## Chapter 9: Phenomenon

Phenomenon: Below is data from three different reactions carried out with three different amounts of reactants. All reactions were carried out in expandable/contractible containers at $25^{\circ} \mathrm{C}$. What patterns do you see in the data? You do not need to know what work, heat, internal energy, or enthalpy are to find patterns in the data.

| $\begin{gathered} \mathrm{C}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \\ \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \end{gathered}$ | Starting Amount of C | Starting Amount of $\mathrm{O}_{2}$ | Observations of Container | Work | Heat | Internal Energy | Enthalpy |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1.00 mol | 1.00 mol | $\begin{gathered} \text { Hot } \\ \text { Same Size } \end{gathered}$ | 0.0 kJ | -394 kJ | -394 kJ | -394 kJ |
|  | 1.00 mol | 2.00 mol | $\begin{gathered} \hline \text { Hot } \\ \text { Same Size } \\ \hline \end{gathered}$ | 0.0 kJ | -394 kJ | -394 kJ | -394 kJ |
|  | 2.00 mol | 2.00 mol | $\begin{gathered} \text { Hot } \\ \text { Same Size } \end{gathered}$ | 0.0 kJ | -788 kJ | -788 kJ | -788 kJ |
| $\begin{aligned} & \mathrm{CO}_{2}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \\ & \quad \rightarrow \mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \end{aligned}$ | Starting Amount of $\mathrm{CO}_{2}$ | Starting Amount of $\mathrm{H}_{2} \mathrm{O}$ | Observations of Container | Work | Heat | Internal Energy | Enthalpy |
|  | 1.00 mol | 1.00 mol | $\begin{aligned} & \text { Cold } \\ & \text { Expanded } \end{aligned}$ | -3.7 kJ | 485 kJ | 481 kJ | 485 kJ |
|  | 1.00 mol | 2.00 mol | Cold Expanded | -7.4 kJ | 970 kJ | 963 kJ | 970 kJ |
|  | 2.00 mol | 2.00 mol | $\begin{aligned} & \text { Cold } \\ & \text { Expanded } \end{aligned}$ | -7.4 kJ | 970 kJ | 963 kJ | 970 kJ |
| $\begin{gathered} \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \\ \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) \end{gathered}$ | Starting Amount of $\mathrm{N}_{2}$ | Starting Amount of $\mathrm{O}_{2}$ | Observations of Container | Work | Heat | Internal Energy | Enthalpy |
|  | 1.00 mol | 1.00 mol | Cold Contract | 1.2 kJ | 34 kJ | 35 kJ | 34 kJ |
|  | 2.00 mol | 1.00 mol | Cold Contract | 1.2 kJ | 34 kJ | 35 kJ | 34 kJ |
|  | 2.00 mol | 2.00 mol | Cold Contract | 2.5 kJ | 68 kJ | 71 kJ | 68 kJ |

Chapter 9: Energy, Enthalpy, and Thermochemistry

## Chapter 9 Energy, Enthalpy, \& <br> Thermochemistry

Big Idea: Heat and work are equivalent ways of changing the energy of a system. The total energy of an isolated system is constant. The change in enthalpy of a reaction indicates whether a reaction is endothermic or exothermic.

## Energy Facts

## WORLD ENERGY <br> CONSUMPTION - 2021



World Consumption

| Source of <br> Energy | Percent |
| :--- | :---: |
| Petroleum | $31 \%$ |
| Coal | $28 \%$ |
| Natural Gas | $25 \%$ |
| Renewable | $12 \%$ |
| Nuclear | $5 \%$ |


| Source of <br> Energy | Percent Change <br> Since 2018 | Percent Change <br> Since 1990 |
| :--- | :---: | :---: |
| Oil | $-6.9 \%$ | $-24.0 \%$ |
| Coal | $-0.5 \%$ | $0.48 \%$ |
| Natural Gas | $3.7 \%$ | $15.2 \%$ |
| Renewables | $11.0 \%$ | $39.8 \%$ |
| Nuclear | $4.9 \%$ | $-23.1 \%$ |


| Energy Focts |  |  |  |
| :---: | :---: | :---: | :---: |
| 2018 |  |  |  |
| Country | Energy Consumption (Quadrillion Btu) | Country | Energy Consumption/person (MBłU) |
| China | 147.6 | Qatar | 704 |
| United States | 101.2 | Iceland | 681 |
| Russia | 33.3 | Singapore | 649 |
| India | 31.3 | Trinidad and | 642 |
| Japan | 19.2 | Tobago | 642 |
| Canada | 15.2 | United Arad | 481 |
| Germany | 14.9 | Emirates | 481 |
| Brazil | 13.8 | Bahrain | 460 |
| Korea, South | 12.4 | Brunei | 425 |
| Iran | 11.7 | Canada | 427 |
|  |  | Kuwait | 398 |
|  |  | Luxembourg | 316 |
|  |  | United States (\#11) | 309 |

## Energy Facts

U.S. energy consumption by source and sector, 2021
quadrillion British thermal units (Btu)


| Source <br> of <br> Energy | World <br> 2021 | $\%$ <br> US | $\%$ <br> US |
| :--- | :---: | :---: | :---: |
| Petroleum | $31 \%$ | $36 \%$ | $37 \%$ |
| Natural <br> Gas | $28 \%$ | $32 \%$ | $25 \%$ |
| Coal | $25 \%$ | $12 \%$ | $21 \%$ |
| Renewable | $12 \%$ | $11 \%$ | $8 \%$ |
| Nuclear | $5 \%$ | $8 \%$ | $9 \%$ |

## Energy Facts

How do we generate electricity?


## Internal Energy

- System: The object of study.
- Surrounding: The region outside the system.
- Internal Energy (E): The capacity to do work or to produce heat.
- Temperature (T): How hot or cold an object is.
- Heat (q): The energy that is transferred as a result of a temperature difference between a system and its surroundings.

Note: If heat enters the system $q$ is positive (endothermic reaction). If heat leaves the system $q$ is negative (exothermic reaction).

- Work (w): The energy expended during the act of moving an object against an opposing force.
Note: If the system expands, $w$ is negative. If the system contracts, $w$ is positive.


## Internal Energy

## Student Question

Which of these changes results in an increase in the internal energy of the system?
a) The system absorbs heat and does work on the surroundings.
b) The system releases heat and does work on the surroundings.
c) The system absorbs heat and has work done on it by the surroundings.
d) The system releases heat and has work done on it by the surroundings.

## Internal Energy

## Student Question

Helium gas, at a pressure of 2 Pa , is placed in a container with a movable piston. On the other side of the piston is a vacuum. The He gas is allowed to expand such that the volume of the helium goes from $2 \mathrm{~m}^{3}$ to $4 \mathrm{~m}^{3}$. How much work does the helium gas do?
a) 8 J
b) 4 J
c) 0 J
d) -4 J
e) None of the above

## Internal Energy

- Heat Capacity (C): The ratio of heat supplied to the temperature rise produced (units $\frac{J}{{ }^{\mathrm{C}}}$ )
- Molar Heat Capacity: The heat capacity per mole of substance (units $\frac{J}{\text { mol.0C }}$ )

Note: Many books use $\mathrm{C}_{\mathrm{m}}$ for molar heat capacity.

- Specific Heat Capacity: The heat capacity per gram of substance (units $\frac{\mathrm{J}}{\mathrm{g} \cdot \mathrm{C}}$ )

Note: Many books use $\mathrm{C}_{\mathrm{S}}$ for specific heat capacity.

Note: If the subscript $V$ is added to any of the heat capacities it is the heat capacity at constant volume. If the subscript $P$ is added to any of the heat capacities it is the heat capacity at constant pressure.

## Internal Energy

## Molar Heat Capacities at 298 K

| Gas | $\mathrm{C}_{\mathrm{V}\left(\frac{1}{\text { motik }}\right)}$ | $\mathrm{C}_{\mathrm{P}\left(\frac{1}{\text { motik }}\right)}$ | $\mathrm{C}_{\mathrm{P}}-\mathrm{C}_{\mathrm{V}\left(\frac{1}{\text { mokik }}\right)}$ | Substances | C $\left(\frac{1}{g, k}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{He}, \mathrm{Ne}, \mathrm{Ar}$ | 12.47 | 20.80 | 8.33 | $\mathrm{H}_{2} \mathrm{O}$ (l) | 4.18 |
| $\mathrm{H}_{2}$ | 20.54 | 28.86 | 8.32 | $\mathrm{H}_{2} \mathrm{O}(\mathrm{s})$ | 2.03 |
| $\mathrm{N}_{2}$ | 20.71 | 29.03 | 8.32 | $\mathrm{Al}(\mathrm{s})$ | 0.89 |
| $\mathrm{N}_{2} \mathrm{O}$ | 30.38 | 38.70 | 8.32 | $\mathrm{Fe}(\mathrm{s})$ | 0.45 |
| $\mathrm{CO}_{2}$ | 28.95 | 37.27 | 8.32 | $\mathrm{Hg}(\mathrm{l})$ | 0.14 |
| $\mathrm{C}_{2} \mathrm{H}_{6}$ | 44.60 | 52.92 | 8.32 | $\mathrm{C}(\mathrm{s})$ | 0.71 |
| $q=n C \Delta T$ |  |  |  | $q=m C \Delta T$ |  |

Note: The smaller the heat capacity, the faster the transfer of heat.

## Internal Energy

$C_{V}$ (Monatomic Ideal Gas)

Know

$$
\Delta E=q+w=\Delta P E+\Delta K E
$$

Potential Energy

Kinetic Energy

Work

Only true for ideal monatomic gases

Heat

## Internal Energy

$C_{p}$ (Monatomic Ideal Gas)

Know

$$
\Delta \mathrm{E}=\mathrm{q}+\mathrm{w}=\Delta \mathrm{PE}+\Delta \mathrm{KE}
$$

Potential Energy

Kinetic Energy

Work
Only true for ideal monatomic gases

Heat

## Internal Energy

- State Function: A property of a substance that is independent of how a substance was prepared.
- Are $\Delta \mathrm{E}, \mathrm{q}$, and w state functions?
- 1 mol of monatomic ideal gas
- Path A
- $1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 1.0 \mathrm{~atm}, 2.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$
- Path B
- $1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$


## Internal Energy

## Path B (Monatomic Ideal Gas)

 $1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$- Step 1 (Constant Volume)

Heat

- $q=n C_{V} \Delta T$
- $C_{V}=\frac{3}{2} R$
(For monatomic ideal gas)
- $q=n \frac{3}{2} R \Delta T$

Problem: We do not know $T$

$$
\text { - }(\Delta P) V=n R \Delta T
$$

- $q=\frac{3}{2}(\Delta P) V=\frac{3}{2}\left(P_{f}-P_{i}\right) V$
- $q=\frac{3}{2}(2.0 \mathrm{~atm}-1.0 \mathrm{~atm})(1.0 \mathrm{~L})$
- $q=1.5 \mathrm{~L} \cdot \mathrm{~atm}=150 \mathrm{~J}$


## Internal Energy

## Path B (Monatomic Ideal Gas)

## $1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$

- Step 2 (Constant Pressure)

Heat

- $q=n C_{P} \Delta T$
- $C_{P}=\frac{5}{2} R$

Work

- $w=-P_{e x} \Delta V$
(For monatomic ideal gas)
- $q=n_{2}^{5} R \Delta T$
- $\mathrm{w}=-(2.0 \mathrm{~atm})(2.0 L-1.0 \mathrm{~L})$
- $w=-2.0 \mathrm{~L} \cdot \mathrm{~atm}=-2.0 \times 10^{2} \mathrm{~J}$
Problem: We do not know T
- $\mathrm{w}=-P_{e x}\left(V_{f}-V_{i}\right)$

Internal Energy

- $q=\frac{5}{2} P \Delta V=\frac{5}{2} P\left(V_{f}-V_{i}\right)$
- $q=\frac{5}{2}(2.0 \mathrm{~atm})(2.0 L-1.0 L)^{\circ} \Delta E=5.0 \times 10^{2} J+-2.0 \times 10^{2} J$
- $q=5.0 \mathrm{~L} \cdot \mathrm{~atm}$
- $q=5.0 \times 10^{2} J$


## Internal Energy

- Path A $1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 1.0 \mathrm{~atm}, 2.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$
- Path B $1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$

| Path B (totals) | Path A (totals) |
| :---: | :---: |
| $q=150 \mathrm{~J}+5.0 \times 10^{2} \mathrm{~J}$ | $\mathrm{q}=550 \mathrm{~J}$ |
| $\mathrm{q}=650 \mathrm{~J}$ |  |
| a <br> $\mathrm{w}=0.0 \mathrm{~J}+-2.0 \times 10^{2} \mathrm{~J}$ <br> $\mathrm{w}=-2.0 \times 10^{2} \mathrm{~J}$ | $w=-1.0 \times 10^{2} \mathrm{~J}$ |
| $\Delta E=150 \mathrm{~J}+3.0 \times 10^{2} \mathrm{~J}$ |  |
| $\Delta E=450 \mathrm{~J}$ | $\Delta E=450 \mathrm{~J}$ |

## Enthalpy

- Path A (Monatomic ideal gas) $1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 1.0 \mathrm{~atm}, 2.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$
- Step 1: $q=250 \mathrm{~J} \quad \mathrm{w}=-1.0 \times 10^{2} \mathrm{~J} \Delta \mathrm{E}=150 \mathrm{~J}$
- Step 2: $q=3.0 \times 10 \mathrm{~J} w=0.0 \mathrm{~J} \quad \Delta \mathrm{E}=3.0 \times 10^{2} \mathrm{~J}$
- Path B (Monatomic ideal gas)
$1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$
- Step 1: $q=150 \mathrm{~J} \quad \mathrm{w}=0.0 \mathrm{~J} \quad \Delta \mathrm{E}=150 \mathrm{~J}$
- Step 2: $q=5.0 \times 10^{2} \mathrm{~J} w=-2.0 \times 10^{2} \mathrm{~J} \Delta \mathrm{E}=3.0 \times 10^{2} \mathrm{~J}$

These values were calculated in class.

## Enthalpy

## Path B (Monatomic Ideal Gas)

 $1.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 1.0 \mathrm{~L} \rightarrow 2.0 \mathrm{~atm}, 2.0 \mathrm{~L}$- Step 1 (Constant Volume)
- $\Delta H=\Delta E+\Delta(P V)=\Delta E+V \Delta P$
- $V \Delta P=(1.0 \mathrm{~L})(2.0 \mathrm{~atm}-1.0 \mathrm{~atm})=1.0 \mathrm{~L} \cdot \mathrm{~atm}$
- $V \Delta P=1.0 \mathrm{~L} \cdot \operatorname{atm}\left(\frac{101.325 \mathrm{~J}}{1 \mathrm{~L} \cdot \mathrm{~atm}}\right)=1.0 \times 10^{2} \mathrm{~J}$
- $\Delta H=150 J+1.0 \times 10^{2} J=250 J$
- Step 2 (Constant Pressure)
- $\Delta H=q=5.0 \times 10^{2} J$
- Total $\Delta H$

$$
0 H_{t o t}=250 \mathrm{~J}+5.0 \times 10^{2} \mathrm{~J}=750 \mathrm{~J}
$$

## Enthalpy

## Heating Curve of $\mathbf{H}_{2} \mathrm{O}$



Heat supplied

- Heat of Fusion ( $\Delta \mathbf{H}_{\text {fus }}$ ): The amount of heat that needs to be supplied to turn a solid into a liquid.
- Heat of Vaporization ( $\Delta \mathbf{H}_{\text {vap }}$ ): The amount of heat that needs to be supplied to turn a liquid into a gas.


## Enthalpy

## Standard State ( ${ }^{\circ}$ )

- For a gas, the standard state is exactly 1 atm.
- For a substance in solution, the standard state is exactly 1 M .
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
- For an element, the standard state is the form in which the element exists (is most stable) under conditions of 1 atm and the temperature of interest.

Note: The temperature of the system is usually noted as a subscript. If no temperature is stated, assume $25^{\circ} \mathrm{C}$.

Note: Only the change in enthalpy is important, therefore, the standard state of elements are set to 0 .

## Enthalpy

## Standard Enthalpy of formation $\left(\Delta H_{f}{ }^{\circ}\right)$ :

- The standard reaction enthalpy per mole of compound for the compound's synthesis from its elements in their most stable form at 1 atm and the specified temperature.

Note: The reaction must be written such that only 1 mole of product forms.

## Enthalpy

## Student Question

For which reaction is $\Delta H_{r x n}^{\circ}=\Delta H_{f}^{\circ}$ ?

$$
\text { a) } 2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

b) 2 C (graphite) $+\mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})$
c) C (diamond) $+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})$
d) $\mathrm{NO}(\mathrm{g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{NO}_{2}(\mathrm{~g})$
e) None of the above

## Enthalpy

## Standard Enthalpy of Combustion ( $\Delta \boldsymbol{H}_{C}^{\circ}$ ):

- The change of enthalpy per mole of substance when it burns (reacts with oxygen) completely under standard conditions.

Note: The reaction is written such that 1 mole of substance combusts.

Note: When carbon is in the reactants, $\mathrm{CO}_{2}$ forms, and when H is in the reactants, $\mathrm{H}_{2} \mathrm{O}$ forms. For standard enthalpies of combustion water is always assumed to be in the liquid phase.

```
Example:
C}\mp@subsup{\textrm{C}}{8}{
```


## Hess's Law

## Hess's Law:

- A reaction's enthalpy is the sum of the enthalpies of any sequence of reactions (at the same temperature and pressure) into which the overall reaction can be divided.
- Things to remember
- If you add reactions together, add $\Delta H$ 's.
- If you flip a reaction, flip the sign of $\Delta H$.
- If you multiply a reaction by a constant, multiply $\Delta H$ by the same constant.


## Hess's Law

1. $\mathrm{CCl}_{4}(\mathrm{~g})+4 \mathrm{HCl}(\mathrm{g}) \rightarrow \mathrm{CH}_{4}(\mathrm{~g})+4 \mathrm{Cl}_{2}(\mathrm{~g})$ $\Delta \mathrm{H}_{1}=397.0 \mathrm{~kJ}$
2. $1 / 2 \mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{HCl}(\mathrm{g})$ $\Delta H_{2}=-92.3 \mathrm{~kJ}$
3. $\mathrm{C}($ graphite $)+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{4}(\mathrm{~g})$

$$
\Delta H_{3}=-74.81 \mathrm{~kJ}
$$

Calculate the standard enthalpy of formation of $\mathrm{CCl}_{4}(\mathrm{~g})$ using the thermochemical equations.

## Hess's Law

- Given
$\mathrm{Na}(\mathrm{s})+\frac{1}{2} \mathrm{H}_{2}(g)+\mathrm{C}($ graphite $)+\frac{3}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{NaHCO}_{3}(\mathrm{~s}) \quad \Delta \mathrm{H}_{f}^{\circ}\left(\mathrm{NaHCO}_{3}\right)$
$2 \mathrm{Na}(\mathrm{s})+\mathrm{C}($ graphite $)+\frac{3}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{~s})$
$\Delta H_{f}^{\circ}\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)$
C (graphite) $+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})$ $\Delta H_{f}^{\circ}\left(\mathrm{CO}_{2}\right)$
$\mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
- What is $\Delta \mathrm{H}^{\circ}{ }_{\mathrm{rxn}}$ of
$2 \mathrm{NaHCO}_{3}(\mathrm{~s}) \rightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
$2 \mathrm{NaHCO}_{3}(\mathrm{~s}) \rightarrow 2 \mathrm{Na}(\mathrm{s})+\mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{C}($ graphite $)+3 \mathrm{O}_{2}(\mathrm{~g})-2 \Delta \mathrm{H}_{f}^{\circ}\left(\mathrm{NaHCO}_{3}\right)$
$2 \mathrm{Na}(\mathrm{s})+\mathrm{C}($ graphite $)+\frac{3}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{~s}) \quad \Delta \mathrm{H}_{f}^{\circ}\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)$
C (graphite) $+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})$ $\Delta H_{f}^{\circ}\left(\mathrm{CO}_{2}\right)$
$\mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
$\Delta H_{f}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}\right)$
$2 \mathrm{NaHCO}_{3}(\mathrm{~s}) \rightarrow \mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$

$$
\Delta H_{r x n}^{\circ}=\Delta H_{f}^{\circ}\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)+\Delta H_{f}^{\circ}\left(\mathrm{CO}_{2}\right)+\Delta H_{f}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}\right)-2 \Delta H_{f}^{\circ}\left(\mathrm{NaHCO}_{3}\right)
$$

$$
\Delta H_{r x n}^{\circ}=\sum \Delta H_{f}^{\circ}(\text { products })-\sum \Delta H_{f}^{\circ}(\text { reactants })
$$

Thermodynamic Dała at 298 K

| Substance | $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\frac{k J}{m o l}\right)$ | $\Delta \mathrm{G}_{\mathrm{f}}^{\circ}\left(\frac{k J}{\mathrm{~mol}}\right)$ | $\Delta \mathrm{S}^{\circ}\left(\frac{\mathrm{J}}{\mathrm{mol} \cdot \mathrm{K}}\right)$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})$ | 52 | 68 | 219 |
| $\mathrm{CH}_{4}(\mathrm{~g})$ | -75 | -51 | 186 |
| $\mathrm{CO}_{2}(\mathrm{~g})$ | -393.5 | -394 | 214 |
| $\mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})$ | -84.7 | -32.9 | 229.5 |
| $\mathrm{O}(\mathrm{g})$ | -110.5 | -137 | 198 |
| $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{l})$ | -484 | -389 | 160. |
| $\mathrm{CH}_{3} \mathrm{OH}^{(\mathrm{g})}$ | -201 | -163 | 240. |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}(\mathrm{l})$ | -278 | -175 | 161 |
| $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(\mathrm{~s})$ | -1275 | -911 | 212 |
| $\mathrm{HCl}_{(\mathrm{g})}$ | -92 | -95 | 187 |
| $\mathrm{H}_{2}(\mathrm{~g})$ | 0 | 0 | 131 |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | -286 | -237 | 70 |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ | -242 | -229 | 189 |
| $\mathrm{Fe}(\mathrm{s})$ | 0 | 0 | 27 |
| $\mathrm{Fe} \mathrm{O}_{2}(\mathrm{O})$ | -826 | -740. | 90. |

Thermodynamic Dała at 298 K

| Substance | $\Delta H_{f}^{\circ}\left(\frac{k J}{m o l}\right)$ | $\Delta G_{f}^{\circ}\left(\frac{k J}{m o l}\right)$ | $\Delta S^{\circ}\left(\frac{J}{\text { mol } \cdot K}\right)$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{N}_{2}(\mathrm{~g})$ | 0 | 0 | 192 |
| $\mathrm{NO}_{2}(\mathrm{~g})$ | 34 | 52 | 240. |
| $\mathrm{NO}^{(\mathrm{g})}$ | 90. | 87 | 211 |
| $\mathrm{~N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ | 10. | 98 | 304 |
| $\mathrm{NH}_{3}(\mathrm{~g})$ | -46 | -17 | 193 |
| $\mathrm{HNO}_{3}(\mathrm{l})$ | -174 | -81 | 156 |
| $\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s})$ | -314 | -203 | 96 |
| $\mathrm{O}_{2}(\mathrm{~g})$ | 0 | 0 | 205 |
| $\mathrm{P}_{4} \mathrm{O}_{10}(\mathrm{~s})$ | -2984 | -2698 | 229 |
| $\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{~s})$ | -1279 | -1119 | 110 |
| $\mathrm{~S}_{\text {thombic }}(\mathrm{s})$ | 0 | 0 | 32 |
| $\mathrm{H}_{2} \mathrm{~S}^{(\mathrm{g})}$ | -21 | -34 | 206 |
| $\mathrm{SO}_{2}(\mathrm{~g})$ | -297 | -300 | 248 |
| $\mathrm{SO}_{3}(\mathrm{~g})$ | -396 | -371 | 257 |

* Other $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$ can be found in appendix 4 in the back of your book.


## Hess's Law

## Student Question

Calculate $\Delta H_{r x n}^{\circ}(\mathrm{kJ})$ for the following reaction from the listed standard enthalpies of formation:
$4 \mathrm{NH}_{3}(\mathrm{~g})+5 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 4 \mathrm{NO}(\mathrm{g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$

$$
\begin{aligned}
& \text { a) }-862 \mathrm{~kJ} \\
& \text { b) }-908 \mathrm{~kJ} \\
& \text { c) }-1,276 \mathrm{~kJ} \\
& \text { d) Not enough information } \\
& \text { e) None of the above }
\end{aligned}
$$

| Substance | $\Delta H^{\circ}\left(\frac{k j}{m o l}\right)$ |
| :---: | :---: |
| $\mathrm{NH}_{3}(\mathrm{~g})$ | -46 |
| $\mathrm{NO}(\mathrm{g})$ | 90. |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ | -242 |

## Calorimetry

Constant Volume
Calorimetry
(Bomb)


Used to find $\Delta \mathrm{E}_{\mathrm{com}}$

- No matter is exchanged
- No heat is exchanged

Constant Pressure Calorimetry (Coffee Cup)


Used to find $\Delta \mathrm{H}\left(\Delta \mathrm{H}_{\text {fus }}\right.$ and $\Delta \mathrm{H}_{\mathrm{rxn}}$ ) and C

- No heat is exchanged


## Calorimetry

- In a constant pressure calorimeter 200. g of ice ( $\mathrm{T}_{\mathrm{i}}$ (ice) $=0.0^{\circ} \mathrm{C}$ ) is combine with 440. g of water $\left(T_{i}(\right.$ water $\left.)=80.0^{\circ} \mathrm{C}\right)$. The final temperature of the system is $30.1^{\circ} \mathrm{C}$. What is $\Delta \mathrm{H}_{\text {fus }}$ of water in $\frac{\mathrm{kJ}}{\mathrm{mol}}$ ? $C_{H_{2} O(l)}=4.18 \frac{\mathrm{~J}}{\mathrm{~g} \cdot{ }^{\circ} \mathrm{C}}$



## Calorimetry

- 100. mL of $0.500 \mathrm{M} \mathrm{HCl}(0.0500 \mathrm{~mol} \mathrm{HCl})$ was mixed with 75.0 mL of $0.500 \mathrm{M} \mathrm{NaOH}(0.0375 \mathrm{~mol}$ NaOH ) in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solution was the same, $22.50^{\circ} \mathrm{C}$, and the final temperature of the mixed solution was $25.86^{\circ} \mathrm{C}$. Calculate the heat change for the neutralization reaction on a molar basis.
- Assume the density and specific heat of the solution are the same as for water ( $1.00 \frac{g}{m L}$ and $4.184 \frac{\mathrm{~J}}{g^{\circ} \mathrm{cC}^{\prime}}$, respectively)


## $\mathrm{H}_{2}$ Fuel

## Energy Released from Different Fuel Sources

- Natural Gas
$\mathrm{CH}_{4}(\mathrm{I})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
$51 \frac{\mathrm{~kJ}}{\mathrm{~g}}$
- Coal
$\mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})$
17 - $33 \frac{k \mathrm{l}}{\mathrm{g}}$ Depending on impurities
- Gasoline
$\mathrm{C}_{x} \mathrm{H}_{y}(\mathrm{l})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ unbalanced $48 \frac{\mathrm{kj}}{\mathrm{g}}$
- Hydrogen

$$
\begin{aligned}
& \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \\
& 141 \frac{k J}{g}
\end{aligned}
$$



## $\mathrm{H}_{2}$ Fuel

Although there is an abundance of hydrogen containing compounds on earth, very little is free hydrogen.
Where do we get $\mathrm{H}_{2}$ from?

- Natural Gas:
$-\mathrm{CH}_{4}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \xrightarrow{1000^{\circ} \mathrm{C}} 3 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{CO}(\mathrm{g})$
Problem: Uses fossil fuels, need heat (energy), more economical to burn the $\mathrm{CH}_{4}$.
- Electrolysis of Water:
- If a current is passed through $\mathrm{H}_{2} \mathrm{O}$ the water breaks down into its elements.

Problem: The price of electricity is too high to make this competitive as a fuel. Most electricity is generated from fossil fuels.

## $\mathrm{H}_{2}$ Fuel

- Thermal Decomposition:
- $\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2}+1 / 2 \mathrm{O}_{2} \quad\left(\mathrm{~T}=3000^{\circ} \mathrm{C} \sim 1 / 2 \mathrm{H}_{2} \mathrm{O}\right.$ dissociates)

$$
\begin{array}{ll}
2 \mathrm{HI} \rightarrow \mathrm{I}_{2}+\mathrm{H}_{2} & \left(435^{\circ} \mathrm{C}\right) \\
2 \mathrm{H}_{2} \mathrm{O}+\mathrm{SO}_{2}+\mathrm{I}_{2} \rightarrow \mathrm{H}_{2} \mathrm{SO}_{4} & \left(90^{\circ} \mathrm{C}\right) \\
\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{SO}_{2}+\mathrm{H}_{2} \mathrm{O}+1 / 2 \mathrm{O}_{2} & \left(825^{\circ} \mathrm{C}\right) \\
\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2}+1 / 2 \mathrm{O}_{2} &
\end{array}
$$

Problem: Still needs very high temperatures

- Biological Hydrogen Production:
- If certain algae are deprived of sulfur they will switch from producing $\mathrm{O}_{2}$ during photosynthesis to $\mathrm{H}_{2}$.


Problem: Currently the yields are to small to be a viable commercial option.

## $\mathrm{H}_{2}$ Fuel

- Other Problems:
- How to transport $\mathrm{H}_{2}$ ?
- $\mathrm{H}_{2}$ decomposes on metal surfaces
- H atoms are so small they can migrate into metal weakening it.



## Take Away from Chapter 9

- Big Idea: Heat and work are equivalent ways of changing the energy of a system. The total energy of an isolated system is constant. The change in enthalpy of a reaction indicates whether a reaction is endothermic or exothermic.
- Energy Facts
- Internal Energy
- Know the $1^{\text {st }}$ law of thermodynamics and its implications (1)
- The energy of the universe is constant
- Be able to calculate internal energy (E) (24\&25)
- $\Delta E=q+w=\Delta K E+\Delta P E$
- Be able to calculate work (w) $(10,20 \& 103)$
- $w=-P_{e x} \Delta V$
- Be able to calculate heat (q) (11)
- $q=C \Delta T$


## Take Away from Chapter 9

## - Enthalpy

- Be able to calculate change in enthalpy ( $\Delta \mathrm{H}$ ) (37,38,39,42\&125)
- $\Delta H=\Delta E+\Delta(P V)$
- $\Delta H=q$ (At constant pressure)
- Know implications of sign of $\Delta H(16,32)$
- $\Delta H$ is -, exothermic reaction
- $\Delta H$ is + , endothermic reaction
- Be able to draw heating curves
- Know the implications/meaning of $\Delta H_{f u s}$ and $\Delta H_{v a p}$
- Be able to draw reaction coordinates diagrams
- Know how to use change in enthalpy as a conversion factor (35,36\&85)
- Hess's Law
- Know how to get $\Delta H_{r x n}^{\circ}$ from other known $\Delta H_{r x n}^{\circ}$ (66,67,68,69\&70)
- Know how to get $\Delta H_{r x n}^{\circ}$ from $\Delta H_{f}^{\circ}(71,76,77,81,82,88 \& 107)$
- $\Delta H_{r x n}^{\circ}=\sum \Delta H_{f}^{\circ}($ prod $)-\sum \Delta H_{f}^{\circ}($ reac $)$


## Take Away from Chapter 9

## - Calorimetry

- Understand the differences/limitations between constant volume and constant pressure calorimetry (43)
- Be able to solve bomb calorimeter (constant volume) problems $(57,58)$

$$
\text { - } \Delta E_{\text {com }}=-C_{\text {cal }} \Delta T
$$

- Be able to solve coffee cup calorimeter (constant pressure) problems
- Solve for C of non soluble substance $(44,46 \& 48)$
- $q_{\mathrm{H}_{2} \mathrm{O}}=-q_{\text {substance }}$ (if needed add heat $q_{\text {cal }}$ to $q_{\mathrm{H}_{2} \mathrm{O}}$ )
- $m_{\mathrm{H}_{2} \mathrm{O}} C_{\mathrm{H}_{2} \mathrm{O}} \Delta T_{\mathrm{H}_{2} \mathrm{O}}=-m_{\text {sub }} C_{\text {sub }} \Delta T_{\text {sub }}$
- Solve for $\Delta H_{\text {fus }}$
- $q_{\text {solid }}=-q_{\text {liquid }}$ (if needed add heat $q_{\text {cal }}$ to $q_{\text {liquid }}$ )
- $q_{s\left(T_{i_{s}} \rightarrow T_{m_{s}}\right)}+q_{\text {fus }}+q_{l(\text { that was })\left(T_{m_{s}} \rightarrow T_{f}\right)}=-q_{l}$
- $m_{s} C_{s}\left(T_{m_{s}}-T_{i_{s}}\right)+n_{s} \Delta H_{f u s}+m_{s} C_{l}\left(T_{f}-T_{m_{s}}\right)=-m_{l} C_{l}\left(T_{f}-T_{i_{l}}\right)$


## Take Away from Chapter 9

- Calorimetry (Continued)
- Be able to solve coffee cup calorimeter problems
- Solve for $\Delta H_{\text {rxn }}(51,54,55 \& 56)$
- $\Delta H_{r x n}=-q_{\text {solution }}$ (if needed add heat $q_{\text {cal }}$ to $q_{\text {solution }}$ )
- $\Delta H_{r x n}=-m_{\text {solution }} C_{H_{2} O} \Delta T_{\text {solution }}$ (Most times need to divide by number of moles. Be careful many of these are limiting reagent problems.)
- $\mathbf{H}_{2}$ Fuel

