## Chapter 19

## Heat and the 1st Law of Thermodynamics

## Heat

- Heat Capacity \& Specific Heat
- Change of Phase and Latent Heat
- Heat Capacities of Gases
- Heat Capacities of Solids
- First Law of Thermodynamics
- Internal Energy of an Ideal Gas
- Work and PV Diagrams for a Gas


## Heat Energy

# Heat is energy in transit between two systems at different temperatures. Heat spontaneously flows from the system at the higher temperature to the system at the lower temperature. 

## Heat Energy

Experiments by Joule showed the equivalence of Work and Energy

A quantity of work done on a system causes the same increase in that system's internal energy as an identical quantity of heat flowing into the system.

Heat is measured in joules or calories.
$1 \mathrm{cal}=4.186 \mathrm{~J}$ (the mechanical equivalent of heat);
1 Calorie $($ used on food packaging $)=1 \mathrm{kcal}$.

## Heat Capacity and Specific Heat

For many substances, under normal circumstances $\Delta T \propto Q$. Or $\mathrm{Q}=\mathrm{C} \Delta \mathrm{T}$ where C is the heat capacity .

The specific heat capacity, or just specific heat, of a substance is the heat capacity per unit mass.

$$
c=\frac{C}{m}=\frac{Q}{m \Delta T} \quad \text { or } \quad Q=m c \Delta T
$$

## Example:

125.6 kJ of heat are supplied to $5.00 \times 10^{2} \mathrm{~g}$ of water at 22 ${ }^{\circ} \mathrm{C}$. What is the final temperature of the water?

$$
\begin{aligned}
Q & =m c \Delta T=m c\left(T_{\mathrm{f}}-T_{\mathrm{i}}\right) \\
T_{\mathrm{f}} & =T_{\mathrm{i}}+\frac{Q}{m c} \\
& =22^{\circ} \mathrm{C}+\frac{125.6 \mathrm{~kJ}}{(0.5 \mathrm{~kg})\left(4.186 \mathrm{~kJ} / \mathrm{kg}^{\circ} \mathrm{C}\right)}=82^{\circ} \mathrm{C}
\end{aligned}
$$

## Example:

A 0.400 kg aluminum tea kettle contains 2.00 kg of water at 15.0 ${ }^{\circ} \mathrm{C}$. How much heat is required to raise the temperature of the water (and kettle) to $100{ }^{\circ} \mathrm{C}$ ?

The heat needed to raise the temperature of the water to $T_{\mathrm{f}}$ is

$$
Q_{\mathrm{w}}=m_{\mathrm{w}} c_{\mathrm{w}} \Delta T_{\mathrm{w}}=(2 \mathrm{~kg})\left(4.186 \mathrm{~kJ} / \mathrm{kg}^{\circ} \mathrm{C}\right)\left(85^{\circ} \mathrm{C}\right)=712 \mathrm{~kJ}
$$

The heat needed to raise the temperature of the aluminum to $T_{f}$ is

$$
Q_{\mathrm{Al}}=m_{\mathrm{Al}} c_{\mathrm{Al}} \Delta T_{\mathrm{Al}}=(0.4 \mathrm{~kg})\left(0.900 \mathrm{~kJ} / \mathrm{kg}^{\circ} \mathrm{C}\right)\left(85^{\circ} \mathrm{C}\right)=30.6 \mathrm{~kJ}
$$

$$
\text { Then } \mathrm{Q}_{\text {total }}=\mathrm{Q}_{\mathrm{w}}+\mathrm{Q}_{\mathrm{Al}}=732 \mathrm{~kJ} \text {. }
$$

## Molar Specific Heat at Constant Volume

The molar specific heat at constant volume is defined below; this is the heat capacity per mole.

$$
C_{\mathrm{v}}=\frac{Q}{n \Delta T}
$$

Heat is allowed to flow into a gas, but the gas is not allowed to expand. If the gas is ideal and monatomic, the heat goes into increasing the average kinetic energy of the particles.

Ideal gas conditions will prevail if we keep the gas density low enough. Examples of monatomic gases are the noble gases such as $\mathrm{He}, \mathrm{Ne}, \mathrm{Ar}, \mathrm{Xe}$; they have no internal degrees of freedom with which to share the energy. Therefore, it all goes into the three translational degrees of freedom.

## Cylinder for Ideal Gas Experiments



## Cylinder for Ideal Gas Experiments



Chamber set constant volume process. The pin prevents the piston from moving.

## Specific Heat of Ideal Gases

The average kinetic energy of a molecule in an ideal gas is

$$
\left\langle K_{\mathrm{tr}}\right\rangle=\frac{3}{2} k T .
$$

And the total kinetic energy of the gas is

$$
K_{\mathrm{tr}}=\frac{3}{2} N k T=\frac{3}{2} n R T .
$$

## Molar Specific Heat

The amount of added heat is $\quad \Delta K_{\mathrm{tr}}=Q=\frac{3}{2} n R \Delta T$.

$$
C_{V}=\frac{Q}{n \Delta T}=\frac{\frac{3}{2} n R \Delta T}{n \Delta T}=\frac{3}{2} R=12.5 \frac{\mathrm{~J}}{\mathrm{~mol}-\mathrm{K}}
$$

If the gas is diatomic: $\quad C_{V}=\frac{5}{2} R=20.8 \frac{\mathrm{~J}}{\mathrm{~mol}-\mathrm{K}}$

## The Equipartition Theorem

"When a substance is in equilibrium, there is an average energy of $\frac{1}{2} k T$ per molecule or $\frac{l}{2} R T$ per mole associated with each degree of freedom." Tipler \& Mosca

## Degrees of Freedom-Molar Specific Heat



This shows the effects of internal degrees of freedom on the molar specific heat at constant volume for a $\mathrm{H}_{2}$ atoms. Below $\mathrm{T}=75 \mathrm{~K}$ the behavior would be similar to that of a monatomic atom.

## Rotational Degrees of Freedom

Internal energy will be distributed equally among all possible degrees of freedom (equipartition of energy). Each degree of freedom contributes $1 / 2 \mathrm{kT}$ of energy per molecule and $1 / 2 R$ to the molar specific heat at constant volume.

Rotational motions of a 2-atom molecule:


## Example:

A container of nitrogen gas $\left(\mathrm{N}_{2}\right)$ at $23^{\circ} \mathrm{C}$ contains 425 L at a pressure of 3.5 atm . If 26.6 kJ of heat are added to the container, what will be the new temperature of the gas?

$$
\text { For a diatomic gas, } \quad Q=n C_{\mathrm{V}} \Delta T .
$$

The number of moles $n$ is given by the ideal gas law

$$
n=\frac{P_{\mathrm{i}} V_{\mathrm{i}}}{R T_{\mathrm{i}}} .
$$

## Example continued:

The change in temperature is

$$
\begin{aligned}
\Delta T & =\left(\frac{Q}{C_{\mathrm{V}}}\right)\left(\frac{R T_{\mathrm{i}}}{P_{\mathrm{i}} V_{\mathrm{i}}}\right) \\
& =\left(\frac{26.6 \times 10^{3} \mathrm{~J}}{2.5 R}\right) \frac{R(296 \mathrm{~K})}{(3.5 \mathrm{~atm})\left(1.013 \times 10^{5} \mathrm{~N} / \mathrm{m}^{2} / \mathrm{atm}\right)(425 \mathrm{~L})\left(10^{-3} \mathrm{~m}^{3} / \mathrm{L}\right)} \\
& =21 \mathrm{~K}
\end{aligned}
$$

The final temperature of the gas is $\mathrm{T}_{\mathrm{f}}$

$$
=\mathrm{T}_{\mathrm{i}}+\Delta \mathrm{T}=317 \mathrm{~K}=44^{\circ} \mathrm{C}
$$

## Specific Heats and Molar Specific Heats

TABLE 18-1
Specific Heats and Molar Specific Heats of Some Solids and Liquids

| Substance | $c, \mathrm{~kJ} / \mathrm{kg} \cdot \mathrm{K}$ | $\mathrm{c}, \mathrm{kcal} / \mathrm{kg} \cdot \mathrm{K}$ <br> or $\mathrm{Bru} / \mathrm{lb} \cdot \mathrm{F}^{\circ}$ | $\mathrm{c}^{\prime}, \mathrm{J} / \mathrm{mol} \cdot \mathrm{K}$ |
| :--- | :--- | :--- | :---: |
| Aluminum | 0.900 | 0.215 | 24.3 |
| Bismuth | 0.123 | 0.0294 | 25.7 |
| Copper | 0.386 | 0.0923 | 24.5 |
| Glass | 0.840 | 0.20 | - |
| Gold | 0.126 | 0.0301 | 25.6 |
| Ice $\left(-10^{\circ} \mathrm{C}\right)$ | 2.05 | 0.49 | 36.9 |
| Lead | 0.128 | 0.0305 | 26.4 |
| Silver | 0.233 | 0.0558 | 24.9 |
| Tungsten | 0.134 | 0.0321 | 24.8 |
| Zinc | 0.387 | 0.0925 | 25.2 |
| Alcohol (ethyl) | 2.4 | 0.58 | 111 |
| Mercury | 0.140 | 0.033 | 28.3 |
| Water | 4.18 | 1.00 | 75.2 |

## Molar Heat Capacities

## TABLE 18-3

Molar Heat Capacities in $\mathrm{J} / \mathrm{mol} \cdot \mathrm{K}$ of Various Gases at $25^{\circ} \mathrm{C}$

| Gas | $c_{p}^{\prime}$ | $c_{v}^{\prime}$ | $c_{v}^{\prime} / R$ | $c_{p}^{\prime}-c_{v}^{\prime}$ | $\left(c_{p}^{\prime}-c_{v}^{\prime}\right) / R$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Monatomic |  |  |  |  |  |
| He | 20.79 | 12.52 | 1.51 | 8.27 | 0.99 |
| Ne | 20.79 | 12.68 | 1.52 | 8.11 | 0.98 |
| Ar | 20.79 | 12.45 | 1.50 | 8.34 | 1.00 |
| Kr | 20.79 | 12.45 | 1.50 | 8.34 | 1.00 |
| Xe | 20.79 | 12.52 | 1.51 | 8.27 | 0.99 |
| Diatomic |  |  |  |  |  |
| $\mathrm{N}_{2}$ | 29.12 | 20.80 | 2.50 | 8.32 | 1.00 |
| $\mathrm{H}_{2}$ | 28.82 | 20.44 | 2.46 | 8.38 | 1.01 |
| $\mathrm{O}_{2}$ | 29.37 | 20.98 | 2.52 | 8.39 | 1.01 |
| $\mathrm{CO}^{2}$ | 29.04 | 20.74 | 2.49 | 8.30 | 1.00 |
| Polyatomic |  |  |  |  |  |
| $\mathrm{CO}_{2}$ | 36.62 | 28.17 | 3.39 | 8.45 | 1.02 |
| $\mathrm{~N}_{2} \mathrm{O}$ | 36.90 | 28.39 | 3.41 | 8.51 | 1.02 |
| $\mathrm{H}_{2} \mathrm{~S}$ | 36.12 | 27.36 | 3.29 | 8.76 | 1.05 |

# Latent heat is the amount of heat per unit mass required to change the phase of a substance. The energy is used to form/break chemical bonds. 

The latent heat of fusion $\left(\mathrm{L}_{\mathrm{f}}\right)$ is the heat per unit mass needed to produce the solid-liquid phase transition. $\mathrm{Q}_{\mathrm{f}}=\mathrm{mL}_{\mathrm{f}}$

The latent heat of vaporization $\left(\mathrm{L}_{\mathrm{v}}\right)$ is the heat per unit mass needed to produce the liquid-gas phase transition. $\mathrm{Q}_{\mathrm{v}}=\mathrm{mL}_{\mathrm{v}}$

## Phase Transitions

A phase transition occurs whenever a substance changes from one phase (solid, liquid, or gas) to another.

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## Example:

A 75 g cube of ice at $-10.0^{\circ} \mathrm{C}$ is placed in 0.500 kg of water at $50.0^{\circ} \mathrm{C}$ in an insulating container so that no heat is lost to the environment. Will the ice melt completely? What will be the final temperature of this system?

The heat required to completely melt the ice is

$$
\begin{aligned}
Q_{\mathrm{ice}} & =m_{\mathrm{icc}} \mathrm{c}_{\mathrm{ice}} \Delta T_{\mathrm{ice}}+m_{\mathrm{ice}} L_{\mathrm{f}} \\
& =(0.075 \mathrm{~kg})\left(2.1 \mathrm{~kJ} / \mathrm{kg}{ }^{\circ} \mathrm{C}\right)\left(10^{\circ} \mathrm{C}\right)+(0.075 \mathrm{~kg})(333.7 \mathrm{~kJ} / \mathrm{kg}) \\
& =27 \mathrm{~kJ}
\end{aligned}
$$

The heat required to cool the water to the freezing point is

$$
\begin{aligned}
Q_{\mathrm{w}} & =m_{\mathrm{w}} c_{\mathrm{w}} \Delta T_{\mathrm{w}} \\
& =(0.5 \mathrm{~kg})\left(4.186 \mathrm{~kJ} / \mathrm{kg}{ }^{\circ} \mathrm{C}\right)\left(50^{\circ} \mathrm{C}\right) \\
& =105 \mathrm{~kJ}
\end{aligned}
$$

## Example continued:

Since $\mathrm{Q}_{\text {ice }}<\mathrm{Q}_{\text {water }}$ the ice will completely melt.
To find the final temperature of the system, note that no heat is lost to the environment; the heat lost by the water is gained by the ice.
$0=\mathrm{Q}_{\text {ice }}+\mathrm{Q}_{\mathrm{w}}$
$0=\mathrm{m}_{\mathrm{ice}} \mathrm{c}_{\mathrm{ice}} \Delta \mathrm{T}+\mathrm{m}_{\mathrm{ice}} \mathrm{L}_{\mathrm{f}}+\mathrm{m}_{\mathrm{ice}} \mathrm{c}_{\mathrm{w}}\left(\mathrm{T}_{\mathrm{f}}-\mathrm{T}_{\mathrm{ice}, \mathrm{i}}\right)+\mathrm{m}_{\mathrm{w}} \mathrm{c}_{\mathrm{w}}\left(\mathrm{T}_{\mathrm{f}}-\mathrm{T}_{\mathrm{w}, \mathrm{i}}\right)$
$0=\mathrm{m}_{\text {ice }} \mathrm{c}_{\mathrm{ice}} \Delta \mathrm{T}+\mathrm{m}_{\mathrm{ice}} \mathrm{L}_{\mathrm{f}}+\left(\mathrm{m}_{\text {ice }}+\mathrm{m}_{\mathrm{w}}\right) \mathrm{c}_{\mathrm{w}} \mathrm{T}_{\mathrm{f}}-\mathrm{m}_{\mathrm{w}} \mathrm{c}_{\mathrm{w}} \mathrm{T}_{\mathrm{w}, \mathrm{i}}$
$0=27 \mathrm{~kJ}+\left(\mathrm{m}_{\mathrm{ice}}+\mathrm{m}_{\mathrm{w}}\right) \mathrm{c}_{\mathrm{w}} \mathrm{T}_{\mathrm{f}}-105 \mathrm{~kJ}$
$78 \mathrm{~kJ}=\left(\mathrm{m}_{\mathrm{ice}}+\mathrm{m}_{\mathrm{w}}\right) \mathrm{c}_{\mathrm{w}} \mathrm{T}_{\mathrm{f}}$
$\mathrm{T}_{\mathrm{f}}=32.4^{\circ} \mathrm{C}$
All $\Delta \mathrm{T}$ factors are $\mathrm{T}_{\mathrm{f}}-\mathrm{T}_{\mathrm{i}}$

## Energy Gained $=$ Energy Lost

$$
\begin{aligned}
& \mathrm{Q}_{\text {ice }}=\mathrm{Q}_{\mathrm{w}} \\
& m_{i c e} c_{\text {ice }} \Delta T+m_{\text {ice }} L_{f}+\left(m_{i c e}+m_{w}\right) c_{w} T_{f}=m_{w} c_{w} T_{w, i} \\
& 27 \mathrm{~kJ}+\left(\mathrm{m}_{\mathrm{ice}}+\mathrm{m}_{\mathrm{w}}\right) \mathrm{c}_{\mathrm{w}} \mathrm{~T}_{\mathrm{f}}=105 \mathrm{~kJ} \\
& \left(\mathrm{~m}_{\mathrm{ice}}+\mathrm{m}_{\mathrm{w}}\right) \mathrm{c}_{\mathrm{w}} \mathrm{~T}_{\mathrm{f}}=105 \mathrm{~kJ}-27 \mathrm{~kJ}=78 \mathrm{~kJ} \\
& \left(\mathrm{~m}_{\text {ice }}+\mathrm{m}_{\mathrm{w}}\right) \mathrm{c}_{\mathrm{w}} \mathrm{~T}_{\mathrm{f}}=78 \mathrm{~kJ} \\
& \mathrm{~T}_{\mathrm{f}}=32.4^{\circ} \mathrm{C}
\end{aligned}
$$

Advantage - all terms start out as positive amount of energy

## Example:

The specific heat of the solid is $0.129 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$. Assume 31.15 kJ will change 0.500 kg of the solid at $21^{\circ} \mathrm{C}$ to liquid at $327^{\circ} \mathrm{C}$, the melting point.
Compute the heat of fusion of a substance from these data.

$$
\begin{aligned}
& Q=m c \Delta T+m L_{\mathrm{f}} \\
& L_{\mathrm{f}}=\frac{Q-m c \Delta T}{m}=22.8 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

On a phase diagram, the triple point is the set of P and T where all three phases can coexist in equilibrium.


Sublimation is the process by which a solid transitions into a gas (and gas $\rightarrow$ solid).

The critical point marks the end of the vapor pressure curve.

A path around this point (i.e. the path does not cross the curve) does not result in a phase transition.


Past the critical point it is not possible to distinguish between the liquid and gas phases.

## Specific Heat Capacity

| Table 10-1 | $\begin{array}{l}\text { Specific Heats and Molar Specific Heats } \\ \text { of Some Solids and Liquids }\end{array}$ |  |  |
| :--- | :--- | :--- | :--- |
|  | c, $\mathrm{kcal} / \mathrm{kg} \cdot \mathrm{K}$ |  |  |$]$.

Liquids are in red typeface and gases are in blue typeface.

## Molar Heat Capacities

## Table 18-3

Molar Heat Capacities in $\mathrm{J} / \mathrm{mol} \cdot \mathrm{K}$ of Various Gases at $25^{\circ} \mathrm{C}$

| Gas | $c_{\mathrm{P}}^{\prime}$ | $c_{\mathrm{V}}^{\prime}$ | $c_{\mathrm{V}}^{\prime} / R$ | $c_{\mathrm{P}}^{\prime}-c_{\mathrm{V}}^{\prime}$ | $\left(c_{\mathrm{P}}^{\prime}-c_{\mathrm{V}}^{\prime}\right) / R$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Monatomic |  |  |  |  |  |
| He | 20.79 | 12.52 | 1.51 | 8.27 | 0.99 |
| Ne | 20.79 | 12.68 | 1.52 | 8.11 | 0.98 |
| Ar | 20.79 | 12.45 | 1.50 | 8.34 | 1.00 |
| Kr | 20.79 | 12.45 | 1.50 | 8.34 | 1.00 |
| Xe | 20.79 | 12.52 | 1.51 | 8.27 | 0.99 |
| Diatomic |  |  |  |  |  |
| $\mathrm{N}_{2}$ | 29.12 | 20.80 | 2.50 | 8.32 | 1.00 |
| $\mathrm{H}_{2}$ | 28.82 | 20.44 | 2.46 | 8.38 | 1.01 |
| $\mathrm{O}_{2}$ | 29.37 | 20.98 | 2.52 | 8.39 | 1.01 |
| $\mathrm{CO}_{\mathrm{O}}$ | 29.04 | 20.74 | 2.49 | 8.30 | 1.00 |
| Polyatomic $_{\text {CO }}$ |  |  |  |  |  |
| $\mathrm{N}_{2}$ | 36.62 | 28.17 | 3.39 | 8.45 | 1.02 |
| $\mathrm{H}_{2} \mathrm{~S}$ | 36.90 | 28.39 | 3.41 | 8.51 | 1.02 |

## Thermal Properties of Various Materials

| Table 18-2 | Melting Point (MP), Latent Heat of Fusion (Lif), Boiling Point (BP), and Latent Heat of Vaporization $\left(L_{\mathrm{v}}\right)$, all at 1 atm , for Various Substances |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Substance | MP, K | $L_{f}, \mathrm{~kJ} / \mathrm{kg}$ | BP, K | $L_{\mathrm{v}}, \mathrm{kJ} / \mathrm{kg}$ |
| Alcohol, ethyl | 159 | 109 | 351 | 879 |
| Bromine | 266 | 67.4 | 332 | 369 |
| Carbon dioxide | de | - | 194.6* | 573* |
| Copper | 1356 | 205 | 2839 | 4726 |
| Gold | 1336 | 62.8 | 3081 | 1701 |
| Helium | - | - | 4.2 | 21 |
| Lead | 600 | 24.7 | 2023 | 858 |
| Mercury | 234 | 11.3 | 630 | 296 |
| Nitrogen | 63 | 25.7 | 77.35 | 199 |
| Oxygen | 54.4 | 13.8 | 90.2 | 213 |
| Silver | 1234 | 105 | 2436 | 2323 |
| Sulfur | 388 | 38.5 | 717.75 | 287 |
| Water (liquid) | 273.15 | 333.5 | 373.15 | 2257 |
| Zinc | 692 | 102 | 1184 | 1768 |

[^0]
## Vibrational Degrees of Freedom

Symmetric stretch mode


Asymmetric stretch mode

(b)

(c)

## Spring Model of a Solid



$$
c^{\prime}=3 R=24.9 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K}
$$

$$
E_{\text {int } m}=6 \times \frac{1}{2} R T=3 R T
$$

## Equipartition Theorem

"It is interesting to note that the successes of the equipartion theorem in explaining the measured heat capacity of gases and solids led to the first real understanding of molecular structure in the 19th century, whereas its failures played an important role in the development of quantum mechanics in the 20th century."

Tipler \& Mosca, p. 614

## Thermodynamics

Thermodynamics is the study of the inter-relation between heat, work and internal energy of a system and its interaction with its environment.

Example systems

- Gas in a container
- Magnetization and demagnetization
- Charging \& discharging a battery


Universe

- Chemical reactions
- Thermocouple operation


## Thermodynamics States

A state variable describes the state of a system at time $t$, but it does not reveal how the system was put into that state.

Examples of state variables:

- $\mathrm{P}=$ pressure ( Pa or $\mathrm{N} / \mathrm{m}^{2}$ ),
- $\mathrm{T}=$ temperature $(\mathrm{K})$,
- $\mathrm{V}=$ volume ( $\mathrm{m}^{3}$ ),
- $\mathrm{n}=$ number of moles, and
- $\mathrm{U}=$ internal energy (J).


## The First Law of Thermodynamics

The first law of thermodynamics says the change in internal energy of a system is equal to the heat flow into the system plus the work done on the system (conservation of energy).

$$
\Delta U=Q+W
$$

## The First Law of Thermodynamics



## First Law of Thermodynamics



## Internal Energy of an Ideal Gas



## Free Expansion - System Isolated

$$
\text { No work done }-\Delta \mathrm{U}=0
$$

$T_{i}=T_{f}$ for an ideal gas - In reality there is cooling, example $\mathrm{CO}_{2} \rightarrow$ Dry Ice

## Sign Conventions

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Table 15.1 Sign Conventions for the First Law of Thermodynamics

| Quantity | Definition | Meaning of + Sign | Meaning of - Sign |
| :--- | :--- | :--- | :--- |
| $Q$ | Heat flow into the system | Heat flows into the <br> system | Heat flows out of the system |
| $W$ | Work done on the system | Surroundings do <br> positive work on the <br> system | Surroundings do negative <br> work on the system (system <br> does positive work on the <br> surroundings) |
| $\Delta U$ | Internal energy change | Internal energy <br> increases | Internal energy decreases |

## Work and an Ideal Gas

$$
\text { Work }=P \Delta V=\frac{F}{A} A \Delta h=F \Delta h=\text { Force } x \text { Distance }
$$

## Thermodynamic Processes

A thermodynamic process is represented by a change in one or more of the thermodynamic variables describing the system.


## Reversible and Irreversible Processes

A process is reversible if it does not violate any law of physics when it is run backwards in time.

For example an ice cube placed on a counter top in a warm room will melt.

The reverse process cannot occur: an ice cube will not form out of the puddle of water on the counter top in a warm room.

A collision between two billiard balls is reversible. Momentum is conserved if time is run forward; momentum is still conserved if time runs backwards.

## Reversible Thermodynamic Process

For a process to be reversible each point on the curve must represent an equilibrium state of the system.


The ideal gas law ( $\mathrm{PV}=\mathrm{nRT}$ ), does not describe the system when it is not in a state of thermal equilibrium.

## Thermodynamic Processes

A PV diagram can be used to represent the state changes of a system, provided the system is always near equilibrium.

The area under a PV curve gives the magnitude of the work done on a system. W>0 for compression and $\mathrm{W}<0$ for expansion.

(b)

## Work for Three Different Pathways

To go from the state $\left(\mathrm{V}_{\mathrm{i}}, \mathrm{P}_{\mathrm{i}}\right)$ by the path (a) to the state $\left(\mathrm{V}_{\mathrm{f}}, \mathrm{P}_{\mathrm{f}}\right)$ requires a different amount of work then by path (b). To return to the initial point (1) requires the work to be nonzero.


The work done on a system depends on the path taken in the PV diagram.
The work done on a system during a closed cycle can be nonzero.

## Isothermal Process



An isothermal process implies that both P and V of the gas change ( $\mathrm{PV} \propto \mathrm{T}$ ).

## Summary of Thermodynamic Processes

| Process | Name | Condition | Consequences |
| :--- | :--- | :--- | :--- |
| Constant temperature | Isothermal | $T=$ constant | $($ For an ideal gas, $\Delta U=0)$ |
| Constant pressure | Isobaric | $P=\mathrm{constant}$ | $W=-P \Delta V$ |
| Constant volume | Isochoric | $V=$ constant | $W=0 ; \Delta U=Q$ |
| No heat flow | Adiabatic | $Q=0$ | $\Delta U=W$ |

## Summary of Thermal Processes

The First Law of Thermodynamics

Type of Thermal Process
Isobaric
$\quad$ (constant pressure)

Isochoric
(constant volume)

Isothermal
(constant temperature)

Adiabatic
(no heat flow)

Work Done
$W=P\left(V_{\mathrm{f}}-V_{\mathrm{i}}\right)$
$W=-P\left(V_{f}-V_{i}\right)$
$W=0 \mathrm{~J}$
$\left.\begin{array}{l}W=n R T \ln \left(\frac{V_{i}}{W}=n R T \ln \left(\frac{V}{V_{i}}\right.\right. \\ V_{i}\end{array}\right)$
(for an ideal gas)
$W=\frac{3}{2} n R\left(T_{\mathrm{f}}-T_{\mathrm{i}}\right)$
(for a monatomic ideal gas)

$$
\begin{aligned}
& \Delta U=Q+W \\
& \Delta U=Q-\underbrace{P\left(V_{\mathrm{f}}-V_{\mathrm{i}}\right)}_{W} \\
& \Delta U=Q-\underbrace{0 \mathrm{~J}}_{W} \\
& \begin{aligned}
\underbrace{0 \mathrm{~J}}_{\begin{array}{c}
\Delta \text { for an } \\
\text { ideal gas }
\end{array}}=Q-\underbrace{\left.\begin{array}{c}
W \\
\\
+n R T \ln \left(\frac{V_{i}}{V_{\mathrm{f}}}\right)
\end{array}\right)}_{W}
\end{aligned} \\
& \Delta U=\underbrace{0 \mathrm{~J}}_{Q}+\frac{3}{2} n R\left(T_{f}-T_{i}\right)
\end{aligned}
$$

## Thermodynamic Processes for an Ideal Gas

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No work is done on a system when its volume remains constant (isochoric process). For an ideal gas (provided the number of moles remains constant), the change in internal energy is

$$
Q=\Delta U=n C_{V} \Delta T .
$$

## Isobaric Process



## Isobaric Process

For a constant pressure (isobaric) process, the change in internal energy is

$$
\Delta U=Q+W
$$

where

$$
W=-P \Delta V=-n R \Delta T \text { and } Q=n C_{P} \Delta T
$$

$C_{P}$ is the molar specific heat at constant pressure. For an ideal gas $\mathrm{C}_{\mathrm{P}}=\mathrm{C}_{\mathrm{V}}+\mathrm{R}$.

## Specific Heats: $\mathrm{C}_{\mathrm{P}}$ and $\mathrm{C}_{\mathrm{V}}$

For an ideal gas $\mathrm{C}_{\mathrm{P}}=\mathrm{C}_{\mathrm{V}}+\mathrm{R}$
Therefore $\mathrm{C}_{\mathrm{P}}$ is always greater than $\mathrm{C}_{\mathrm{V}}$
For a constant pressure process the volume can change and work can be done.

For a constant volume process the volume cannot change and NO work can be done.

$$
\Delta U=Q+W
$$

For a constant V process all the energy goes into raising T .
For a constant P process some of the energy goes into work.
If it takes more energy to reach a given $T$, then C is larger.

## Isothermal Process



## Isothermal Process

For a constant temperature (isothermal) process, $\Delta \mathrm{U}=0$ and the work done on an ideal gas is

$$
W=n R T \ln \left(\frac{V_{\mathrm{i}}}{V_{\mathrm{f}}}\right) .
$$

## Isometric Process



## Isochoric Process

Example: An ideal monatomic gas is taken through a cycle in the PV diagram.
(a) If there are 0.0200 mol of this gas, what are the temperature and pressure at point $C$ ?


From the graph: $\mathrm{P}_{\mathrm{c}}$
$=98.0 \mathrm{kPa}$
Using the ideal gas law

$$
T_{\mathrm{c}}=\frac{P_{\mathrm{c}} V_{\mathrm{c}}}{n R}=1180 \mathrm{~K}
$$

Example continued:
(b) What is the change in internal energy of the gas as it is taken from point $A$ to $B$ ?

This is an isochoric process so $\mathrm{W}=0$ and $\Delta \mathrm{U}=\mathrm{Q}$.

$$
\begin{aligned}
\Delta U & =Q=n C_{V} \Delta T=n\left(\frac{3}{2} R\right)\left(\frac{P_{B} V_{B}}{n R}-\frac{P_{A} V_{A}}{n R}\right) \\
& =\frac{3}{2}\left(P_{B} V_{B}-P_{A} V_{A}\right) \\
& =\frac{3}{2} V\left(P_{B}-P_{A}\right)=-200 \mathrm{~J}
\end{aligned}
$$

Example continued:
(c) How much work is done by this gas per cycle?

The work done per cycle is the area between the curves on the PV diagram. Here $\mathrm{W}=1 / 2 \Delta \mathrm{~V} \Delta \mathrm{P}=66 \mathrm{~J}$.
(d) What is the total change in internal energy of this gas in one cycle?

$$
\begin{aligned}
\Delta U & =n C_{V} \Delta T=n\left(\frac{3}{2} R\right)\left(\frac{P_{\mathrm{f}} V_{\mathrm{f}}}{n R}-\frac{P_{\mathrm{i}} V_{\mathrm{i}}}{n R}\right) \\
& =\frac{3}{2}\left(P_{\mathrm{f}} V_{\mathrm{f}}-P_{\mathrm{i}} V_{\mathrm{i}}\right)=0 \quad \begin{array}{l}
\text { The cycle ends where it } \\
\text { began }(\Delta \mathrm{T}=0)
\end{array}
\end{aligned}
$$

## Isothermal Process

Example:
An ideal gas is in contact with a heat reservoir so that it remains at constant temperature of 300.0 K . The gas is compressed from a volume of 24.0 L to a volume of 14.0 L . During the process, the mechanical device pushing the piston to compress the gas is found to expend 5.00 kJ of energy.

How much heat flows between the heat reservoir and the gas, and in what direction does the heat flow occur?

This is an isothermal process, so $\Delta \mathrm{U}=\mathrm{Q}+\mathrm{W}=0$ (for an ideal gas) and $\mathrm{W}=-\mathrm{Q}=-5.00 \mathrm{~kJ}$. Heat flows from the gas to the reservoir.

## Adiabatic Process



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## Extra Slides

## Isotherms of a Pure Substance



## P-V-T Surface for Helium



The top surface is characteristic of water while the surface on the bottom is characteristic of most other substances.


Fig. 11.8. $P-V-T$ surface for a substance which expands upon freezing.


Fig. 11.9. $P-V-T$ surface for a substance which contracts upon freezing.

## The Very Complex P-V-T Surface for Water



Fig. 11.10. $P$ - $V$ - $T$ surface for water, showing all the triple points. Constructed by Verwiebe on the basis of measurements by Bridgman.


[^0]:    * These values are for sublimation. Carbon dioxide does not have a liquid state at 1 atm .

