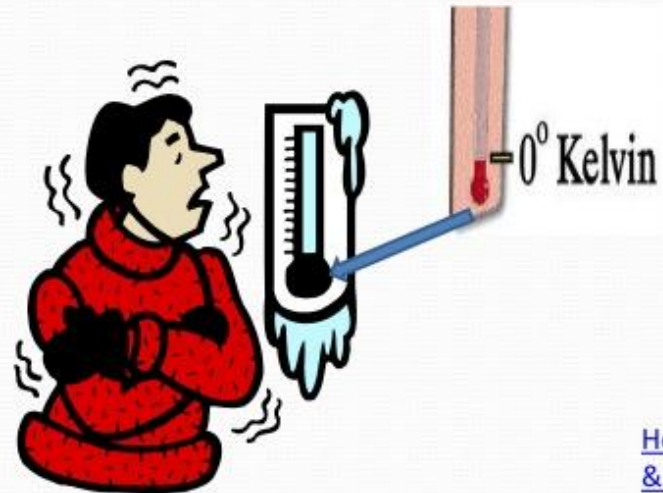
The process is spontaneous, as reflected in the negative value of ΔG .

You can't get out (3rd Law)

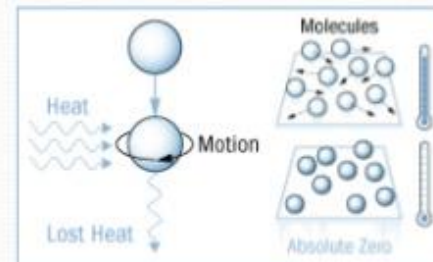
- ▶ No system can reach absolute zero
- ▶ This is one reason we use the Kelvin temperature scale. Not only is the internal energy proportional to temperature, but you never have to worry about dividing by zero in an equation!
- ▶ There is no formula associated with the 3rd Law of Thermodynamics
- ▶ <https://www.youtube.com/watch?v=kuGmsnzjbpE>

3rd Law of Thermodynamics

Absolute zero can't be reached - who would want to!



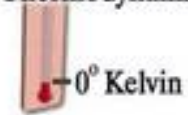
$$0^{\circ} \text{K} = -273^{\circ} \text{C} = -459^{\circ} \text{F}$$



[How Stuff Works: 10 Scientific Laws & Theories You Really Should Know](#)

3rd Law of Thermodynamics

Third Law of
Thermodynamics



- ▶ It says that however it is impossible to reach absolute zero, but at which (0 Kelvin), there will be no entropy (S) and a pure crystalline structure of matter will form.

