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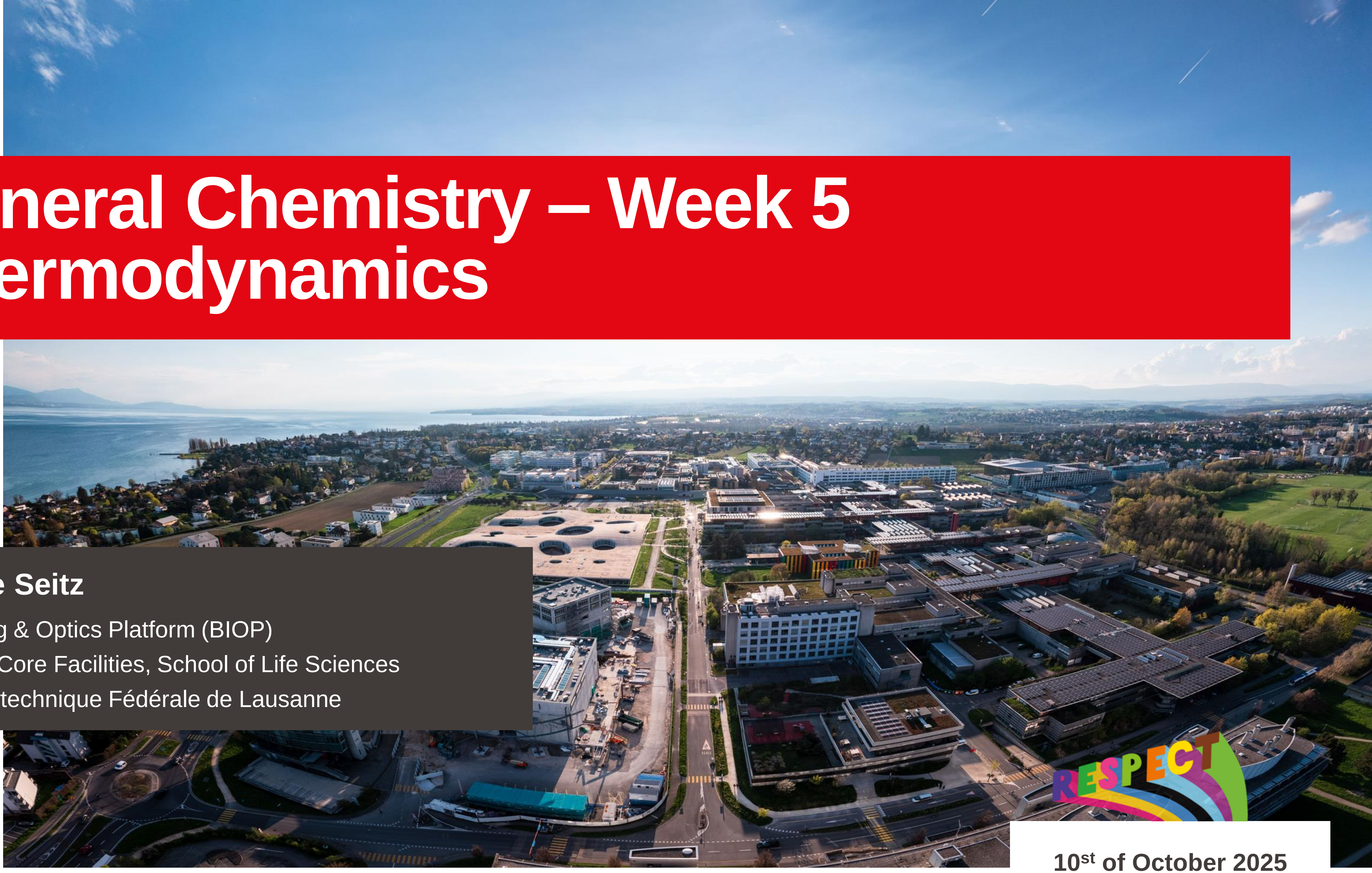

General Chemistry – Week 5
Thermodynamics

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Recap last week

Behaviour of gases

- Behaviour of ideal gases
- The Ideal Gas Law
- The Kinetic Model of Gases
  - Pressure and Temperature can be deduced from the kinetic behavior of gas molecules.

$$PV = n \cdot R \cdot T$$

$$R = 8.314\, J \cdot K^{-1} \cdot mol^{-1}$$

$$PV = \frac{1}{3} n M {v_{\mathrm{rms}}}^2$$

$$v_{\mathrm{rms}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} \qquad T = \frac{M {v_{\mathrm{rms}}}^2}{3R}$$

The Maxwell Distribution of Speeds

- The root mean square speed equation is like cars in traffic: individual molecules have speeds that vary over a wide range.
- The formula for calculating the fraction of gas molecules having a given speed, v, at any instant was derived by the Scottish scientist James Clerk Maxwell.

$$\Delta N = Nf(v)\Delta v \quad \text{with} \quad f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 e^{-Mv^2/2RT}$$

- ΔN is the number of molecules with speeds in the between v and $v + \Delta v$, M is molar mass, and R is the gas constant.

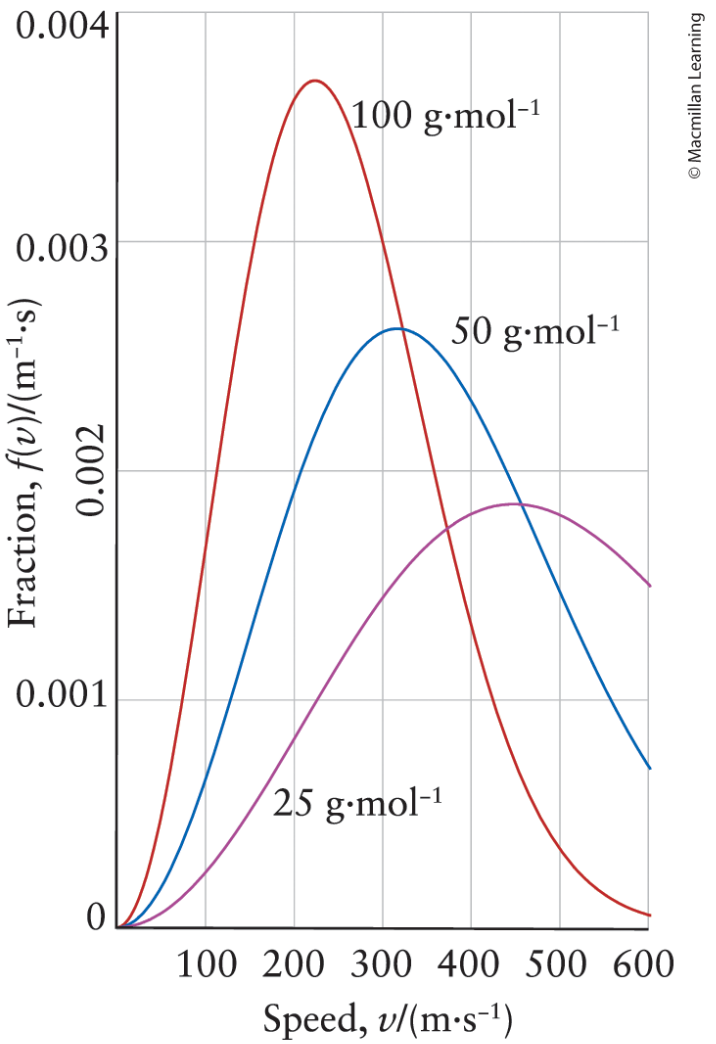
The Maxwell Distribution of Speeds

$\Delta N = Nf(v)\,\Delta v$ with $$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-Mv^2/2RT}$$

- The exponential factor (which falls rapidly toward zero as v increases) means that very few molecules have very high speeds.
- The factor v^2 that multiplies the exponential factor goes to zero as v goes to zero, so it means that very few molecules have very low speeds.
- The factor $4\pi(M/2\pi RT)^{3/2}$ simply ensures that the total probability of a molecule having a speed between zero and infinity is 1.

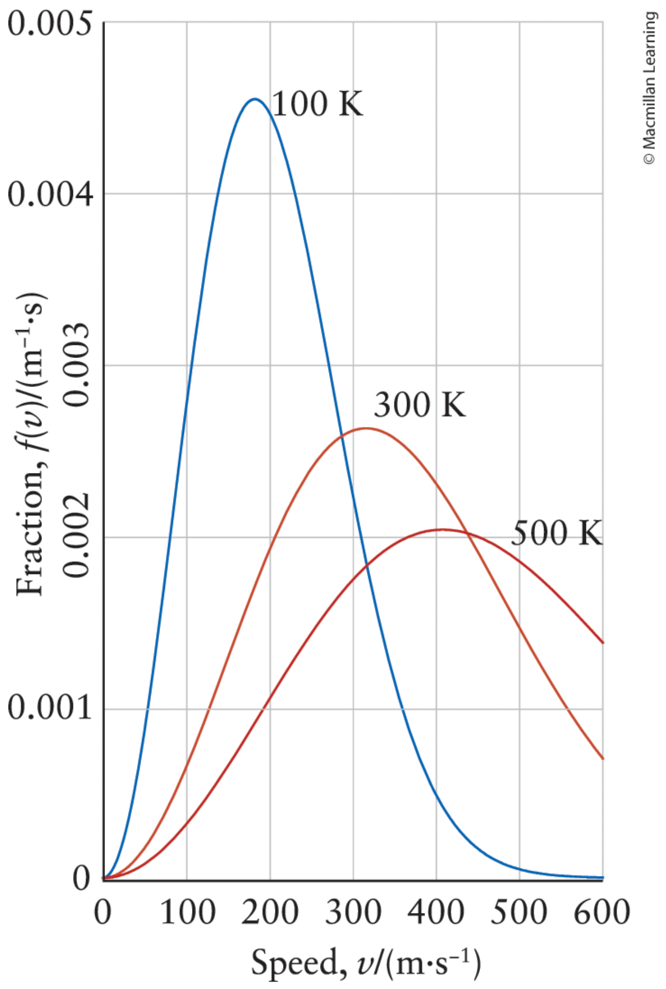
Velocity of Different Masses

- Maxwell distribution gives the range of molecular speeds for three gases.
- All are for the same temperature, 300 K.
- The greater the molar mass, the lower the average speed.



Velocity of Same Mass

- In the Maxwell distribution, the curves correspond to the speeds of a single substance (of molar mass 50 g·mol−1) at different temperatures.
- The higher the temperature, the higher the average speed and the broader the spread of speeds.



Intermolecular Forces

- Intermolecular forces are attractions and repulsions between molecules. They are responsible for the different phases of matter (solid, liquid, gas).
- Phases are uniform throughout in chemical composition and physical state.
- Intermolecular forces are most prevalent in the condensed phases, solid and liquid.
- The strongest forces are the interionic forces: forces between ions. These are the forces of ionic solids.

The Origin of Intermolecular Forces

- Attractive force arises from Coulombic interaction

$$E_p = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$

  - E_p = potential energy
  - Q_1 and Q_2 = charge of each atom
  - r = distance between Q_1 and Q_2
- The strength (E_p) is determined by both q and r.
- Temperature is an indicator of the strength of the attractive forces: Temp ↓ (boiling point) means attractive forces ↓

The Origin of Intermolecular Forces: Radius

$$E_p = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$

Type of interaction	Typical energy ($kJ \cdot mol^{-1}$)	Distance dependence
Ion-ion	250	$1/r$
Ion-dipole	15	$1/r^2$
∗Dipole-dipole (stationary solids/liquids)	2	$1/r^3$
Dipole-dipole (rotating gases)	0.3	$1/r^6$
Dipole-induced-dipole	2	
London or induced (or dispersion)	2	

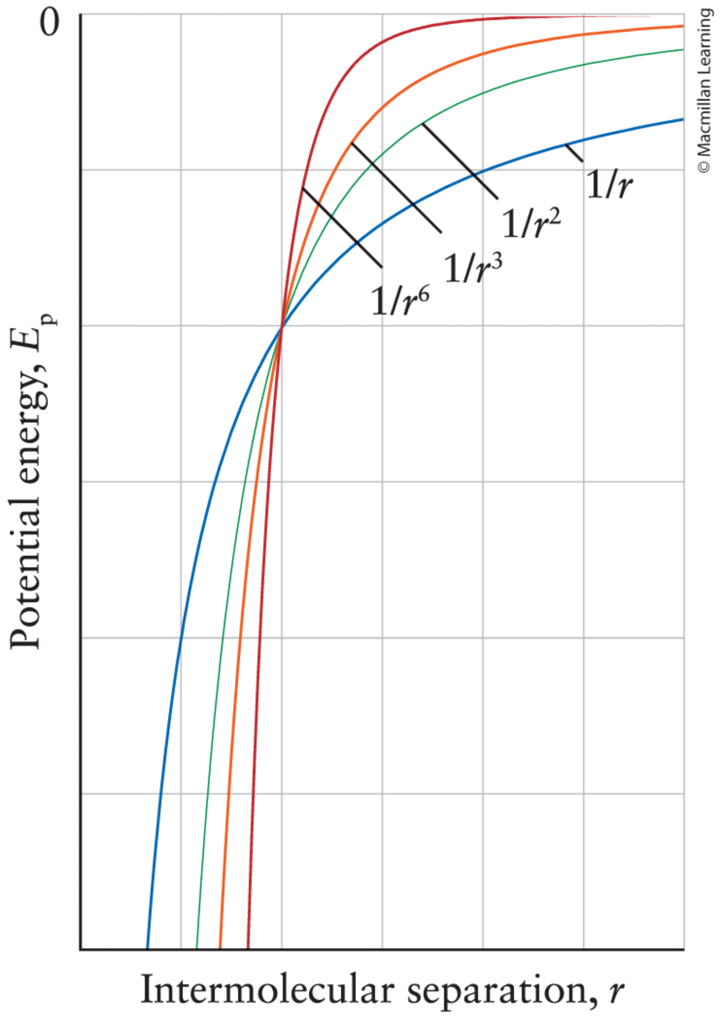
- ∗Hydrogen bonding is a special case of dipole-dipole; typical energy, 20 $kJ \cdot mol^{-1}$.

The Origin of Intermolecular Forces: Radius

- The distance across which the potential energy interaction is felt.

Ion-ion	$1/r$
Ion-dipole	$1/r^2$
Dipole-dipole (stationary)	$1/r^3$
Dipole-dipole (rotating)	$1/r^6$

- For $1/r^6$, the interaction falls off rapidly as distance increases just a little.



$$E_p = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$

Ideal Gas Law: Deviations from Ideality

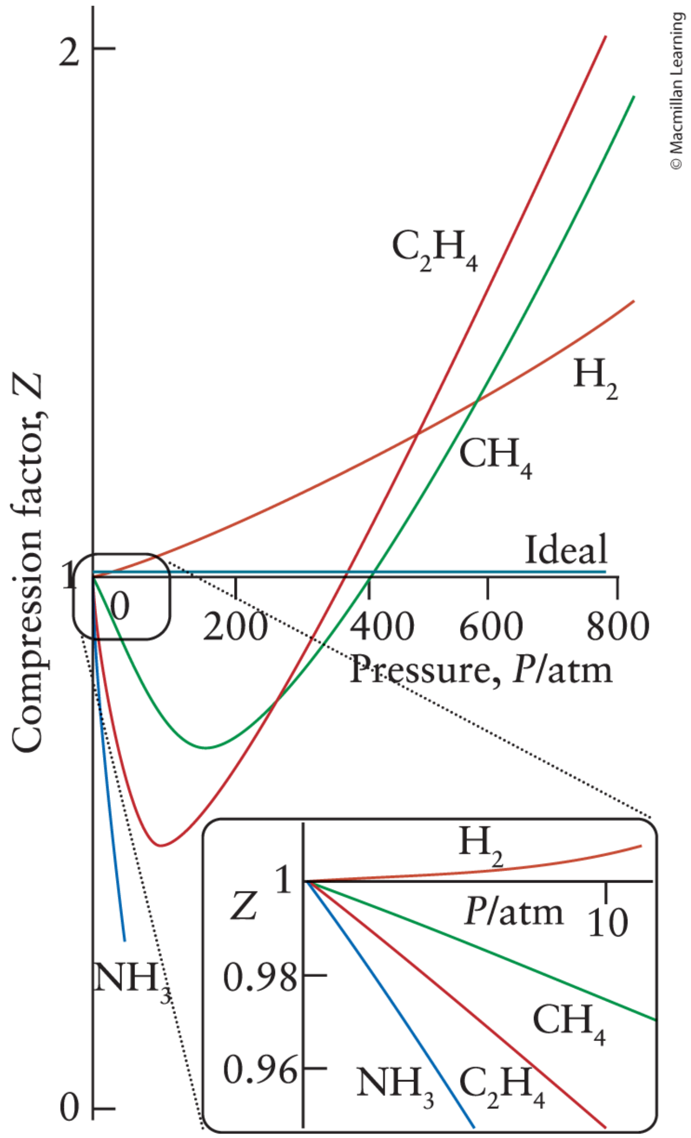
- In industry and in many research laboratories, gases must be used under high pressures, when the ideal gas law is not followed closely.
- The ideal gas law is a limiting law, valid only as $P \rightarrow 0$.
- All actual gases, which are called real gases, have properties that differ from those predicted by the ideal gas law.
- These differences are significant at high pressures and low temperatures.

Deviations from Ideality: Compressibility

- The presence of intermolecular forces can be detected by measuring the compression factor, Z.

$$Z = \frac{V_m}{V_m^{\text{ideal}}}$$

- Z = 1 for an ideal gas, so deviations from Z = 1 are a sign of nonideality.
- For most gases, at low pressures, the attractive forces are dominant and Z < 1.
- At high pressures, repulsive forces become dominant and Z > 1 for all gases.



Equations of State of Real Gases

- A common procedure to describe the behavior of real gases is to write the following expression

$$PV = nRT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^{\ 2}} + \dots\right)$$

- This expression is called the virial equation. The coefficients B, C, ... are called the second virial coefficient, third virial coefficient, and so on.
- However, the virial coefficients are not always known for each gas at a given temperature.

Equations of State of Real Gases

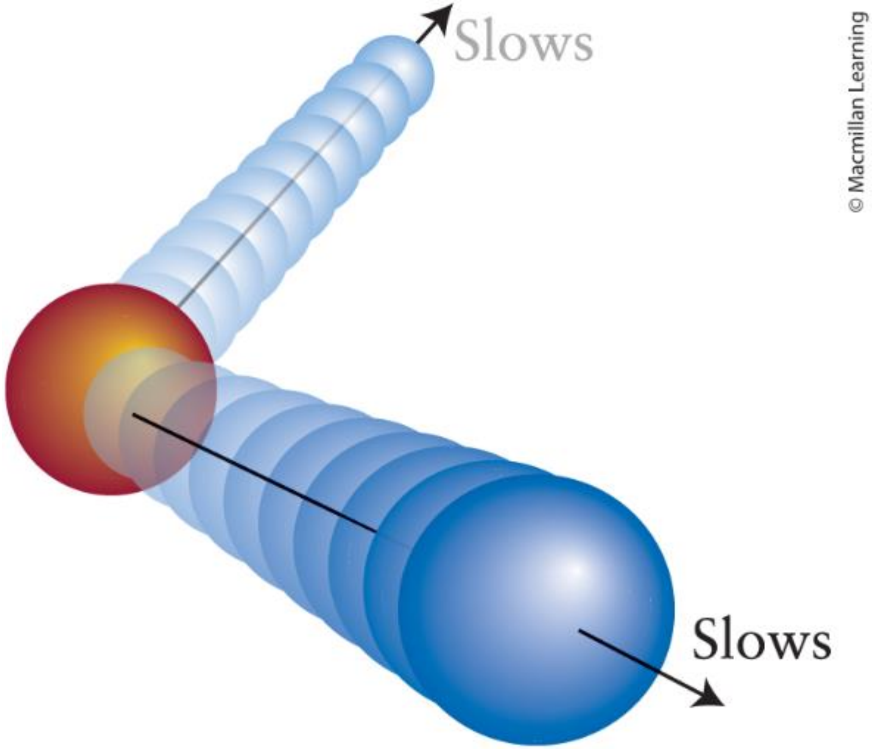
- So, a less accurate but more common form is used, the temperature-independent van der Waals equation:

$$\left(P + a\frac{n^2}{V^2}\right)\left(V - nb\right) = nRT$$

- (values for a and b are found experimentally, or, for well know molecules, in tables)
- Parameter “a” represents the attraction between molecules; the value is large for strongly attracting molecules.
- Parameter “b” represents the role of repulsions; it can be thought of as representing the volume.

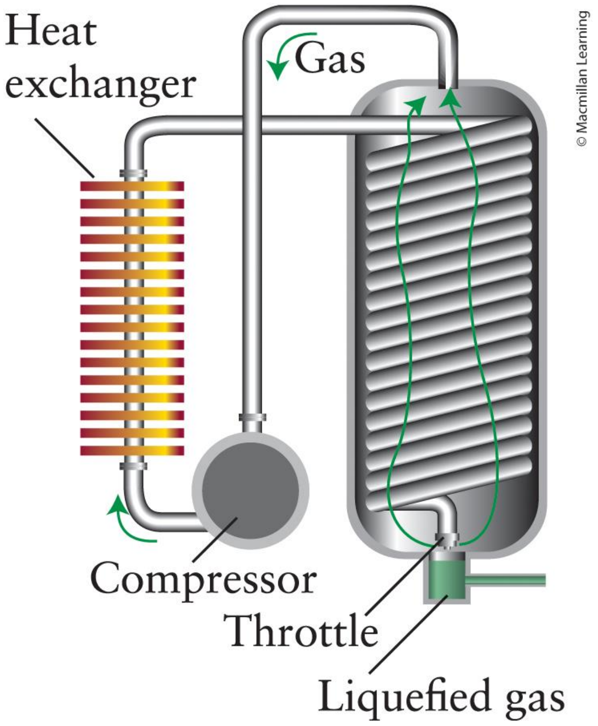
The Joule-Thomson Effect

- The Joule-Thomson effect is used in some commercial refrigerators to liquefy gases
- When molecules of a real gas climb away from one another's attractive forces (expand), they exert a force on one another just as a ball pulling away the surface of the Earth feels the gravitational pull.
- For real gases, attractive forces dominate, slowing the molecules average speed, and so they cool as they expand.
- The Joule-Thomson effect is named in honor of the scientists James Joule and William Thomson (later to become Lord Kelvin), who first observed this.



The Joule-Thomson Effect in Commercial Refrigerators

- The gas is compressed, then allowed to expand through a small hole, called the throttle.
- The gas cools as it expands, and the cooled gas circulates past the incoming compressed gas, cooling the incoming gas still further.
- The process continues and the temperature progressively falls until the gas finally condenses.
- This technique is used for harvesting nitrogen, oxygen, neon, argon, krypton, and xenon from the atmosphere.
- This will not work with H_2 or He, which are ideal and actually become warm.



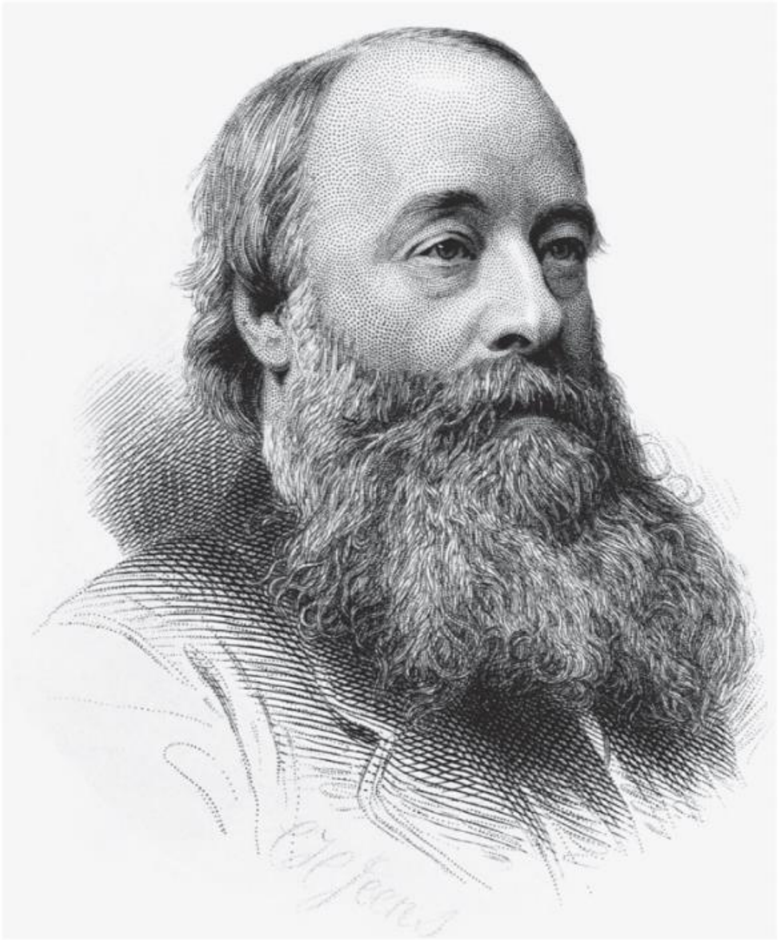
Introduction to Thermodynamics

- Thermodynamics studies the transformations of energy.
- The two fundamental parts of energy are work and heat.
- Work is the process of achieving motion against an opposing force.
- A transfer of energy that results in a temperature difference is heat.

Systems and Surroundings

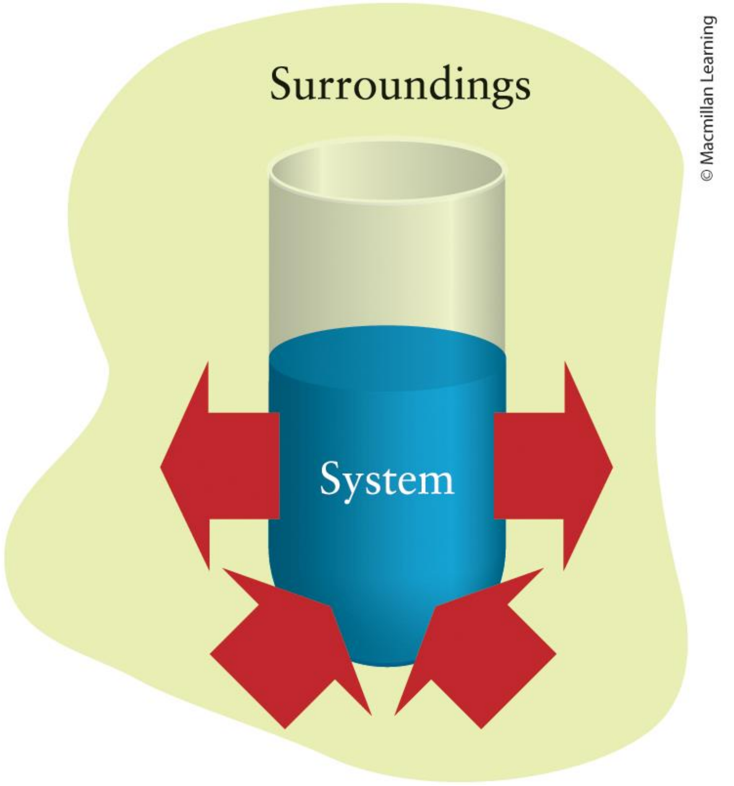
James Joule

- Heat was thought of as a material fluid, flowing from a hot to a cold substance.
- In the middle of the nineteenth century, James Joule, an English physicist, showed that heat and work are simply two ways in which energy can be transferred.



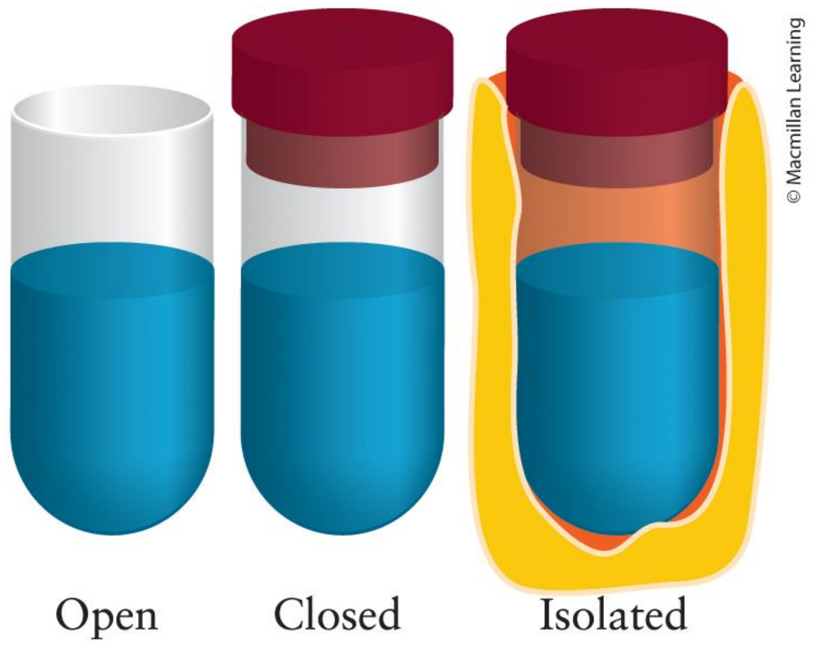
Systems and Surroundings

- In thermodynamics, the world is divided into two parts: the system and the surroundings.
- The system is the region of interest, such as a flask of gas, a reaction mixture, or a muscle fiber. The surroundings include everything else, such as a water bath in which a reaction mixture may be immersed.
- The system and the surroundings jointly make up the universe.



Open, Closed, and Isolated Systems

- An open system can exchange both matter and energy with the surroundings. (Examples: automobile engines and the human body.)
- A closed system has a fixed amount of matter, but it can exchange energy with the surroundings. (Example: a cold pack used to treat athletic injuries.)
- Isolated systems cannot exchange matter or energy with the surroundings. (Example: a sealed, insulated, rigid container like a thermos.)



Work and Energy

- The work required to move an object a certain distance against an opposing force is calculated from

  Work = opposing force × distance moved

- The unit for work (energy) is the joule, J, where $1\ J = 1\ kg \cdot m^2 \cdot s^{-2}$.
- Energy is the capacity of some system to do work.

Work and Energy

- If a system can do a lot of work, it has a lot of energy.
- A hot, compressed gas can do more work than the same gas after it has cooled and expanded. Therefore, it has more energy initially. A tightly wound spring can do more work than an unwound spring. Therefore, the would spring has more energy.
- Work is positive if energy is supplied to the system by doing work on it.
- Work is negative if energy is lost from the system by doing work on the surroundings.

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Types of Molecular Energy

- Gaseous molecules have three different types of energy.
- **Translational energy** is the energy of an atom or molecule due to its motion through space.
- **Rotational energy** is the energy of a molecule due to its rotational motion.
- **Vibrational energy** is the energy stored by a molecule as the oscillation of its atoms relative to one another.

Equipartition Theorem

- The equipartition theorem states that the average value of each quadratic contribution to the energy of a molecule in a sample at a temperature T is equal to ½kT.
- In the expression, k is Boltzmann's constant, which has a value of 1.381×10^{-23} $J \cdot K^{-1}$.

Internal Energy, U

- In thermodynamics, the total energy of a system is called internal energy, U.
- The molar internal energy, U_m, is the internal energy per mole of molecules in a sample. If the internal energy of a sample is U and the number of molecules (in moles) of a sample is n, then $U_m = U/n$.
- In thermodynamics, the symbol ΔX indicates $\Delta X = X_{final} - X_{initial}$.
- Therefore, a negative value of ΔX, as in $\Delta U = -15$ J, means that the value of X has decreased.

Internal Energy, U

- When work is done on a system, energy is transferred from the surroundings into the system. Since the system can do more work, the energy has increased. The energy transferred to a system as work is denoted w, so the change in internal energy is $\Delta U = w$.
- If +15 kJ of work is done on the system, its internal energy increases with $w = +15$ kJ and $\Delta U = +15$ kJ.
- If the system does 15 kJ of work, its internal energy decreases with $w = -15$ kJ and $\Delta U = -15$ kJ.

Heat

- Heat is the transfer of energy as a result of a temperature difference.
- Energy flows as heat from a high-temperature region to a low-temperature region.
- The energy transferred to a system from its surroundings as heat is denoted q.

Heat and Internal Energy

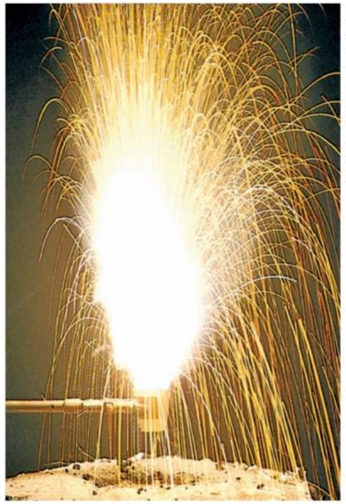
- When the internal energy changes of a system changes as a result of transferring energy as heat (without other processes such as compression taking place), $\Delta U = q$.
- If energy enters the system as heat, the internal energy increases, and q is positive. For example, if 10 J enters the system as heat, $q = +10$ J and $\Delta U = +10$ J.
- If energy leaves the system as heat, the internal energy decreases, and q is negative. For example, if 10 J leaves the system as heat, $q = -10$ J and $\Delta U = -10$ J.

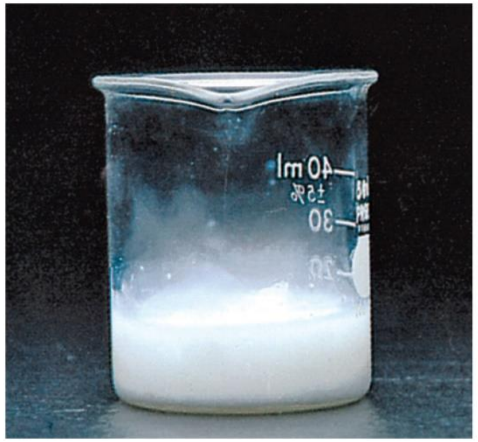
The Calorie

- Like work, the unit for heat is the joule, J. However, in biochemistry and related fields, the unit calorie (cal) is common.
- Originally, 1 cal was the energy needed to raise the temperature of 1 g of water by 1 °C.
- The modern definition is 1 cal = 4.184 J (exactly).
- The nutritional calorie, Cal, is 1 kilocalorie (kcal).

Endothermic and Exothermic Processes

- An exothermic process is a process that releases energy as heat into the surroundings. Combustion reactions are an example of exothermic processes.

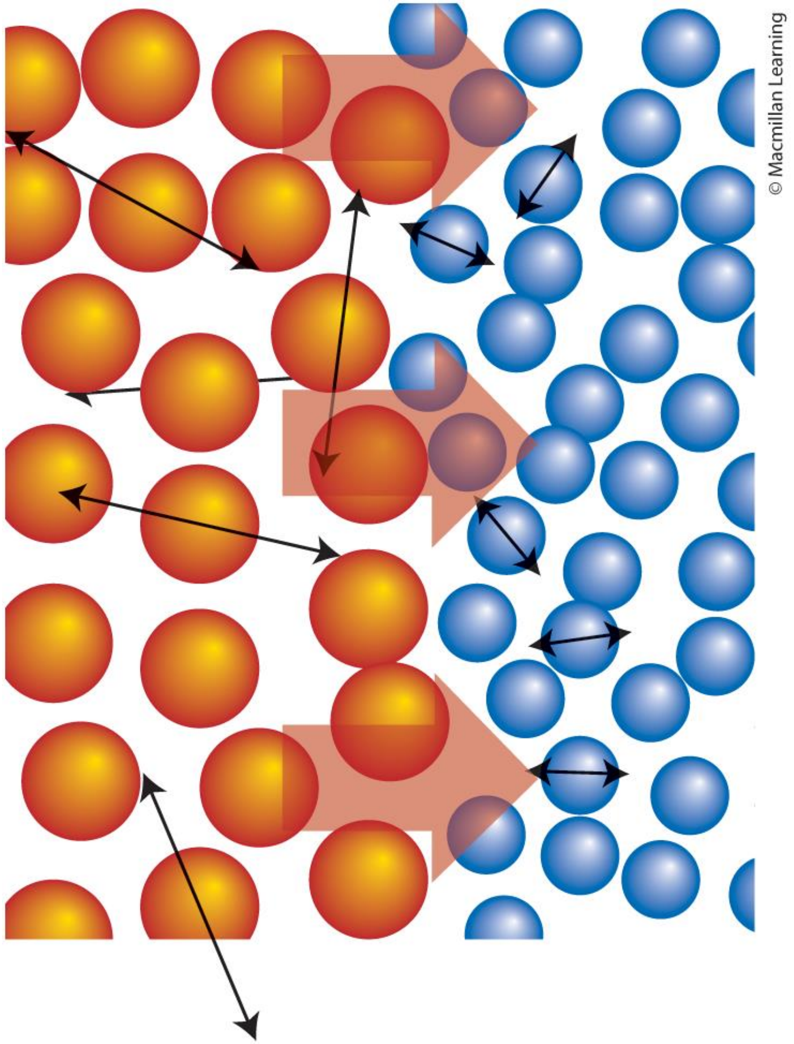




- An endothermic process is a process that absorbs heat from the surroundings. Vaporization is an example of an endothermic process.

Atomic View of Heat

- Energetic molecules in higher- temperature regions vigorously stimulate slower-moving molecules in the lower-temperature region into higher energetic states.
- The double-headed arrows represent the motion of some of the atoms. The large arrows represent the direction of heat transfer.



https://de.wikipedia.org/wiki/Joseph_Louis_Gay-Lussac

Joseph Louis Gay-Lusac (1778-1850)

First law of Thermodynamic

The First Law of Thermodynamics

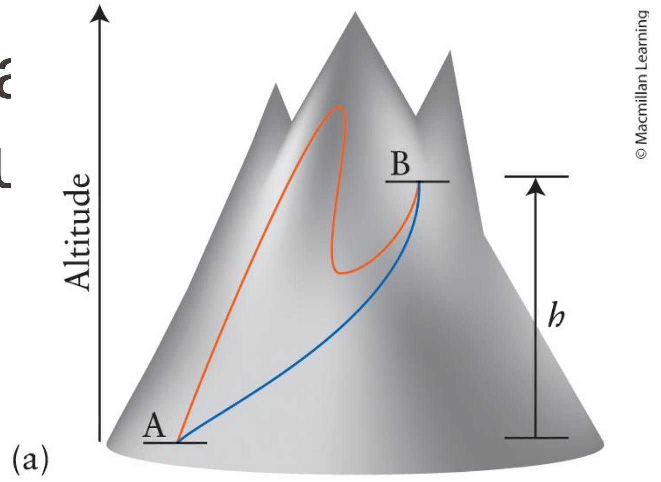
- So far, we have considered energy transfer as work or heat, separately.
- However, for a closed system, the change in internal energy, ΔU, is the sum of both kinds of energy transfer (heat and work).
- $\Delta U = q + w$
- The first law of thermodynamics states that the internal energy of an isolated system is constant. The first law of thermodynamics is closely related to the law of conservation of energy.

State Functions

- According to the first law of thermodynamics, if an isolated system has a certain internal energy at a certain point in time and then is inspected again later, it will be found to have exactly the same internal energy regardless of any changes it may go through, as long as it returns to its original state. Because of this, internal energy is a state function.
- A state function is a property that only depends on the system's current state and is independent on how that state was prepared.
- Other examples of state functions are pressure, volume, temperature, and density of a system.

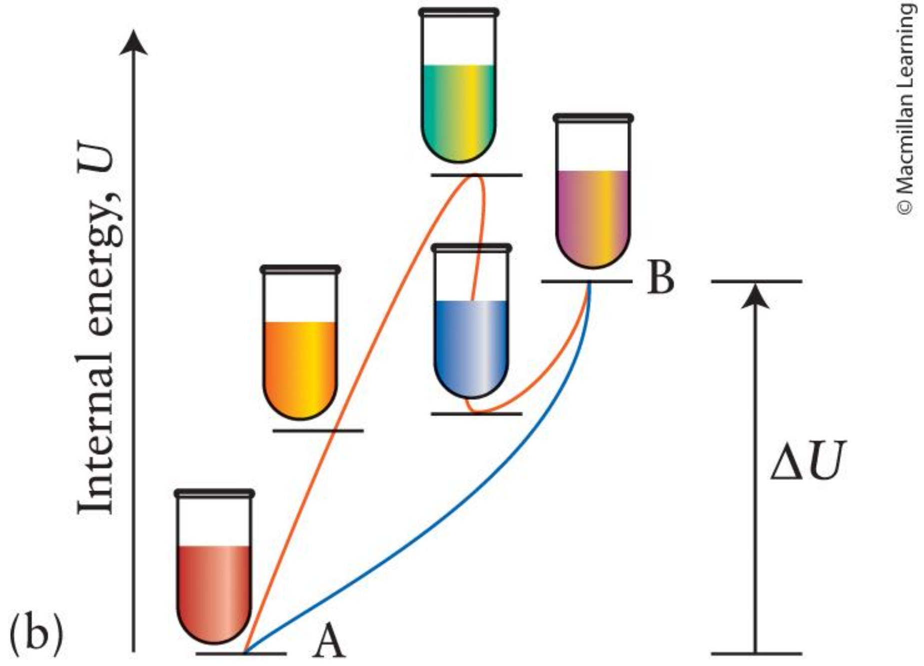
State Functions

- Since a state function depends only on the current state of the system, any change in its value depends only on its initial and final value and is independent of how the change occurred.
- A state function is like the altitude of a mounta any number of different paths between two hu mountain, but the change in altitude between same regardless of the path taken.



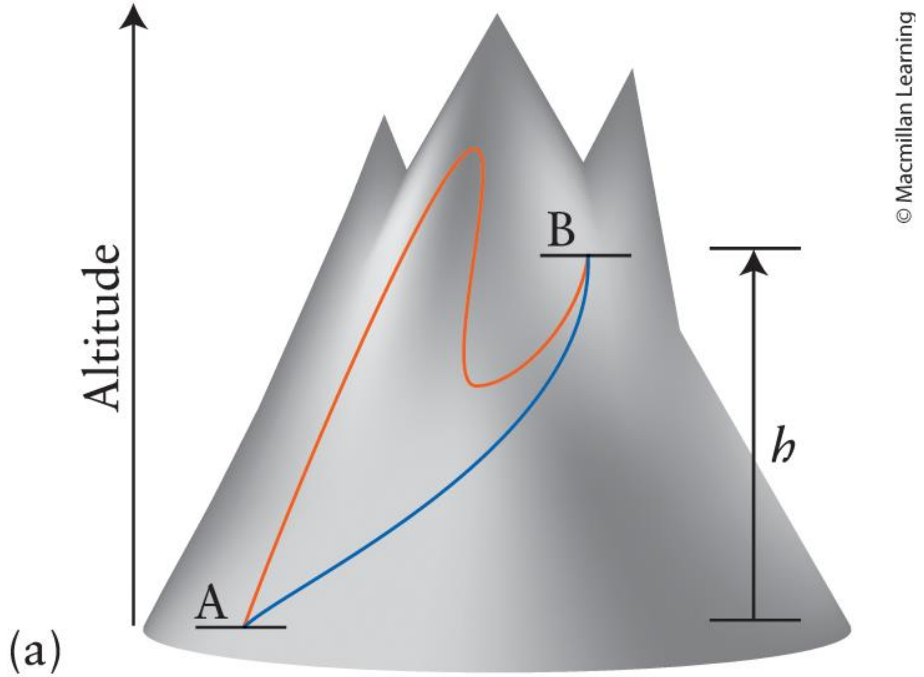
State Functions

- Internal energy is a state function.
- If a system changes from state A to state B in one step or in multiple steps, the net change in internal energy is the same. It does not matter the sequence of steps between the two states.



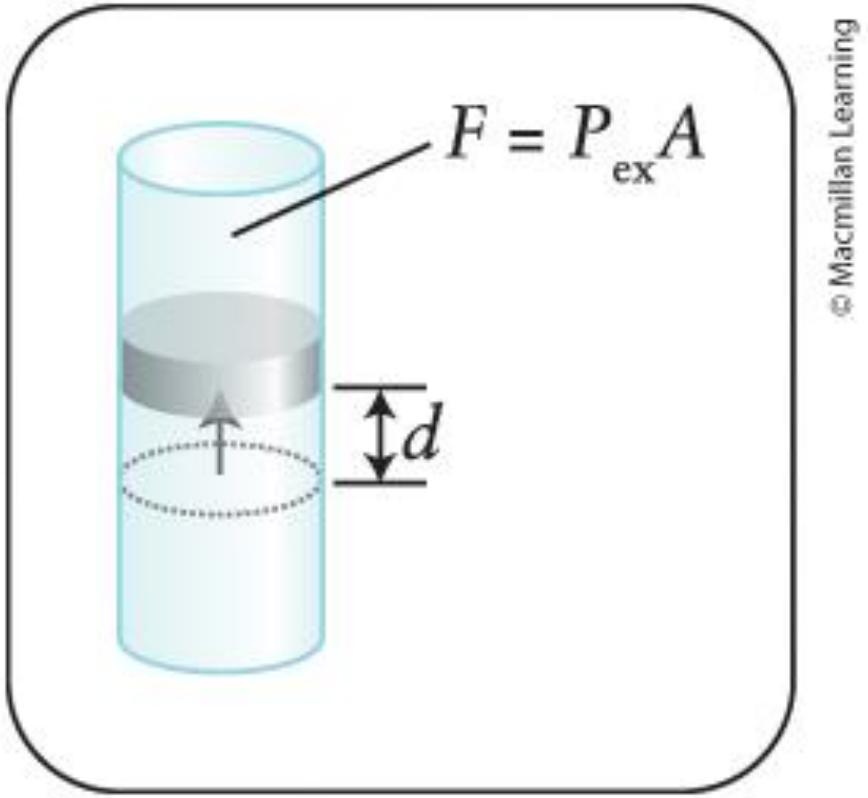
Path Functions

- The work done by a system is not a state function because it depends on how the change occurs. For example, the distance traveled between the two huts, A and B, is different even though the change in altitude is the same.
- Work (w) and heat (q) are path functions because the value is dependent on the path taken.



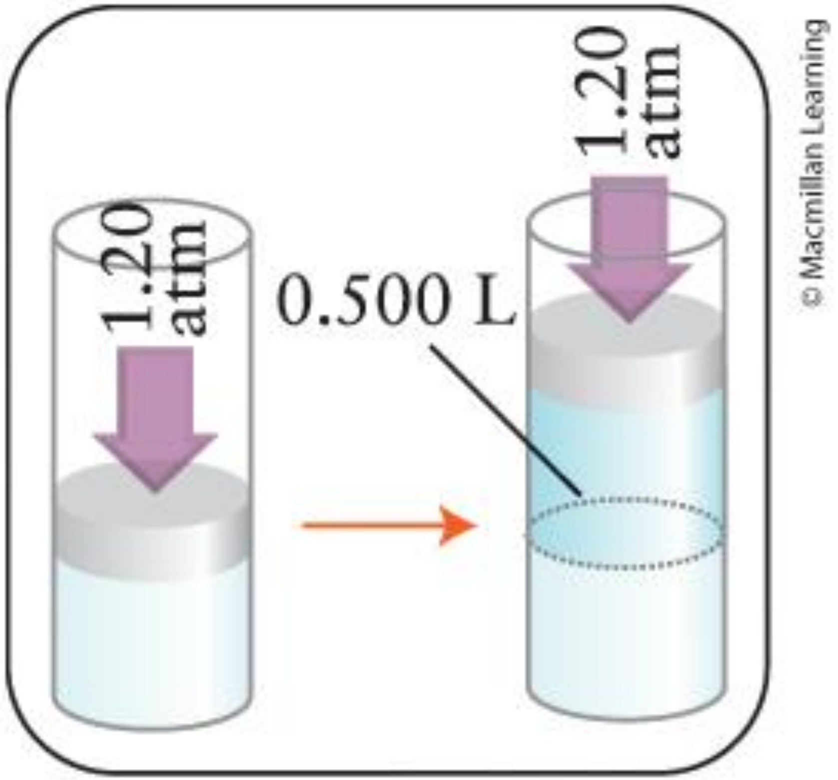
Categories of Work

- Expansion work is work arising from a change in volume of a system. Expansion work occurs when a gas expands in a cylinder, pushing back a piston which pushes out against the atmosphere.
- Nonexpansion work is work that does not involve a change in the system's volume. Chemical reactions do nonexpansion work by causing electrical current to flow.
- Table 4B.1 lists some of the kinds of work that a system can do.

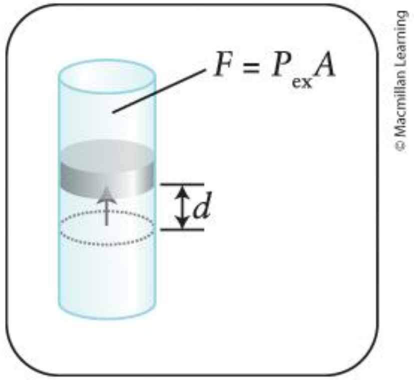


Expansion Work

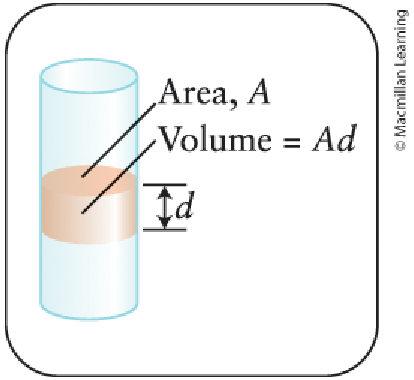
- Work = opposing force × distance moved
- The opposing force is the external pressure pushing against the outer face of the piston.
- How much expansion work is done is seen when the system expands, ΔV, against the external pressure P_{ex}.
- Work is done when the gas expands and the piston pushes against the opposing force (atmospheric pressure).



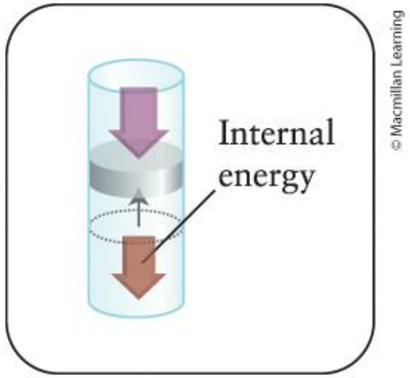
The Pressure—Work Relationship: Volume Expansion



$\text{work} = P_{ex}A \times d$



$A \times d = \Delta V$



$w = -P_{ex}\,\Delta V$

$\Delta U < 0$ when $\Delta V > 0$

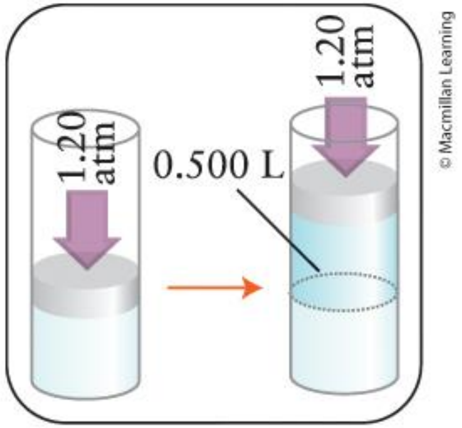
- The system does expansion work by pushing against the opposing pressure (force), so the system loses energy as work: ΔU is negative
- If ΔV is positive (an expansion), w is negative.
- If ΔV is negative (contraction), w is positive.

Free Expansion

- If the external pressure is zero (P_{ex} = 0, a vacuum), then w = 0. In other words, a system does no expansion work when it expands in a vacuum.
- There is no opposing force; therefore, no work is done by pushing if there is nothing to push against.
- Expansion against zero pressure is called free expansion.

Example: Expansion

Suppose a gas expands by 500. mL against the opposing force due to transmission, which is modelled as a pressure of 1.20 atm, and that no heat is exchanged with the surroundings during the expansion.
(a) How much work is done in the expansion?
(b) what is the change in internal energy of the system?

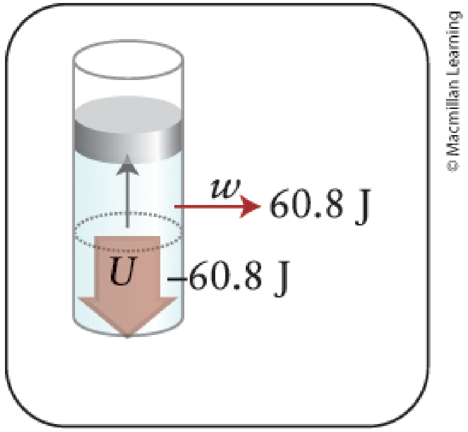


(a) $w = -P_{ex}\,\Delta V = -1.20\text{ atm} \times 0.500\text{ L} = -0.600\text{ L·atm}$

Convert to joules using 101.325 J = 1 L·atm.

$$-0.600\text{ L}\cdot\text{atm} \times \frac{101.325\text{ J}}{1\text{ L}\cdot\text{atm}} = -60.8\text{ J}$$

(b) Because no energy is transferred as heat, w = ΔU.



w = −60.8 J
ΔU = −60.8 J

Reversible and Irreversible Processes

- In thermodynamics, a reversible process is one that can be reversed by an infinitely small change in a variable (an “infinitesimal” change).
- An irreversible process is one that is not reversed by an infinitesimal change in a variable.

Reversible Isothermal Expansion

- The simplest reversible change is reversible isothermal expansion of an ideal gas. Expansion is carried out at constant temperature (isothermal) against an external pressure that is matched at all times by the pressure of the system.
- In isothermal expansion, the pressure of the gas falls as it expands. Therefore, to achieve reversible expansion, the external pressure must be reduced in step with the change in volume so that at every stage the external pressure is the same as the pressure of the gas.

Isothermal Work with Changing External Pressure

- The symbol for infinitesimal change is d (calculus) so small changes in volume is dV.
- Infinitesimal change in work is then $dw = -P_{ex}dV$.
- Matching external to the internal pressure, so $P = P_{ex}$ and $dw = -PdV$.
- Since PV = nRT we can substitute

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

Isothermal Work with Changing External Pressure

- For an ideal gas, PV = nRT, we can replace P:

$$dw = -P_{ex}dV$$

- The total work done is the sum (integral) of these infinitesimal contributions as the volume changes from its initial value V_1 to its final value V_2.

$$dw = -\frac{nRT}{V}dV$$

Isothermal Work with Changing External Pressure

- From w=∫dw, with nRT a constant:

$$w = -nRT \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = -nRT \ \mathrm{In} \frac{V_2}{V_1}$$

- The final step used the standard integral

$$\int \frac{\mathrm{d}x}{x} = \mathrm{In}\ x + \mathrm{constant}$$

- and then ln x – ln y = ln(x/y).

Isothermal Work with Changing External Pressure

- The result of this calculation shows that the work of reversible, isothermal expansion of an ideal gas from V_1 to V_2 is

$$w = -nRT\text{In}\frac{V_2}{V_1}$$

- where n is the amount of gas molecules (in moles) in the system and T is the absolute temperature (in kelvins).

Example: Irreversible vs. Reversible

A piston confines 0.100 mol Ar(g) in 1.00 L at 25 °C. Two experiments are performed.
(a) The gas is allowed to expand through an additional 1.00 L against a constant pressure of 1.00 atm. (b) The gas is allowed to expand reversibly and isothermally to the same final volume. Which process does more work?

- Irreversible path:

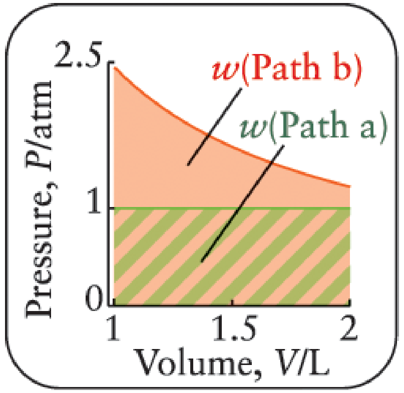
$w = -P_{ex}\Delta V$

$$w = -(1.00\ \text{atm}) \times (1.00\ \text{L}) = -1.00 \times 1.00\ \text{L} \cdot \text{atm} \times \frac{101.325\ \text{J}}{1\ \text{L} \cdot \text{atm}} = -101\ \text{J}$$

- Reversible isothermal path:

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

$$w = (-0.100\ \text{mol}) \times (8.3145\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \times (298\ \text{K}) \times \ln \frac{2.00\ \text{L}}{1.00\ \text{L}} = -172\ \text{J}$$



- The gas does more work in the reversible process.

Summary: Expansion and Work

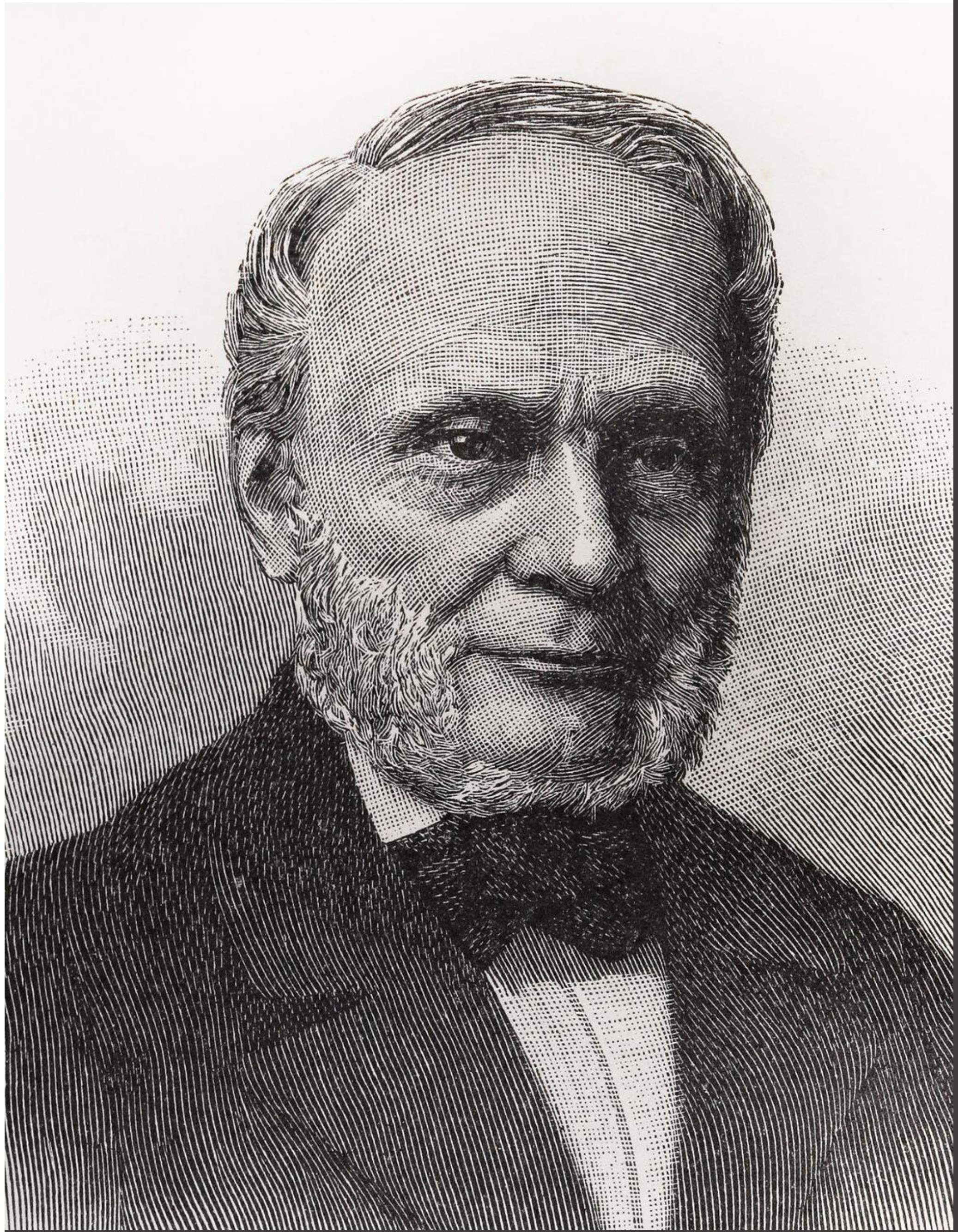
Two Ways to Calculate Work

1. For expansion against constant external pressure:

$$w = -P\Delta V$$

2. For reversible, isothermal expansion:

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



Rudolf Claudius (1822-1888)

https://www.britannica.com/science/first-law-of-thermodynamics

The Second Law of Thermodynamics

Measurement of Heat: Types of Boundaries

- There are two types of boundaries between systems and their surroundings.
- Adiabatic walls do not allow for the transfer of heat between a system and its surroundings, even if there is a temperature difference between the two. Adiabatic walls are insulating.
- Diathermic walls allow heat transfer between a system and its surroundings.

The Measurement of Heat: Heat Capacity

- Heat capacity, C, measures heat transferred (q), as energy to a system (or surroundings) to a corresponding change in temperature (ΔT):

$$\text{Heat capacity } (C) = \frac{\text{heat transferred}}{\text{change in temperature}} = \frac{q}{\Delta T}$$

$$q = C\Delta T$$

- A larger heat capacity produces only a slight temperature rise.
- Temperature is measured with a thermometer.

Specific Heat and Molar Heat Capacity

- The specific heat capacity, C_s, is the heat capacity divided by the mass of the sample.

$$C_s = \frac{C}{m}$$

- The molar heat capacity, C_m, is the heat capacity divided by the amount (in moles) of the sample.

$$C_m = \frac{C}{n}$$

- For water the specific heat is 4.18 $J \cdot (°C)^{-1} \cdot g^{-1}$ (or 4.18 $J \cdot K^{-1} \cdot g^{-1}$), and the molar heat capacity is 75 $J \cdot K^{-1} \cdot mol^{-1}$.

Specific Heat and Molar Heat Capacity

- If the mass, the specific heat capacity, and the temperature rise in the process are known, then the energy supplied as heat by the substance is

$$q = C\Delta T = mC_s\Delta T$$

- Similarly, the amount (in moles), the molar heat capacity, and the temperature rise in the process are known, then the energy supplied as heat by the substance is

$$q = C\Delta T = nC_m\Delta T$$

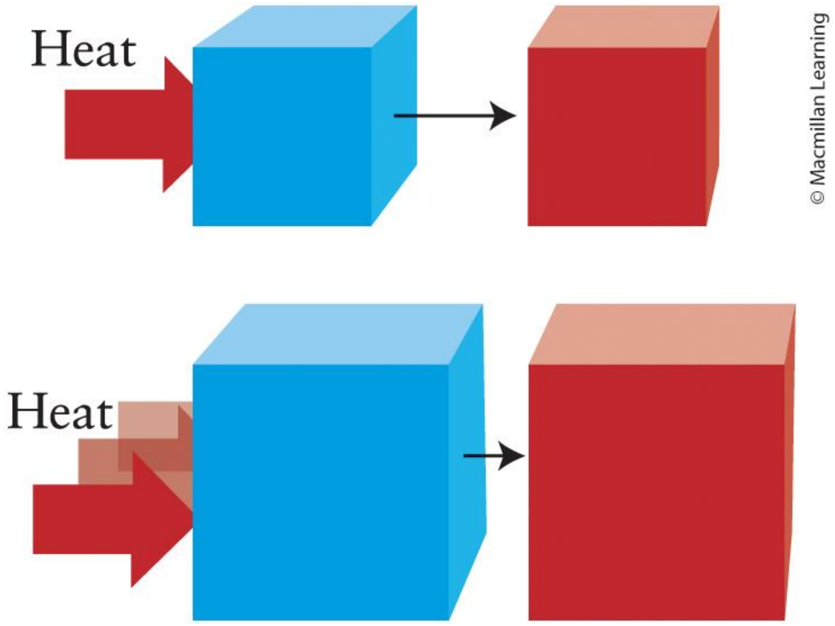
Heat Capacities of Selected Substances

Specific and Molar Heat Capacities of Common Materials

Material	Specific heat capacity, C_s ($J \cdot (°C)^{-1} \cdot g^{-1}$)	Molar heat capacity, C_m ($J \cdot K^{-1} \cdot mol^{-1}$)
air	1.01	–
benzene	1.74	136
brass	0.37	–
copper	0.38	24
ethanol	2.42	111
glass (Pyrex)	0.78	–
granite	0.80	–
marble	0.84	–
polyethylene	2.3	–
stainless steel	0.51	–
water: solid	2.03	37
liquid	4.184	75
vapor	2.01	34

Heat Capacity is an Extensive Property

- Heat capacity is an extensive property. For two objects made of the same material, the larger piece of the material has a greater heat capacity.
- This is why it is convenient to use specific heat capacity (C/m) and molar heat capacity (C/n) for particular substances.



Example Heat increase

Calculate the heat necessary to increase the temperature of
(a) 100. g of water and
(b) 2.00 mol $H_2O(l)$ from 20. °C to 100. °C .

- In each case the change in temperature (ΔT) is 80. °C (80. K).
- a) Use the equation for specific heat capacity:
  $q = C\Delta T = mC_s\Delta T$.

$$q = mC_s\Delta T = 100.\ \mathrm{g} \times 4.18\ \mathrm{J \cdot K^{-1} \cdot g^{-1}} \times 80.\ \mathrm{K}$$
$$= \ +33\ \mathrm{kJ}$$

- b) Use the equation for molar heat capacity: $q = nC_m\Delta T$.

$$q = nC_\mathrm{m}\Delta T = 2.00\ \mathrm{mol} \times 75\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \times 80.\ \mathrm{K}$$
$$= \ +12\ \mathrm{kJ}$$

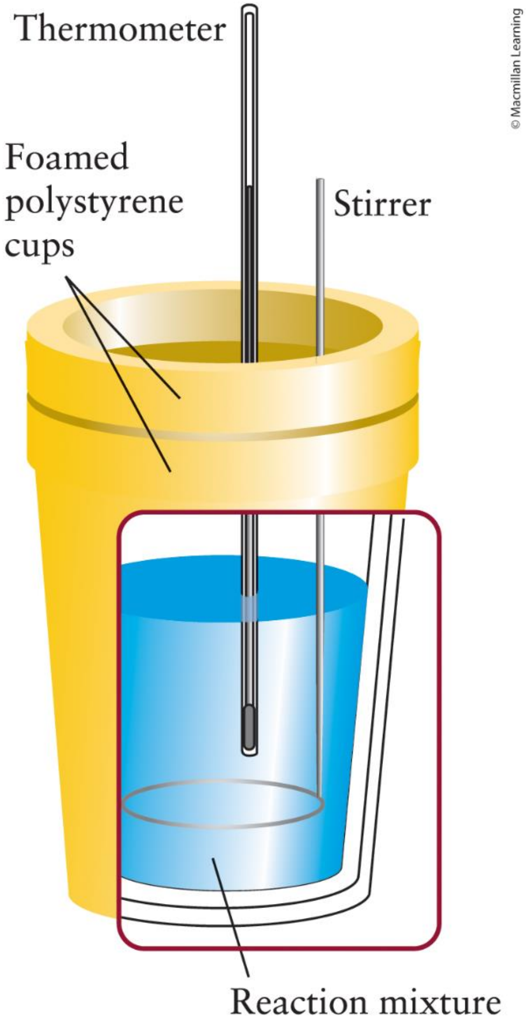
Temperature Change

- The temperature change, ΔT, is the same in degrees Celsius and in kelvins.
- $\Delta T(°C) = \Delta T(K)$
- For example, in the previous example, the temperature increased from 20. °C to 100. °C.
- $\Delta T(°C) = T_{final} - T_{initial} = 100.\ °C - 20.\ °C = 80.\ °C$
- Consider if the temperature is converted to kelvins.
- $\Delta T(K) = T_{final} - T_{initial} = (100.\ °C + 273) - (20.\ °C + 273) = 80.\ K$

➔The change in temperature in degrees Celsius is equivalent to the change in temperature in kelvins.

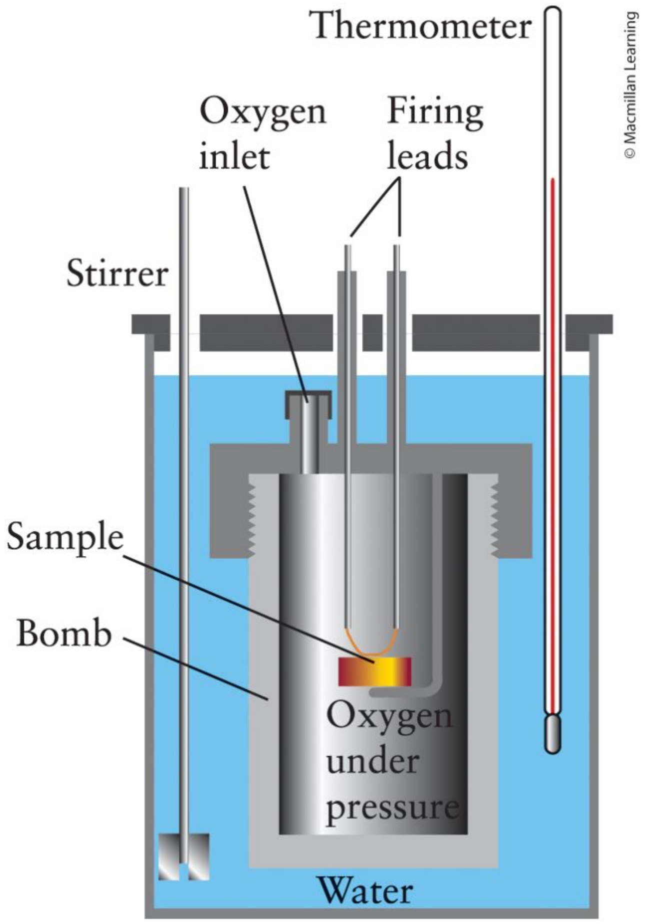
Calorimeters

- Transfers of energy as heat are often measured using a calorimeter, a device in which energy transferred as heat is monitored by recording the temperature change.
- A calorimeter has a known C_{cal}.
- When a sample is placed in the calorimeter, heat from the experiment goes into the calorimeter.
- ΔT of the calorimeter is the heat lost by the experiment into the calorimeter.
- By knowing information about the calorimeter and temperature changes, we can calculate $q = -C_{cal}\Delta T$, the heat from our experiment.



Calorimetry

- Calorimeters are calibrated with a known specific heat, usually water.
- The heat lost by a reaction is gained by the calorimeter.
- $-q = q_{cal}$
- The heat gained by the calorimeter is calculated using $q_{cal} = C_{cal}\Delta T$. When combined with $-q = q_{cal}$, the heat lost or gained by the reaction can be calculated using $q = -C_{cal}\Delta T$.



Example Calorimetry

- A constant-volume calorimeter was calibrated by carrying out a reaction known to release 1.78 kJ of heat in 0.100 L of solution in the calorimeter, resulting in a temperature rise of 3.65 °C.
  Next, 50.0 mL of 0.200 m HCl(aq) and 50.0 mL of 0.200 m NaOH(aq) were mixed in the same calorimeter and the temperature rose by 1.26 °C.
- What is the change in the internal energy of the neutralization reaction? (1 of 2)
- Calculate q_{cal} using the given heat released and the equation −q = qcal.
- $q_{cal} = -q = -(-1.78\ \text{kJ}) = +1.78\ \text{kJ}$
- Then, calculate Ccal using the equation $C_{cal} = q_{cal}/\Delta T$.

$$C_{\text{cal}} = \frac{1.78\ \text{kJ}}{3.65\ °\text{C}} = 0.488\ \text{kJ} \cdot °\text{C}^{-1}$$

Example Internal Energy

- A constant-volume calorimeter was calibrated by carrying out a reaction known to release 1.78 kJ of heat in 0.100 L of solution in the calorimeter, resulting in a temperature rise of 3.65 °C. Next, 50.0 mL of 0.200 m HCl(aq) and 50.0 mL of 0.200 m NaOH(aq) were mixed in the same calorimeter and the temperature rose by 1.26 °C. What is the change in the internal energy of the neutralization reaction?
- Here we notice the calorimeter's temperature rose by 1.26 °C.
- Next, we find the heat the sample generated. We do this by measuring the amount of heat that was absorbed by the calorimeter.
- $q = -C_{cal}\,\Delta T = -(0.488\ \text{kJ}\cdot{}^\circ\text{C}-1) \times (1.26\ {}^\circ\text{C}) = -0.614\ \text{kJ}$
- For our reaction, heat is leaving the reaction, so $q = \Delta U = -0.614$ kJ.

Measuring Changes in Internal Energy, ΔU

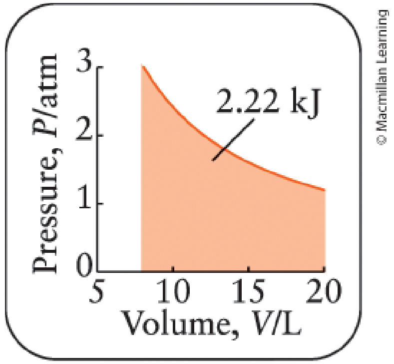
- For the isothermal expansion or compression of an ideal gas, there is no change in the total kinetic or potential energy of the gas molecules.
- Therefore, the internal energy of the gas is also unchanged.
- $\Delta U = 0$ for an isothermal gas expansion or compression

Measuring Changes in Internal Energy, ΔU

- In the next example, internal energy, $\Delta U = q + w$, is calculated by two different paths, both over the same range.
- One path calculates internal energy only reversibly.
- The other path is a combination of both reversible and irreversible.
- The biggest difference between the two is that for a reversible process, the temperature remains constant (isothermal).
- Also, remember that all isothermal expansions are the most efficient (though not common).

Example: Internal Energy

- Suppose that 1.00 mol of ideal gas molecules at an initial pressure of 3.00 atm and 292 K expands against a constant external pressure of 0.20 atm from 8.00 L to 20.00 L by two different paths. (a) Path A is an isothermal, reversible expansion. (b) Path B, a hypothetical alternative to path A, has two steps. In step 1, the gas is cooled at a constant volume until its pressure has fallen to 1.20 atm. In step 2, it is heated and allowed to expand against a constant pressure of 1.20 atm until its volume is 20.00 L and T = 292 K. Determine for each path the work done (w), the heat transferred (q), and the change in internal energy (ΔU).

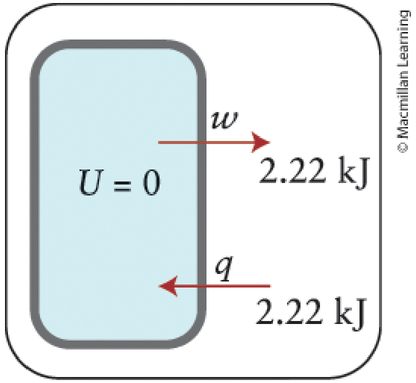


- (a) Path A is an isothermal, reversible expansion.

$$w = -nRT\text{In}\frac{V_2}{V_1}$$

$$w = -(1.00\ \text{mol}) \times (8.3145\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \times \left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right) \times (292\ \text{K}) \times \ln\frac{20.00\ \text{L}}{8.0\ \text{L}}$$

$$= -2.22\ \text{kJ}$$



- And from ΔU = q + w = 0, q = −w = +2.22 kJ

Example: Internal Energy

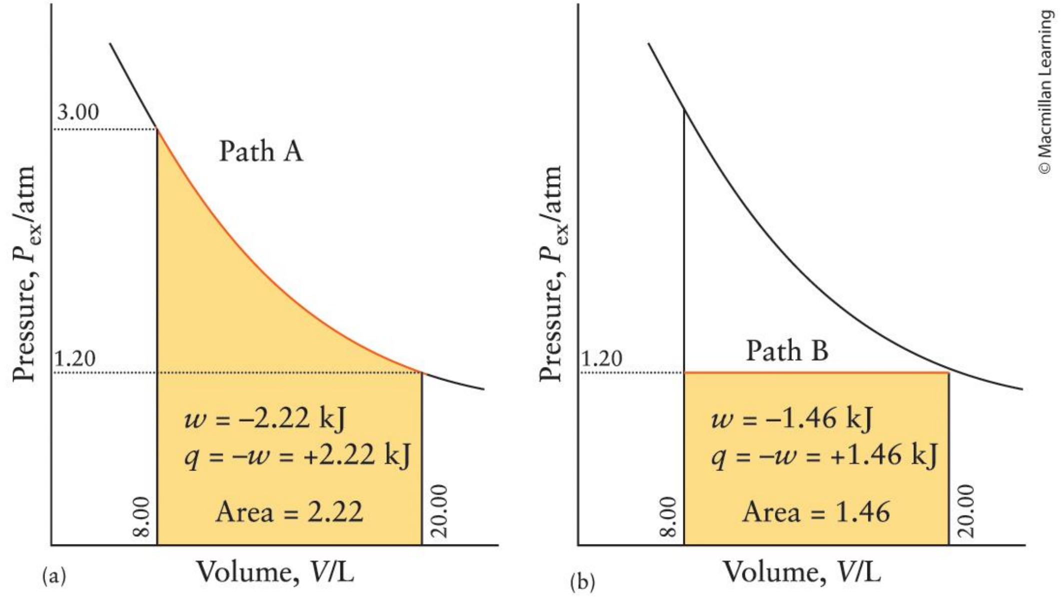
- Path B: $\Delta U = q + w$
- Step 1 work: cooling at constant V, no work or $w = 0$
- Step 2 work: $w = -P_{ex}\Delta V$ where $\Delta V = (20.00 - 8.00\ )L = 12.00\ L$

$$w = -P_{ex}\Delta V = \ -1.20\ \text{atm} \times 12.00\ \text{L} \times \frac{101.323\ \text{J}}{1\ \text{L}\cdot\text{atm}} = -1.46\ \text{kJ}$$

- Step 1 + Step 2: $w = 0 + -1.46\ kJ\ = -1.46\ kJ$
- $\Delta U = q + w$, note that for an isothermal expansion $\Delta U = 0$ (same as in in Part A).
- $0 = q + w$ or $q = -w$ so here $q = -(-1.46\ kJ) = +1.46\ kJ$

Example: Internal Energy

- Path A: since ΔU = 0, heat flows to maintain constant temperature and constant internal energy.
- Path B: overall, the outflow of heat in the cooling step combined with the work done corresponding to the area under the curve is less than Path A.
- ΔU = 0 for both
- Isothermal, reversible does more work, +2.22 kJ.
- Nonreversible does less work, +1.46 kJ.



EPFL

Enthalpy

- In a chemistry lab, many reactions are done in open containers, under nonexpansion ($\Delta V = 0$) work conditions at a constant pressure of 1 atm.
- $\Delta U = q + w$, and for nonexpansion work $w = 0$
- So at constant volume, $\Delta U = q + w$
- $\Delta U = q$
- In this case, energy supplied is strictly heat, q only.

Enthalpy

- Gases are free to expand (or contract), but they are working against the atmosphere, which is acting as the opposing force in a piston.
- So, for chemists, we must use another state function to keep track of our energy at constant pressure.

Enthalpy: Heat Transfers at Constant Pressure

- The new state function is called enthalpy, H:
- $H = U + PV$
- U, P, and V are the internal energy, pressure, and volume of the system.
- Enthalpy is a state function because U (from the first law), P, and V are also state functions.
- Constant pressure means the system is open, and the work is pushing against the atmosphere; that is, the constant pressure is the constant pressure of the atmosphere.

Enthalpy: Heat Transfers at Constant Pressure

- It follows from enthalpy, $H = U + PV$, that changes at constant pressure are expressed as: $\Delta H = \Delta U + P\Delta V$.
- We substitute for $\Delta U = q + w$ to get $\Delta H = q + w + P\Delta V$.
- For a system doing expansion work only, we substitute for
- $w = -P_{ex}\Delta V$ to get:
- $\Delta H = q - P_{ex}\Delta V + P\Delta V$

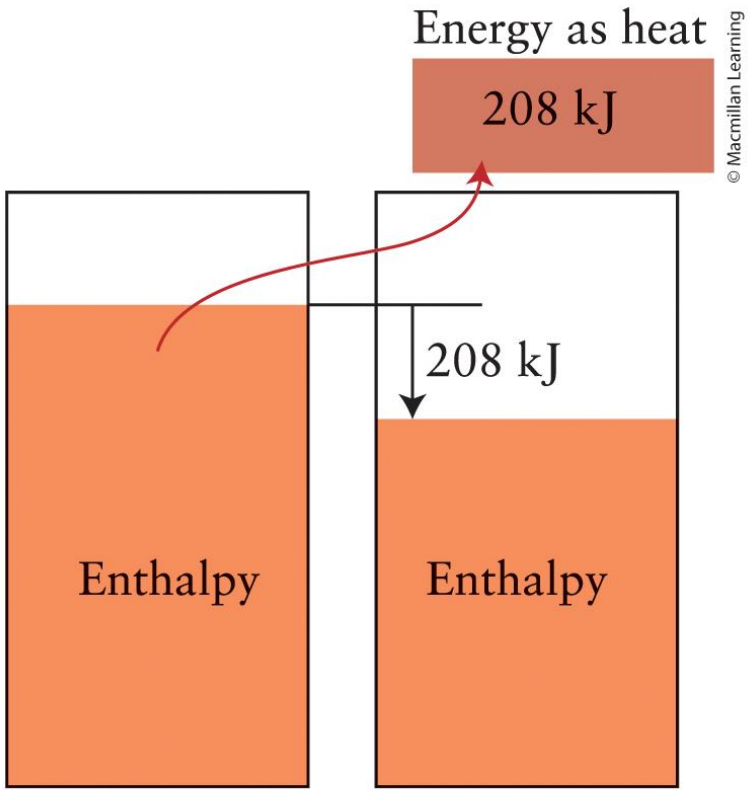
Enthalpy: Heat Transfers at Constant Pressure

- $\Delta H = q - P_{ex}\,\Delta V + P\Delta V$
- Now, if we leave our system open to the atmosphere, the pressure of the system is the same as the external pressure, so $P_{ex} = P$, and $\Delta H = q + -P\Delta V + P\Delta V$. The last two terms cancel to give us:
- $\Delta H = q$ (constant pressure)
- Previously: $\Delta U = q$ (constant volume)

Enthalpy: $\Delta H = q$

- For a chemical reaction open to the atmosphere, or at constant pressure, the heat released or required is the enthalpy of the system.
- We note that:
- $\Delta H < 0$ for exothermic reactions
- $\Delta H > 0$ for endothermic reactions
- Note: We have ΔH, and this follows the first law even though there is no work term. Remember that ΔH is a constant pressure (open to the atmosphere) scenario.

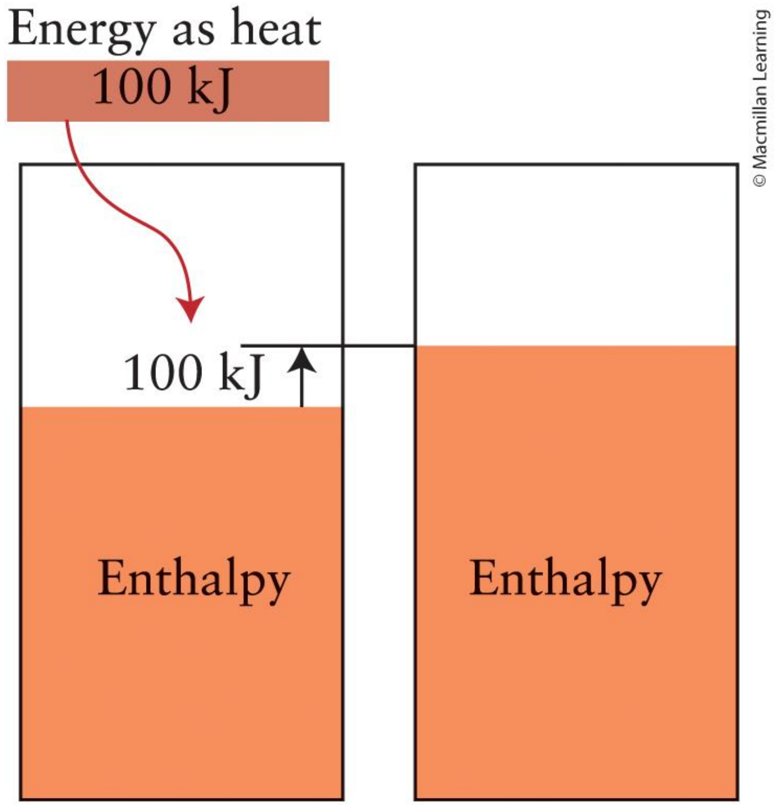
Enthalpy: ΔH = q



The enthalpy of a system is like a measure of the height of water in a reservoir. When a reaction releases 208 kJ of heat at constant pressure, the "reservoir" falls by 208 kJ and Δ*H* = −208 kJ.

Enthalpy: ΔH = q

- If an endothermic reaction absorbs 100 kJ of heat at constant pressure, the height of the enthalpy “reservoir” rises by 100 kJ and ΔH = +100 kJ.



endothermic reactions

Heat Capacities at Constant Volume and Constant Pressure

- Our definition of heat capacity is q = CΔT.

At constant volume: $\Delta U = q$

$$C_V = \frac{\Delta U}{\Delta T}$$

At constant pressure: $\Delta H = q$

$$C_P = \frac{\Delta H}{\Delta T}$$

- For an ideal gas, the PV in the definition of enthalpy, $H = U + PV$, can be replaced by nRT, and so $H = U + nRT$.

$$C_P = \frac{\Delta H}{\Delta T} = \frac{\Delta U + nR\Delta T}{\Delta T} = \frac{\Delta U}{\Delta T} + nR = C_V + nR$$

- For molar heat capacity $C_{P,\mathrm{m}} = C_{V,\mathrm{m}} + R$

The Origin of the Heat Capacities of Gases

- Heat capacities are helpful to find the internal energy of at different temperatures: $C_{P,m} = C_{V,m} + R$.
- Monoatomic Gas:
  - $(3/2)RT$ is the molar internal energy for a monoatomic ideal gas. Therefore, the change in molar internal energy, ΔU_m, is

$$\Delta U_\mathrm{m} = \frac{3}{2} R\Delta T$$

$$C_{V,\mathrm{m}} = \frac{\Delta U_\mathrm{m}}{\Delta T} = \frac{\frac{3}{2}R\Delta T}{\Delta T} = \frac{3}{2}R$$

  - From $C_{P,m} = C_{V,m} + R$, we get

$$C_{P,\mathrm{m}} = \frac{3}{2}R + R = \frac{5}{2}R$$

The Origin of the Heat Capacities of Gases

- Linear molecules:

$$C_{V,\mathrm{m}} = \frac{\frac{3}{2}R\Delta T + R\Delta T}{\Delta T} = \frac{5}{2}R$$

$$C_{P,\mathrm{m}} = \frac{5}{2}R + R = \frac{7}{2}R$$

- Nonlinear molecules:

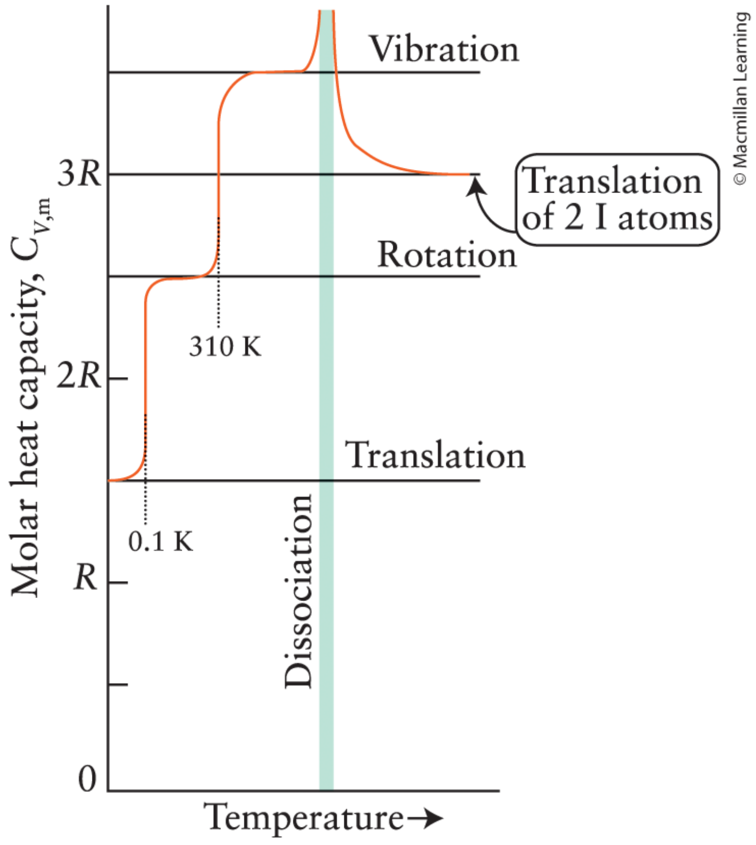
$$C_{V,\mathrm{m}} = \frac{\frac{3}{2}R\Delta T + \frac{3}{2}R\Delta T}{\Delta T} = 3R$$

$$C_{P,\mathrm{m}} = 3R + R = 4R$$

	Atoms	Linear Molecules	Nonlinear Molecules
$C_{V,\mathrm{m}}$	(3/2)R	(5/2)R	3R
$C_{P,\mathrm{m}}$	(5/2)R	(7/2)R	4R

The Origin of the Heat Capacities of Gases

- Variation in the molar heat capacity for molecular iodine, I_2.
- The translational motion contributes to the heat capacity at very low temperatures.
- Vibrational energy contributes only at high temperatures (above about 310 K).
- At dissociation, the heat capacity becomes very large.



The Enthalpy of Physical Change

- A phase of matter indicates how far apart molecules are.
- A phase change in which the attractions between molecules decrease, such as melting or vaporization, requires energy and is endothermic. A phase change in which the attractions between molecules increase, such as condensation or freezing, is exothermic.
- Phase changes usually take place at constant pressure; the heat transfer is due to changes in enthalpy.

Enthalpy of Vaporization, Δ_{Hvap}

- Vaporization is the transition of a liquid to a gas. The difference in molar enthalpy between the vapor and liquid states is called the enthalpy of vaporization, ΔH_{vap}.
- $\Delta H_{vap} = H_m(\text{vapor}) - H_m(\text{liquid})$
- For water at its boiling point, 100 °C, ΔH_{vap} = 40.7 kJ·mol^{-1}, and at 25 °C the value is ΔH_{vap} = 44.0 kJ·mol^{-1}.
- This means that vaporizing 1.00 mol H_2O(l) (18.02 g of water) at 25 °C and constant pressure requires 44.0 kJ of energy as heat.

Intermolecular Forces and ΔH_{vap}

- All enthalpies of vaporization are positive. Substances with stronger intermolecular forces, such as hydrogen bonds*, have the highest enthalpies of vaporization and deeper potential energy plots.

Substance	Formula	Freezing/Boiling Points (K)	$\Delta H_{fus}°/\Delta H_{vap}°$
Argon	Ar	83.8/87.3	1.2/6.5
Methane	CH_4	90.7/112	0.94/8.2
Acetone	CH_3COCH_3	178/329	5.72/29.1
Methanol*	CH_3OH	175/338	3.16/35.3
Ammonia*	NH_3	195/240	5.65/23.4
Water*	H_2O	273/373	6.01/40.7

Enthalpy of Fusion, ΔH_{fus}

- Melting (fusion) is the transition of a solid to a liquid. The molar enthalpy change that accompanies melting is called the enthalpy of fusion, ΔH_{fus}.
- $\Delta H_{fus} = H_m(\text{liquid}) - H_m(\text{solid})$

- The enthalpy of fusion of water at 0.0 °C is 6.0 $kJ \cdot mol^{-1}$: to melt 1.0 mol H_2O (s) (18 g of ice) at 0.0 °C, we have to supply 6.0 kJ of heat.
- Vaporizing water takes much more energy (more than 40 kJ) than melting because to vaporize a gas, its molecules are separated completely, and its KE increases dramatically. In melting, the molecules stay close together, so the forces of attraction and repulsion are nearly as strong as in the solid.

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Enthalpy of Freezing

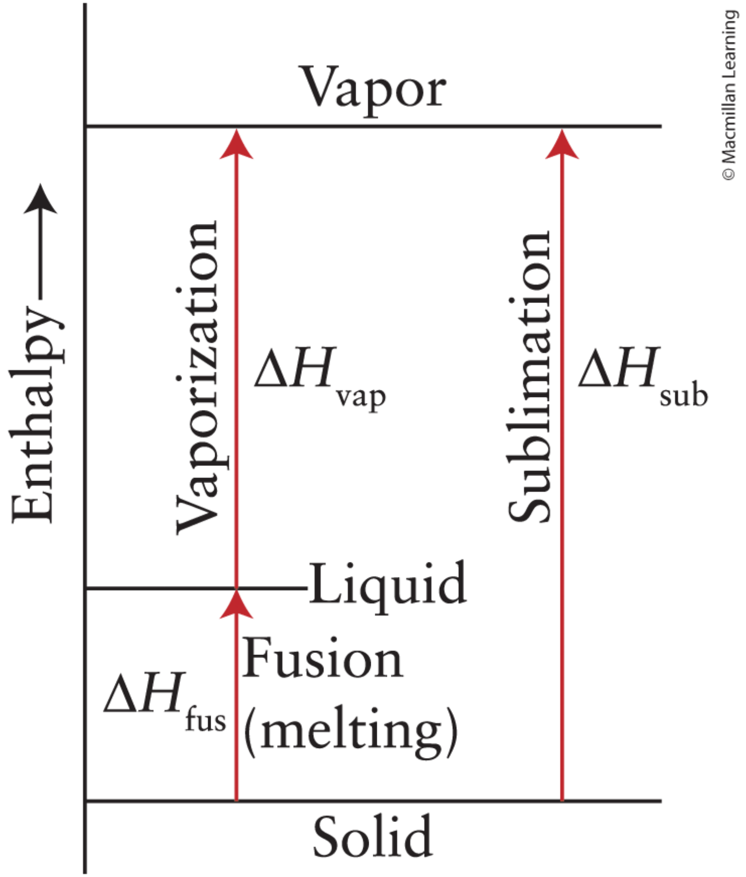
- Freezing is the change from liquid to solid.

- Because enthalpy is a state function, the enthalpy of freezing a substance is the negative of its enthalpy of fusion.
- $\Delta H_{\text{reverse process}} = -\Delta H_{\text{forward process}}$

- The enthalpy of fusion of water at 0.0 °C is +6.0 $kJ{\cdot}mol^{-1}$, so the enthalpy of freezing for water at 0.0 °C is −6.0 $kJ{\cdot}mol^{-1}$.

Enthalpy of Sublimation, ΔHsub (1 of 2)

- Sublimation is the direct conversion of a solid into its vapor. The enthalpy of sublimation, ΔH_{sub}, is the molar enthalpy change when a solid sublimes.
- $\Delta H_{sub} = H_m(\text{vapor}) - H_m(\text{solid})$
- Frost disappears on a cold, dry morning as the ice sublimes directly into water vapor. Solid carbon dioxide also sublimes, which is why it is called “dry ice.”



Enthalpy of Sublimation, ΔHsub

- Since enthalpy is a state function, the enthalpy of sublimation of a substance is the same whether the transition takes place in one step, directly from solid to gas, or takes place in two steps, first from solid to liquid and then from liquid to gas.

- The enthalpy of sublimation of a substance must therefore be equal to the sum of the enthalpies of fusion and vaporization.

- $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$