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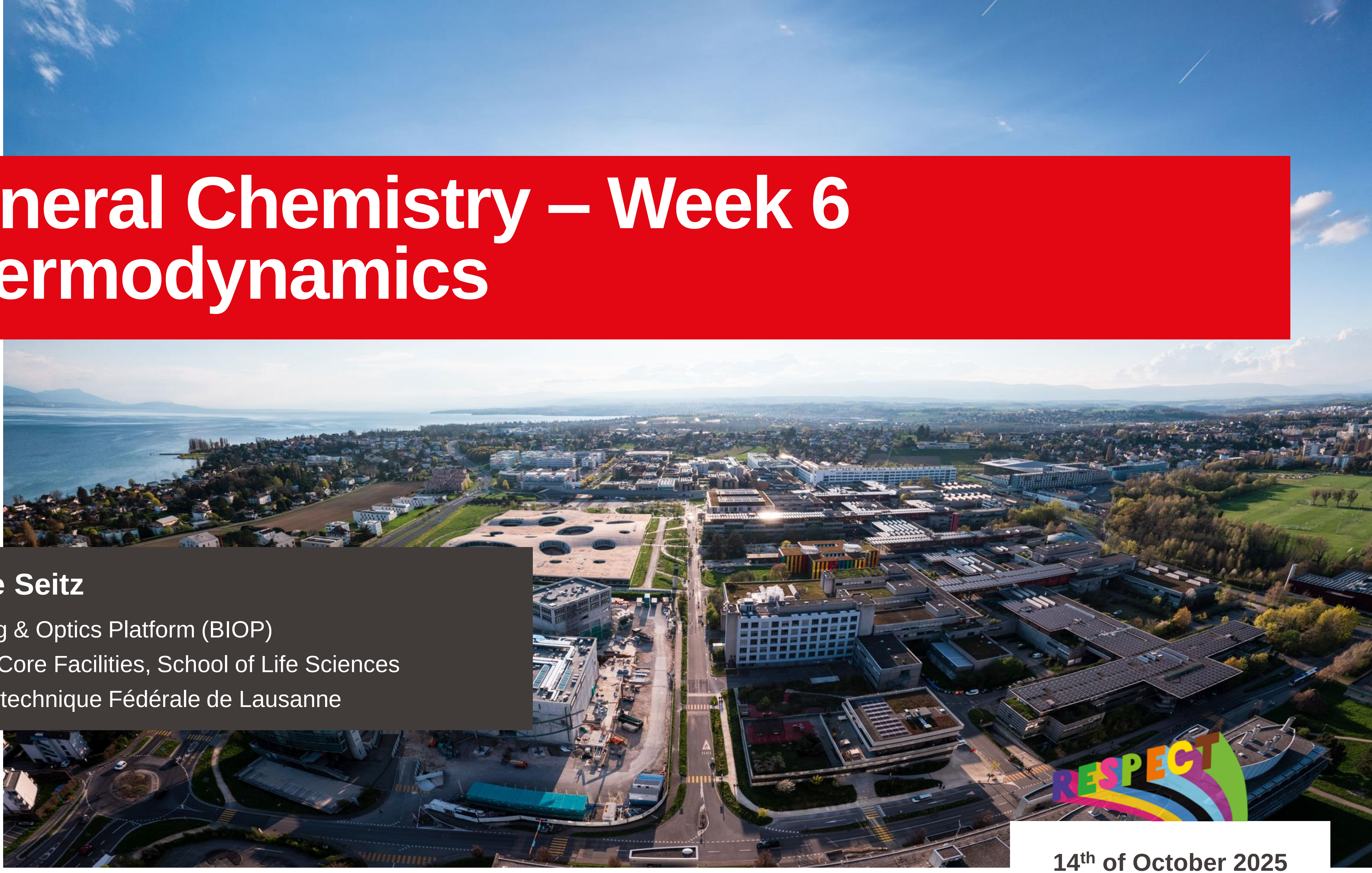

General Chemistry – Week 6
Thermodynamics

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RESPECT

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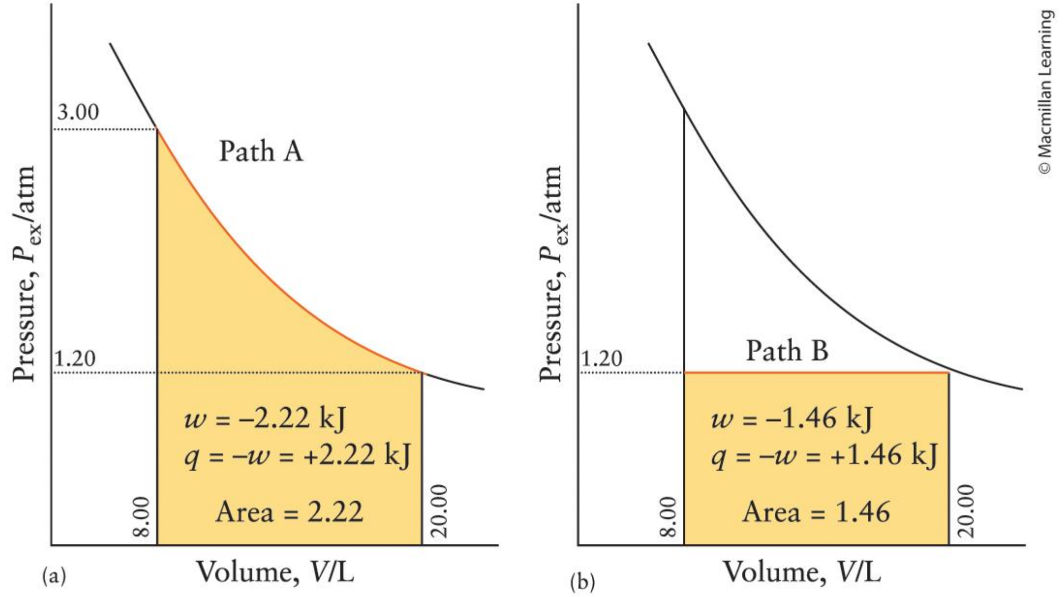
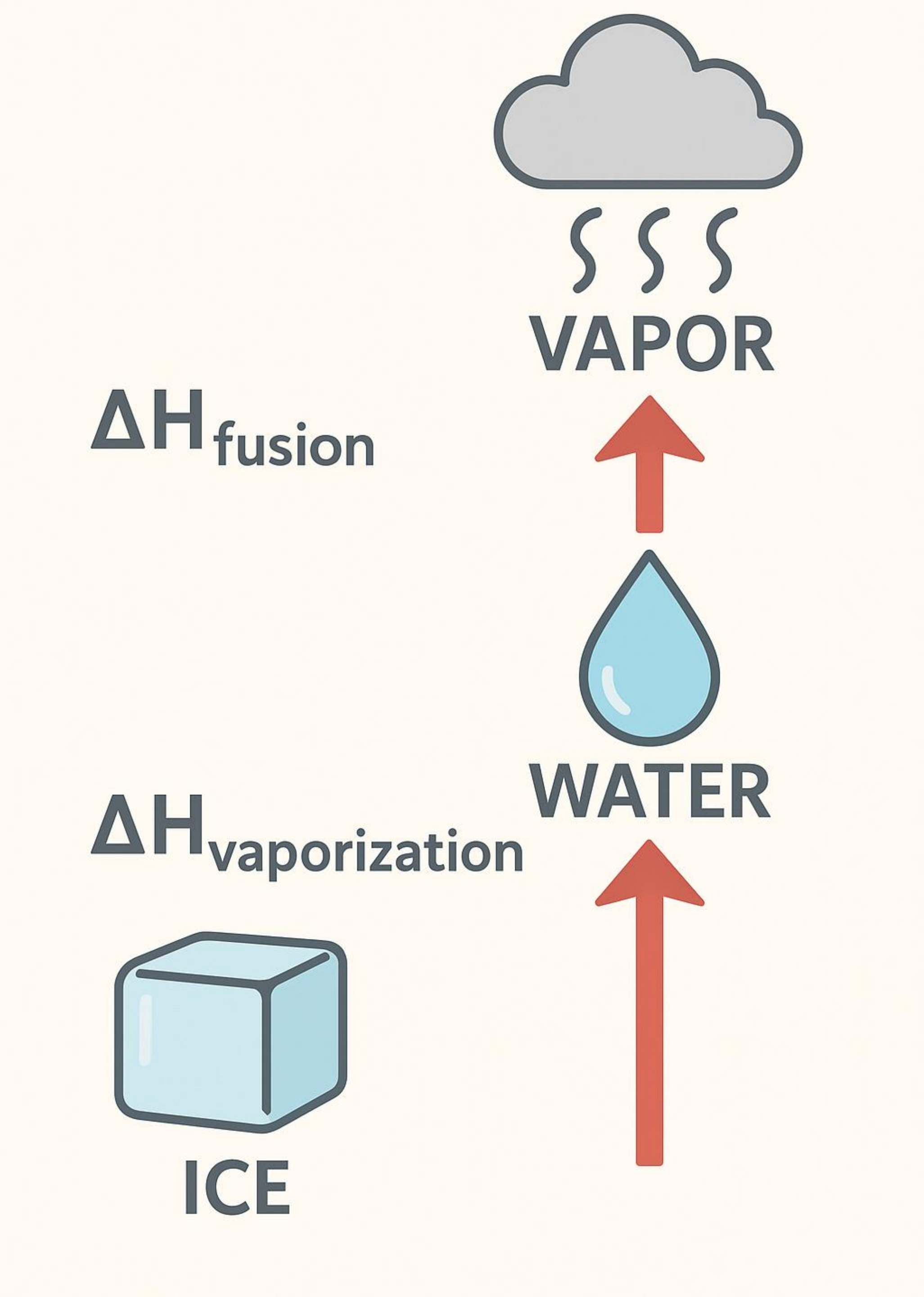
Recap last week

Thermodynamics

- Heat and work are different forms of energy transfer, but they are interconvertible under the First Law of Thermodynamics.
- Internal energy (U) is a state function.
- Expansion work (path function) can be done reversibly or irreversibly.
- Heat capacity





Enthalpy

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:
- $\Delta H = q - P_{ex}\Delta V + P\Delta V$

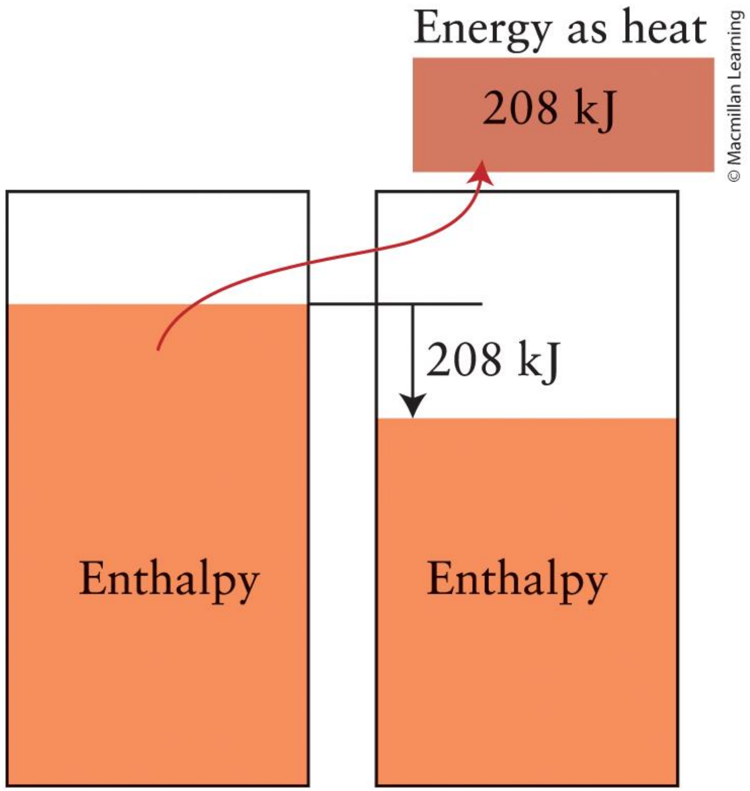
Enthalpy: Heat Transfers at Constant Pressure

- $\Delta H = q - P_{ex}\,\Delta V + P\Delta V$
- 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.

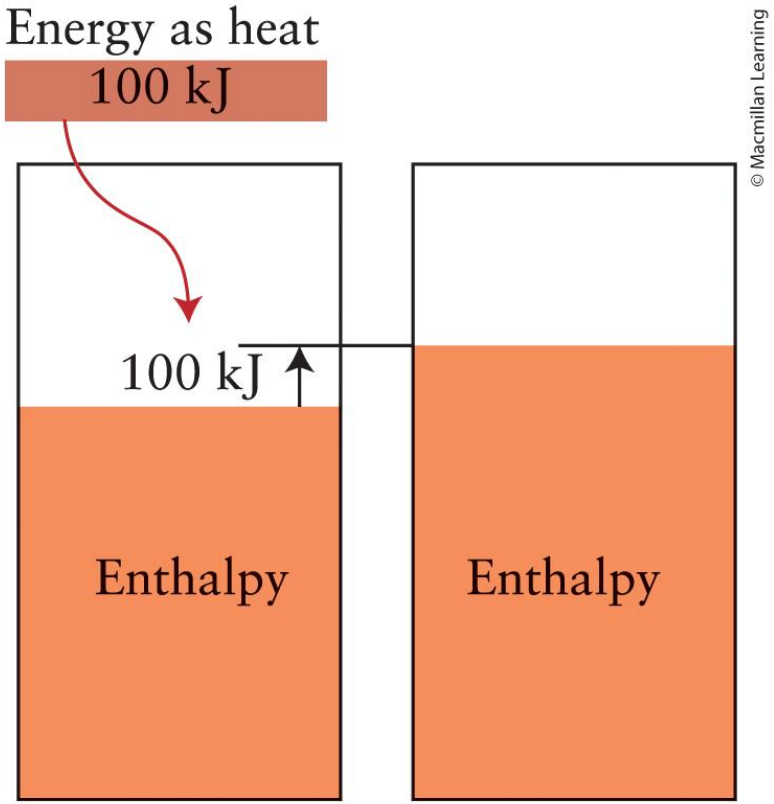
Enthalpy: ΔH = q



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 $\Delta H = -208$ 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:

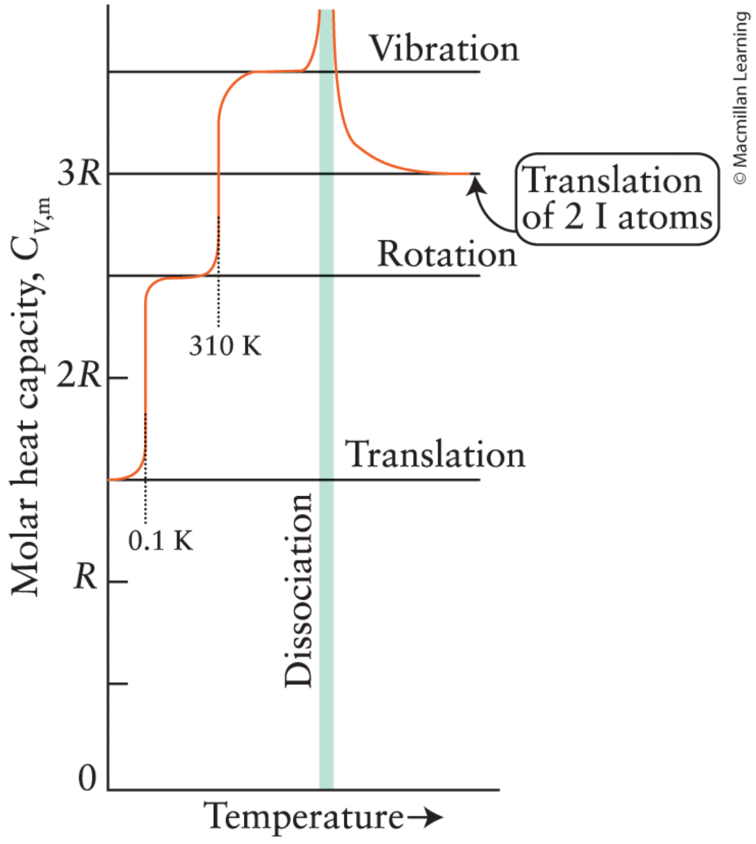
$$C_{V,\mathrm{m}} = \frac{\frac{3}{2}R\Delta T + \frac{3}{2}R\Delta T}{\Delta T} = 3R$$

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

	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, $\Delta H_{vap} = 40.7\ \text{kJ}\cdot\text{mol}^{-1}$, and at 25 °C the value is $\Delta H_{vap} = 44.0\ \text{kJ}\cdot\text{mol}^{-1}$.
- 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.

Enthalpy of Freezing

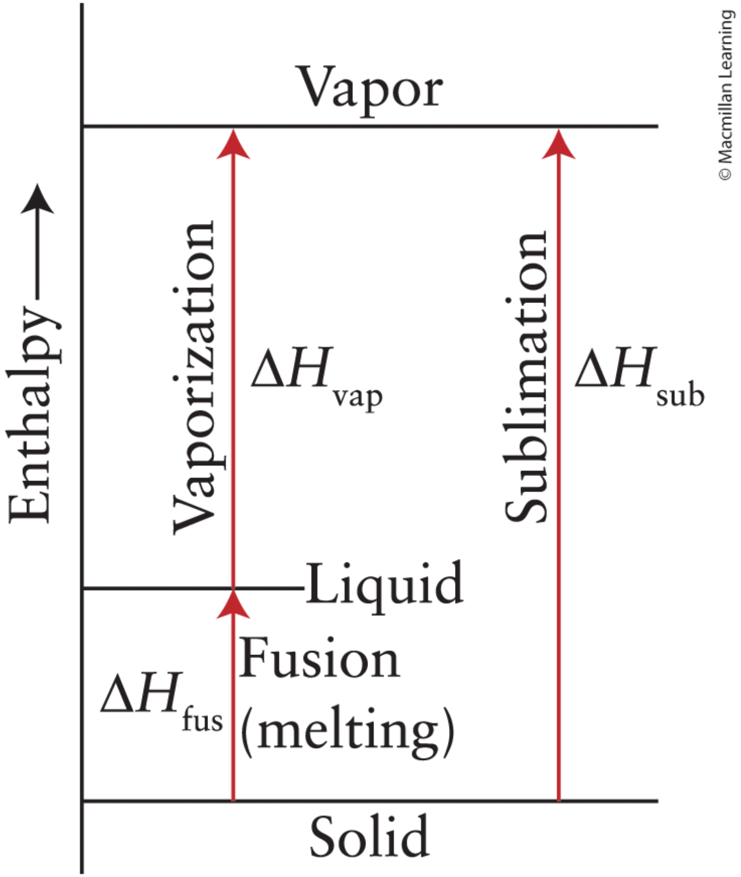
- Freezing is the change from liquid to solid.

- 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·mol^{-1}, so the enthalpy of freezing for water at 0.0 °C is −6.0 kJ·mol^{-1}.

Enthalpy of Sublimation, ΔH_{sub}

- 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."



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- 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.

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

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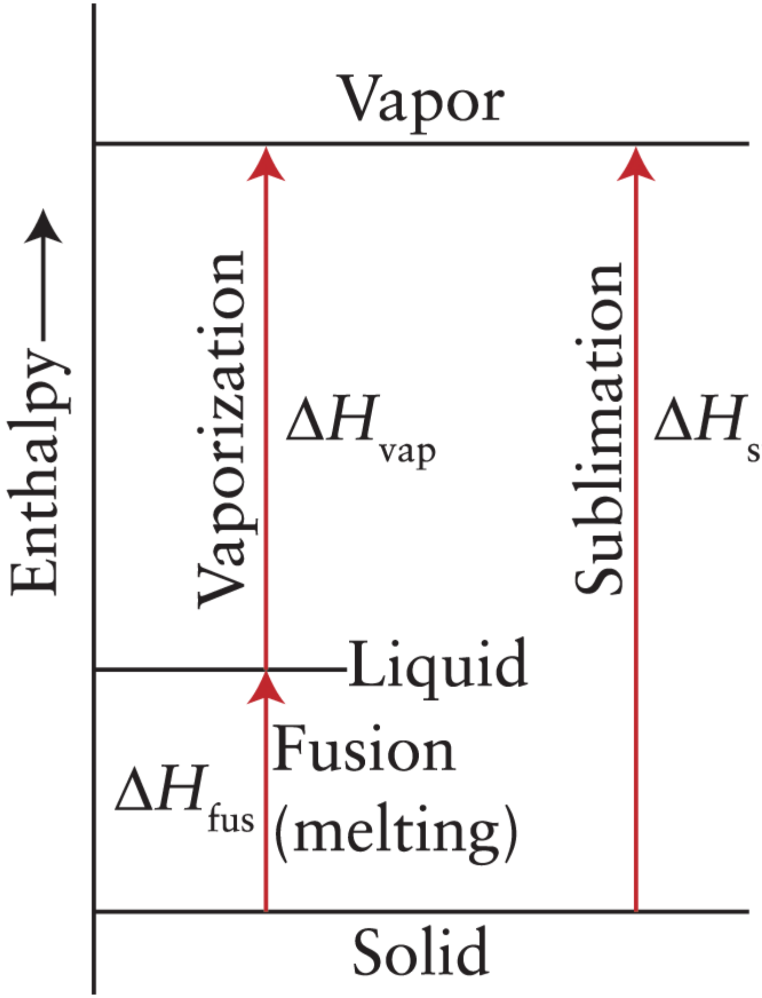

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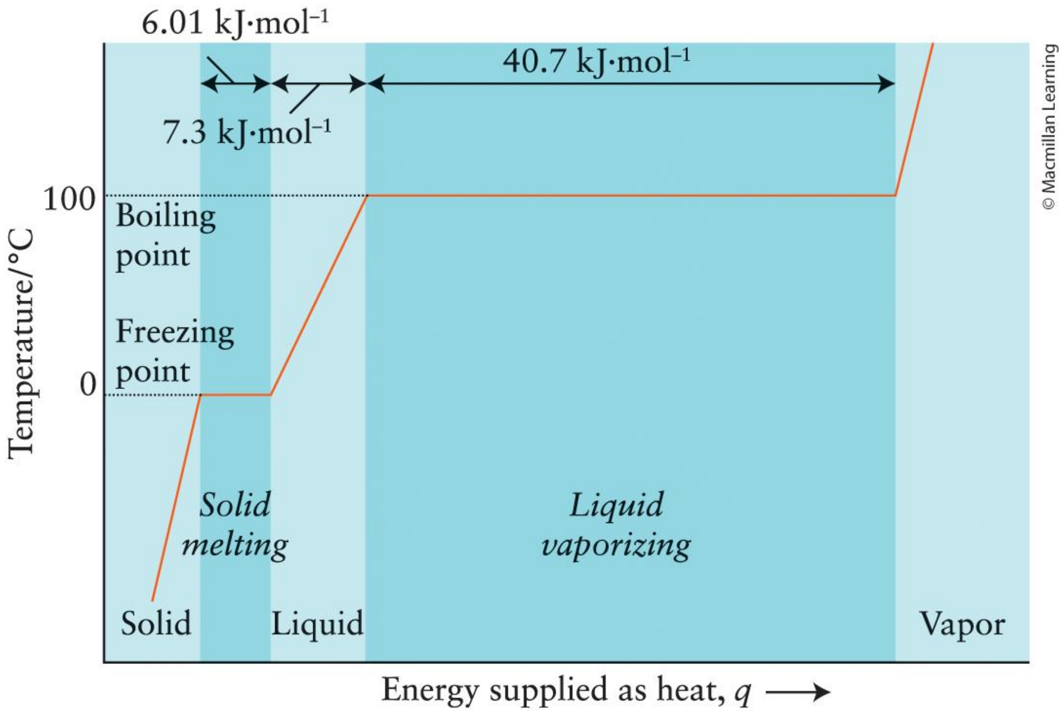
- $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$

Heating Curves

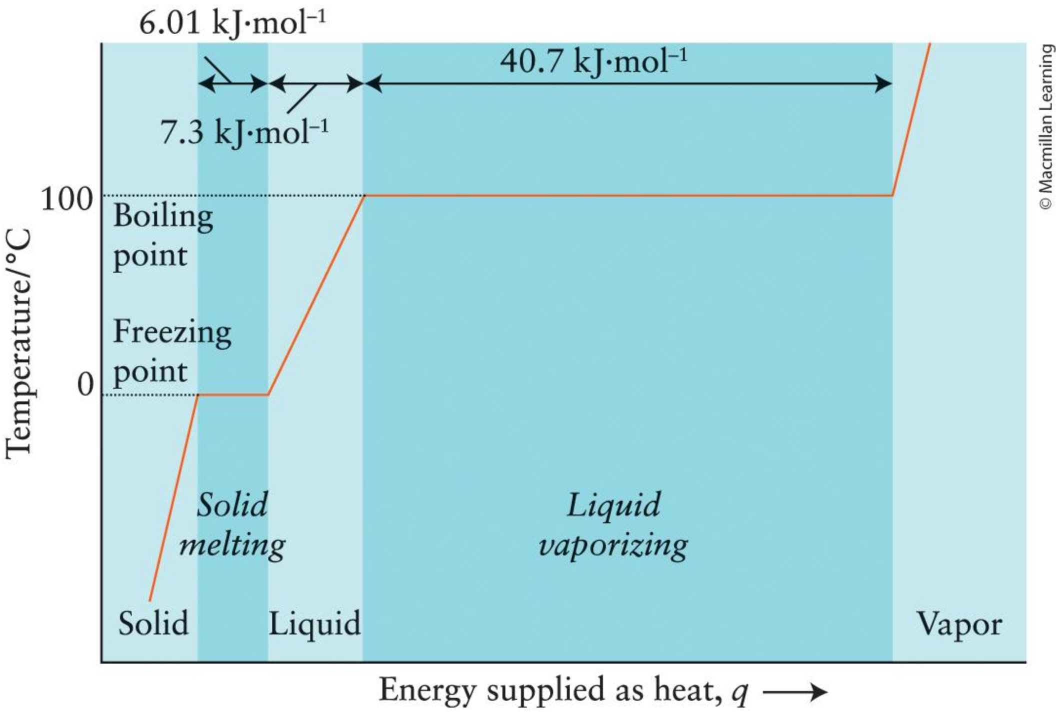
- A heating curve shows the variation in the temperature of a heated sample.
- As a sample of ice is heated the temperature rises steadily.
- In a solid the molecules are still locked together as they oscillate vigorously around their mean positions.
- As the temperature rises, reaching the melting point, the molecules have enough energy to move past one another, overcoming the attractive forces between molecules.



Heating Curves

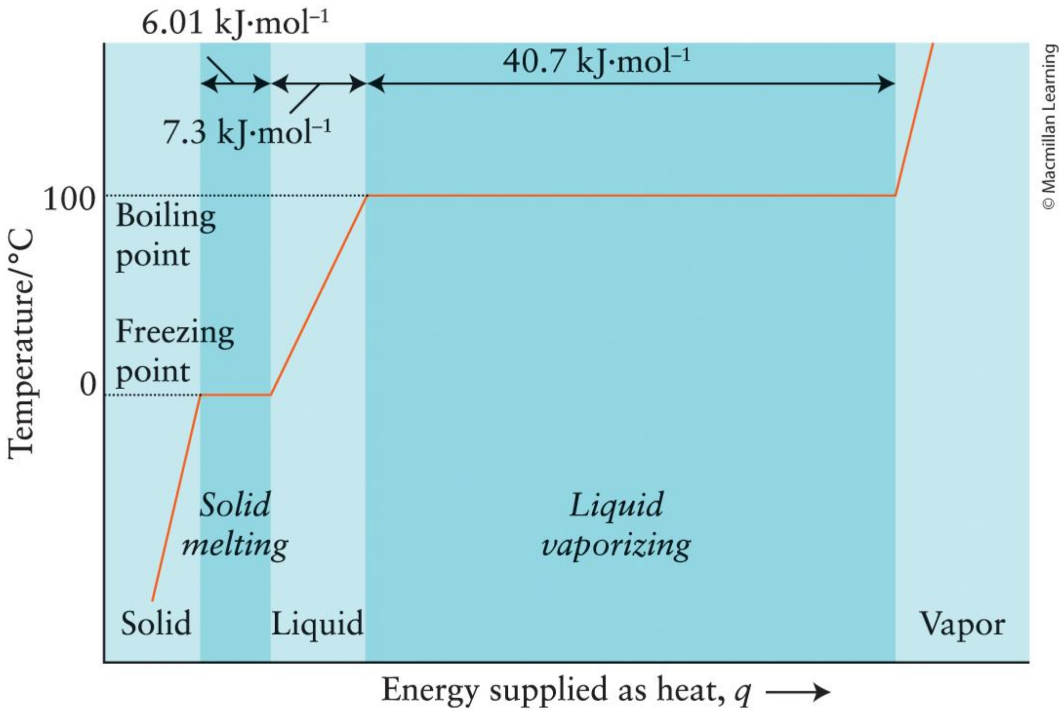
- At this temperature, all the added energy is used to break all the attractive forces; the temperature remains constant at the melting point until all the ice has melted.
- Only then does the temperature rise again, and the rise continues right up to the boiling point.
- At the boiling point, the temperature rises again and comes to a halt.

- Now the water molecules have enough energy to escape into the vapor state, and all the heat supplied is used to form the vapor.



Heating Curves

- After the sample has evaporated and heating continues, the temperature of the vapor rises again.
- The steeper the slope, the lower the heat capacity. Both the solid and vapor phases have steeper slopes than liquid, so the liquid has a greater heat capacity.
- The liquid's high heat capacity is due largely to presence of intermolecular hydrogen bonds that can break and re-form as the molecules rotated. It requires more energy to break them.



Thermochemistry

- Enthalpy changes apply to chemical changes as well as physical processes.
- Thermochemistry is the branch of thermodynamics that deals with the heat absorbed or required when chemical reactions take place.
- For example, the combustion (the complete reaction with oxygen) of methane, releases 890. kJ of energy as heat.
- $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + \ 2\ H_2O(l) \quad \Delta H = -890.\ \text{kJ}$
- The equation for the combustion of methane is an example of a thermochemical equation which consists of a chemical equation together with a state of the reaction enthalpy.

Reaction Enthalpy

- The stoichiometric coefficients corresponding to an enthalpy change. For example, 1 mol CH_4 (g) and 890. kJ of heat.
- $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \qquad \Delta H = -890.\ \text{kJ}$
- If the same reaction is multiplied by 2, then the change in enthalpy will be twice as great.
  $2\ CH_4(g) + 4\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(l) \qquad \Delta H = -1780.\ \text{kJ}$
- For the reverse reaction, the change is enthalpy is the negative of the enthalpy of the forward process.
- $CO_2(g) + 2\ H_2O(l) \rightarrow CH_4(g) + 2\ O_2(g) \quad \Delta H = +890.\ \text{kJ}$

The Relation Between ΔH and ΔU

- We have measured heat with bomb calorimeter.
- At constant volume, the heat transfer is ΔU;

$$C_{V,\mathrm{m}} = \frac{\Delta U}{\Delta T}$$

- At constant pressure, it is ΔH; $C_{P,m} = C_{V,m} + R$
- However, it is sometimes necessary to convert the measured value of ΔU into ΔH.
- For example, it is easy to measure the heat released by the combustion of glucose in a bomb calorimeter, but to use that information in studying metabolism, which takes place at constant pressure, we need the enthalpy of reaction.

The Relation Between ΔH and ΔU

- For reactions in which no gas is generated or consumed, little expansion work is done—the difference between ΔH and ΔU is negligible, so we can set ΔH = ΔU.
- However, if a gas is formed in the reaction and expansion work is done, the difference can be significant.
- We can use the ideal gas law to relate the values of ΔH and ΔU for gases that behave ideally.

The Relation Between ΔH and ΔU (3 of 3)

- The relation between ΔH and ΔU is $H = U + PV$, or $H = U + nRT$.

- We suppose initial amount of reactant gas is $n_{initial}$.
- $H_{initial} = U_{initial} + PV_{initial}$ or $= U_{initial} + n_{initial}RT$

- and after the reaction, the amount of ideal gas product molecules is nfinal.
- $H_{final} = U_{final} + PV_{final} = U_{final} + n_{final}RT$

- The difference is $\Delta H = H_{final} - H_{initial} = \Delta U + (n_{final} - n_{initial})RT$ or
- $\Delta H = \Delta U + \Delta n_{gas}RT$.

Standard Reaction Enthalpies

- Always specify the state of each substance: for methane,
  - $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$ $\Delta H = -802.\ kJ$
  - $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta H = -890.\ kJ$

- The difference between $H_2O(g)$ and $H_2O(l)$ is 88 kJ of energy so for transforming just one mole of $H_2O(g)$ to $H_2O(l)$, the ΔH_{vap} is 44.0 $kJ \cdot mol^{-1}$.

Standard Reaction Enthalpies

- Always specify the state of each substance: for methane,
  - $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$ ΔH = −802. kJ
  - $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ ΔH = −890. kJ

- For the oxidation of methane to $H_2O(l)$ the ΔH° = −890. kJ. The heat output of 890. kJ indicates that 1 mol CH_4 (g) as pure methane gas at 1 bar is allowed to react with pure oxygen gas at 1 bar to produce 1 mol CO_2 (g) and 2 mol of H_2O (l) under standard state conditions.

- Standard state conditions exactly 1 bar at 298 K.

- The standard reaction enthalpy (also known as "standard enthalpy of reaction"), ΔH°, is the reaction enthalpy when the reactants are in their standard states.

What Does This Have to Do with Renewable Fuels?

- We could not live without combustion reactions: the oxidation of glucose powers our bodies and the burning of fossil fuels (coal, petroleum, and natural gas) powers our homes and vehicles.
- Three alternative fuels are hydrogen, from ocean water by electrolysis; ethanol, from fermenting biomass; and methane, generated from bacterial digestion of wastes.
- Note: Ethanol, CH_3CH_2OH, makes up about 10% by volume of gasoline. One bushel of corn (30 L) produces 10 L of ethanol.

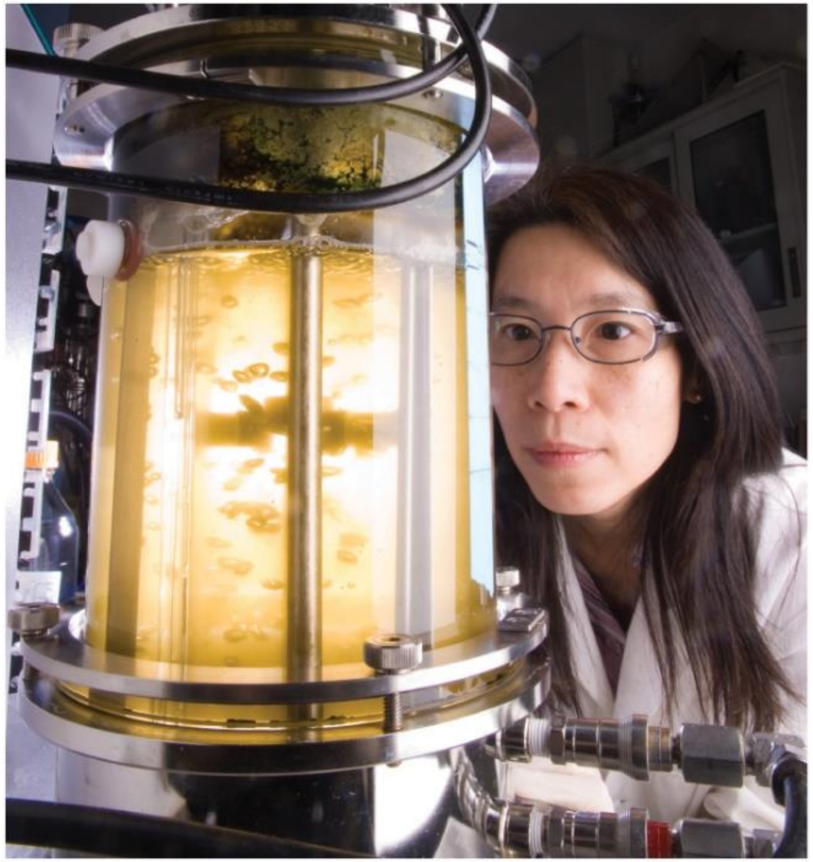


Photo by Pat Corkery/NREL.

What Does This Have to Do with Renewable Fuels?

- Methane, CH_4, is found underground in natural gas, but it is also obtained from biological materials.
- The “digestion” of the biomaterials by bacteria is anaerobic, which means that it takes place in the absence of oxygen.
- Many sewage treatment plants have anaerobic digesters that digest sewage to produce the methane used to operate the plants.

What Does This Have to Do with Renewable Fuels?

- Biodiesel is the term used for diesel fuel that comes from renewable, biological sources, such as algae or vegetable oil. Diesel engines are more efficient than gasoline engines because the fuel has a high energy density (enthalpy of combustion per liter).
- Some difficulties with biodiesel include that it is more viscous than traditional diesel and that it solidifies at low temperatures.
- These renewable fuels do produce carbon dioxide when burned and thus contribute to the greenhouse effect and global warming.

Enthalpy of Combustion

- The standard enthalpy of combustion, ΔHc°, is the change in enthalpy per mole of a substance that is burned in a combustion reaction under standard conditions.
- The specific enthalpy is the standard enthalpy of reaction divided by the mass of the sample and reported in kilojoules per gram.
- The enthalpy density is the enthalpy of reaction of a sample divided by the volume of the sample and is reported in kilojoules per liter.

The Heat Output of Reactions

Substance	Formula	$\Delta H_c°$/kJ·mol^{-1}	Specific enthalpy/kJ·g^{-1}
Hydrogen	$H_2(g)$	−286	142
Methane	$CH_4(g)$	−890	55
Ethanol	$CH_3CH_2OH(l)$	−1368	29.7
Propane	$CH_3CH_2CH_3(g)$	−2220	50.35
Glucose	$C_6H_{12}O_6(s)$	−2808	15.59
Benzene	$C_6H_6(l)$	−3268	41.8
Octane	$C_8H_8(l)$	−5471	48

- For example, the heat output from combusting 150. g of methane $CH_4 + 2\ O_2 \rightarrow 2\ H_2O + CO_2$: 1 mol CH_4 is chemically equivalent to 890. kJ.

$$\frac{890.\ \text{kJ}}{1\ \text{mol CH}_4} \times \frac{\text{mol CH}_4}{16.04\ \text{g CH}_4} \times \frac{150.\ \text{g}}{1} = 8.32\ \text{kJ}$$