## Chapter 19 The Kinetic Theory of Gases

- 3 variables associated with a gas:
(1) volume: a result of the freedom the atoms have to spread throughout the container
(2) pressure: a result of the collisions of the atoms with the container's walls
(3) temperature: related to the kinetic energy of the atoms


## Avogadro's Number

One mole is the number of atoms in a 12 g sample of carbon- 12 .

- Avogadro's number $N_{A}=6.02 \times 10^{23} / \mathrm{mole}$ Avogadro's number
- Avogadro suggested that all gases occupying the same volume under the same conditions of temperature and pressure contain the same number of atoms or molecules.
- The number of moles $n=\frac{N}{N_{A}}$
- the number of moles $n$ in a sample from the mass $M_{\text {sam }}$ of the sample and either the molar mass $M$ (the mass of 1 mole) or the molecular mass $m$ (the mass of one molecule):

$$
n=\frac{M_{\mathrm{sam}}}{M}=\frac{M_{\mathrm{sam}}}{m N_{A}} \Leftarrow \Leftarrow \quad M=m N_{A}
$$

## Ideal Gases

- At low enough densities, all real gases tend to obey the relation

$$
p V=n R T \text { ideal gas law }
$$

$R$ is the gas constant $R=8.31 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$.

- We can rewrite the equation in terms of the Boltzmann constant, $k=\frac{R}{N_{A}}=\frac{8.31 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}}{6.02 \times 10^{23} \mathrm{~mol}^{-1}}=1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}$
$\Rightarrow n R=N k \quad p \quad p V=N k T$ ideal gas law
- An ideal gas is defined as a gas which behavior follows the above equation.
- All real gases approach the ideal state at low enough densities and at high enough temperature.

Work Done by an Ideal Gas at Constant Temperature

- isothermal expansion (or isothermal compression): A process carried out from an initial volume $V_{i}$ to a final volume $V_{f}$ at constant temperature.
- On a $p$ - $V$ diagram, an isotherm is a curve that connects points that have the same temperature, ie, a graph of pressure versus volume for a gas whose temperature $T$ is held constant.

$$
p=n R T \frac{1}{V}=(\mathrm{a} \text { constant }) \frac{1}{V}
$$

- the isotherms with different temperatures doesn't cross each other.
- the work done by an ideal gas during an isothermal process

$$
W=\int_{V_{i}}^{V_{f}} p \mathrm{~d} V=\int_{V_{i}}^{V_{f}} \frac{n R T}{V} \mathrm{~d} V \Leftarrow p V=n R T
$$

- For an isothermal process: $T=$ const $\Rightarrow W=n R T \int_{V_{i}}^{V_{f}} \frac{\mathrm{~d} V}{V}=\left.n R T \ln V\right|_{V_{i}} ^{V_{f}}$

$$
\Rightarrow W=n R T \ln \frac{V_{f}}{V_{i}}
$$

- For $V_{f}>V_{i}$ (expansion), the work $W$ done by an ideal gas is positive; For $V_{f}<V_{i}$ (compression), the work $W$ done by an ideal gas is negative.


## Work Done at Constant Volume and at Constant Pressure

- If the volume of the gas is constant, then $W=0$ constant-volume process
- If the volume changes while the pressure $p$ of the gas is held constant, then
$W=p\left(V_{f}-V_{i}\right)=p \Delta V \quad$ constant-pressure process problem 19-1 problem 19-2


## Pressure, Temperature, and RMS Speed

- $n$ moles of an ideal gas are confined in a cubicä̃ 1.0 box of volume $V$. The walls of the box are held at temperature $T$. We need to relate the macroscopic quantity - pressure $p$, to the microscopic quantity - the velocity of the molecule $v$.
- the momentum $\Delta p_{x}$ delivered to the wall by the molecule is $+2 m v_{x}$.
- The molecule of will hit the wall repeatedly. The time $\Delta t$ between collisions is the time the molecule takes to travel to the opposite wall and back again (a distance $2 L$ ) at speed $v_{x}$

$$
\Delta t=\frac{2 L}{v_{x}}
$$

- the average rate at which momentum is delivered to the wall by this single molecule is

$$
\frac{\Delta p_{x}}{\Delta t}=\frac{2 m v_{x}}{2 L / v_{x}}=\frac{m v_{x}^{2}}{L}
$$

- From Newton's $2^{\text {nd }}$ law, the rate at which momentum is delivered to the wall is the force acting on that wall.
- Dividing the magnitude of the total force $F_{x}$ by the area of the wall $\left(=L^{2}\right)$ gives the pressure $p$ on that wall.
- we can write this pressure: $p=\frac{F_{x}}{L^{2}}=\frac{m v_{x 1}^{2} / L+\cdots+m v_{x \mathrm{~N}}^{2} / L}{L^{2}}=\frac{m}{L^{3}} \sum_{i=1}^{N} v_{x i}^{2}$

$$
\begin{aligned}
& \left(v_{x}^{2}\right)_{\mathrm{avg}}=\frac{1}{N} \sum_{i=1}^{N} v_{x i}^{2}, \quad N=n N_{A} \text { and } M=N_{A} m \quad \text { the molar mass } \\
& \Rightarrow \quad p=\frac{m}{L^{3}} \sum_{i=1}^{N} v_{x i}^{2}=\frac{m}{V} N\left(v_{x}^{2}\right)_{\mathrm{avg}}=\frac{n m N_{A}}{V}\left(v_{x}^{2}\right)_{\mathrm{avg}}=\frac{n M\left(v_{x}^{2}\right)_{\mathrm{avg}}}{V}
\end{aligned}
$$

- For any molecule, $v^{2}=v_{x}^{2}+v_{y}^{2}+v_{z}^{2}$. Because there are many molecules and because they are all moving in random directions, the average values of the squares of their velocity components are equal, so that $v_{x}^{2}=v^{2} / 3$,

$$
p=\frac{n M\left(v^{2}\right)_{\mathrm{avg}}}{3 V}
$$

$p=\frac{n M\left(v^{2}\right)_{\text {avg }}}{3 V}$

- root-mean-square speed $v_{\mathrm{rms}} \equiv \sqrt{\left(v^{2}\right)_{\text {avg }}}=\sqrt{\frac{1}{N} \sum_{i=1}^{N} v_{i}^{2} \Rightarrow \mathrm{p}=\frac{n M v_{\text {rms }}^{2}}{3 V}}$
- The equation tells how the pressure of the gas (a purely macroscopic quantity) depends on the speed of the molecules (a purely microscopic quantity).
- Using the ideal gas law ( $p V=n R T$ ) gives $v_{\mathrm{rms}}=\sqrt{\frac{3 R T}{M}}$
- The rms speed is only a kind of average speed; many molecules move much faster than this, and some much slower.
- The speed of sound in a gas is closely related to the rms speed of the molecules of that gas.
- If molecules move so fast, why does it take as long as a minute or so before you can smell perfume when someone opens a bottle across a room?
problem 19-3


## Translational Kinetic Energy

- consider a single molecule of an ideal gas, Its average translational kinetic energy over the time is

$$
\begin{aligned}
& K_{\text {avg }}=\left(\frac{1}{2} m v^{2}\right)_{\text {avg }}=\frac{1}{2} m\left(v^{2}\right)_{\text {avg }}=\frac{1}{2} m v_{\mathrm{rms}}^{2}=\frac{1}{2} m \frac{3 R T}{M}=\frac{3 R T}{2 N_{A}} \\
& k=\frac{R}{N_{A}} \Rightarrow K_{\text {avg }}=\frac{3}{2} k T
\end{aligned}
$$

At a given temperature $T$, all ideal gas molecules - no matter what their mass - have the same average translational kinetic energy - namely, 3kT/2. When we measure the temperature of a gas, we are also measuring the average translational kinetic energy of its molecules.

## Mean Free Path

- the mean free path $\lambda$ : is one useful parameter to describe this random motion of the molecules; it is the average distance traversed by a molecule between collisions.
- We expect (1) $\lambda \propto V / N(2) \lambda \propto 1 / d^{2}$, the cross section of a molecule determines its effective target area, thus

$$
\lambda=\frac{V}{\sqrt{2} \pi N d^{2}} \quad \text { mean free path }
$$

## justification

- A collision will then take place if the centers of 2 molecules come within a distance $d$ of each other.
- As a single molecule zigzags through the gas, it sweeps out a cylinder of cross-sectional area $\pi d^{2}$ between successive collisions.
- For a time interval $\Delta t$, it moves a distance $v_{\text {avg }} \Delta t$.
- The volume of the cylinder is $\left(\pi d^{2}\right)\left(v_{\text {avg }} \Delta t\right)$.
- The number of collisions that occur in time $\Delta t$ is equal to the number of molecules that lie within this cylinder,
$\lambda=\frac{\text { length of path during } \Delta t}{\text { number of collisions in } \Delta t}=\frac{v_{\text {avg }} \Delta t}{\pi d^{2} v_{\text {rel }} \Delta t N / V}=\frac{v_{\text {avg }}}{\pi d^{2} v_{\text {rel }} N / V}$
$v_{\text {avg }}$ : the mean speed of the molecules relative to the container;
$v_{\text {rel }}$ : the mean speed of a single molecule relative to the other molecules.

- A detailed calculation, taking into account the actual speed distribution of the molecules, gives

$$
v_{\mathrm{rel}}=\sqrt{2} v_{\mathrm{avg}} \quad \Rightarrow \quad \lambda=\frac{V}{\sqrt{2} \pi N d^{2}}
$$

- The mean free path of air molecules: $0.1 \mu \mathrm{~m}$ for $\mathrm{H}=0 ; 16 \mathrm{~cm}$ for $\mathrm{H}=100 \mathrm{~km}$; 20 km for $\mathrm{H}=300 \mathrm{~km}$.
problem 19-4


## The Distribution of Molecular Speeds




- Maxwell's speed distribution law, thee speed distribution of gas molecules, is

$$
P(v)=\sqrt{\frac{2 M^{3}}{\pi R^{3} T^{3}}} v^{2} e^{-M v^{2} / 2 R T}
$$

Random molecular velocities


$$
\begin{aligned}
v_{\text {rel }}^{2}=\vec{v}_{\text {rel }}^{2} & =\left(\vec{v}_{1}-\vec{v}_{2}\right) \cdot\left(\vec{v}_{1}-\vec{v}_{2}\right)=\vec{v}_{1} \cdot \vec{v}_{1}-2 \vec{v}_{1} \cdot \vec{v}_{2}+\vec{v}_{2} \cdot \vec{v}_{2} \\
\Rightarrow \quad \bar{v}_{\text {rel }} & =\sqrt{\vec{v}_{1} \cdot \vec{v}_{1}-2 \vec{v}_{1} \cdot \vec{v}_{2}+\vec{v}_{2} \cdot \vec{v}_{2}} \\
& =\sqrt{\overrightarrow{\vec{v}}_{1} \cdot \vec{v}_{1}-2 \vec{v}_{1} \cdot \vec{v}_{2}+\overrightarrow{\vec{v}}_{2} \cdot \vec{v}_{2}} \\
& =\sqrt{\bar{v}_{1}^{2}+\bar{v}_{2}^{2}} \\
& =\sqrt{\bar{v}^{2}+\bar{v}^{2}} \\
& =\sqrt{2} \bar{v}
\end{aligned}
$$

- The quantity $P(v)$ is a probability distribution function: For any speed $v$, the product $P(v) \mathrm{d} v$ (a dimensionless quantity) is the fraction of molecules with speeds in the interval $\mathrm{d} v$ centered on speed $v, \int_{0}^{\infty} P(v) \mathrm{d} v=1$
- The fraction (frac) of molecules with speeds in an interval of $v_{1}$ to $v_{2}$ is

$$
\mathrm{frac}=\int_{v_{1}}^{v_{2}} P(v) \mathrm{d} v
$$

## Average, RMS, and Most Probable Speeds

- find the average speed $v_{\text {avg }}$ of the molecules in a gas with the distribution law

$$
v_{\text {avg }}=\int_{0}^{\infty} v P(v) \mathrm{d} v
$$

- Substituting for $P(v)$ from the Maxwell's speed distribution law and find

$$
v_{\mathrm{avg}}=\sqrt{\frac{8 R T}{\pi M}} \text { average speed }
$$

- Similarly, $\left(v^{2}\right)_{\text {avg }}=\int_{0}^{\infty} v^{2} P(v) \mathrm{d} v=\frac{3 R T}{M} \Rightarrow v_{\mathrm{rms}}=\sqrt{\left(v^{2}\right)_{\text {avg }}}=\sqrt{\frac{3 R T}{M}} \mathrm{rms}$ speed
- The most probable speed $v_{P}$ is the speed at which $P(v)$ is maximum, therefore solve it to find

$$
\frac{\mathrm{d} P}{\mathrm{~d} v}=0 \Rightarrow v_{P}=\sqrt{\frac{2 R T}{M}} \text { most probable speed }
$$

Gaussian Integral $\quad \int_{-\infty}^{\infty} e^{-x^{2}} \mathrm{~d} x=2 \int_{0}^{\infty} e^{-x^{2}} \mathrm{~d} x=\sqrt{\pi}$
Proof:

$$
\begin{aligned}
&\left(\int_{-\infty}^{\infty} e^{-x^{2}} \mathrm{~d} x\right)^{2}=\int_{-\infty}^{\infty} e^{-x^{2}} \mathrm{~d} x \int_{-\infty}^{\infty} e^{-y^{2}} \mathrm{~d} y=\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\left(x^{2}+y^{2}\right)} \mathrm{d} x \mathrm{~d} y \\
&= \int_{0}^{\infty} \int_{0}^{2 \pi} e^{-r^{2}}(r \mathrm{~d} \theta)(\mathrm{d} r) \Leftarrow \begin{array}{l}
r^{2}=x^{2}+y^{2} \\
\mathrm{~d} x \mathrm{~d} y=(r \mathrm{~d} \theta)(\mathrm{d} r)=r \mathrm{~d} r \mathrm{~d} \theta \\
\\
=
\end{array} \\
&=\int_{0}^{2 \pi} \mathrm{~d} \theta \int_{0}^{\infty} e^{-r^{2}} r \mathrm{~d} r=2 \pi \cdot \frac{1}{2} \int_{0}^{\infty} e^{-q} \mathrm{~d} q \Leftarrow q \equiv r^{2} \\
&=-\pi e^{-\left.q\right|_{0} ^{\infty}=\pi}
\end{aligned}
$$

$$
\begin{aligned}
& s \equiv \sqrt{\frac{2 M^{3}}{\pi R^{3} T^{3}}}, \quad u^{2}=\frac{2 R T}{M} \quad \Rightarrow \quad P(v)=s v^{2} e^{-v^{2} / u^{2}} \\
& \int_{0}^{\infty} P(v) \mathrm{d} v=s \int_{0}^{\infty} v^{2} e^{-v^{2} / u^{2}} \mathrm{~d} v=\frac{s}{2} \int_{0}^{\infty} v e^{-v^{2} / u^{2}} \mathrm{~d} v^{2}=-\frac{s u^{3}}{2} \int_{0}^{\infty} \frac{\nu}{u} \mathrm{~d} e^{-v^{2} / u^{2}} \\
& =-\frac{s u^{3}}{2}\left[\left.\frac{v}{u} e^{-v^{2} / u^{2}}\right|_{0} ^{\infty}-\int_{0}^{\infty} e^{-v^{2} / u^{2}} \mathrm{~d} \frac{v}{u}\right]=\frac{s u^{3}}{2} \int_{0}^{\infty} e^{-v^{2} / u^{2}} \mathrm{~d} \frac{v}{u}=\frac{s u^{3}}{2} \frac{\sqrt{\pi}}{2}=1 \\
& \bar{v}=\int_{0}^{\infty} v P(v) \mathrm{d} v=s \int_{0}^{\infty} v^{3} e^{-v^{2} / u^{2}} \mathrm{~d} v=\frac{s u^{4}}{2} \int_{0}^{\infty} q e^{-q} \mathrm{~d} q \Leftarrow q \equiv \frac{v^{2}}{u^{2}} \\
& =-\frac{s u^{4}}{2}\left[\left.q e^{-q}\right|_{0} ^{\infty}-\int_{0}^{\infty} e^{-q} \mathrm{~d} q\right]=-\left.\frac{s u^{4}}{2} e^{-q}\right|_{0} ^{\infty}=\sqrt{\frac{8 R T}{\pi M}} \\
& \overline{v^{2}}=\int_{0}^{\infty} v^{2} P(\nu) \mathrm{d} v=s \int_{0}^{\infty} \nu^{4} e^{-v^{2} / u^{2}} \mathrm{~d} \nu=\frac{s u^{5}}{2} \int_{0}^{\infty} x^{3} e^{-x^{2}} \mathrm{~d} x^{2} \Leftarrow x \equiv \frac{\nu}{u} \\
& =-\frac{s u^{5}}{2}\left[\left.x^{3} e^{-x^{2}}\right|_{0} ^{\infty}-\frac{3}{2} \int_{0}^{\infty} x e^{-x^{2}} \mathrm{~d} x^{2}\right]=-\frac{3 s u^{5}}{4} \int_{0}^{\infty} x \mathrm{~d} e^{-x^{2}}=\frac{3 s u^{5}}{4} \frac{2}{s u^{3}}=\frac{3 R T}{M}
\end{aligned}
$$

- some molecules will have speeds that are many times of $v_{P}$. These molecules form the high-speed tail of a distribution curve, useful for rain \& sunshine.
problem 19-5, 19-6


## The Molar Specific Heats of an Ideal Gas

## Internall Energy $\boldsymbol{E}_{\text {int }}$

- assume that our ideal gas is a monatomic gas and the internal energy $E_{\text {int }}$ of the ideal gas is simply the sum of the translational kinetic energies of its atoms.
- The average translational kinetic energy of a single atom depends only on the gas temperature, ie, $K_{\text {avg }}=3 k T / 2$. The internal energy of a sample of $n$ moles of the gas is

$$
\begin{aligned}
& E_{\mathrm{int}}=\left(n N_{A}\right) K_{\mathrm{avg}}=\left(n N_{A}\right)\left(\frac{3}{2} k T\right)=\left(n N_{A}\right)\left(\frac{3 R}{2 N_{A}} T\right) \\
& \Rightarrow \quad E_{\mathrm{int}}=\frac{3}{2} n R T \text { monatomic ideal gas }
\end{aligned}
$$

The internal energy $E_{\text {int }}$ of an ideal gas is a function of the gas temperature only; it does not depend on any other variable.

- 2 types of the molar specific heat of an ideal gas:
$C_{V}$ : molar specific heat at constant volume;
$C_{p}$ : molar specific heat at constant pressure.


## Molar Specific Heat at Constant Volume

- the heat $Q$ is related to the temperature change $\Delta T$ by

$$
Q=n C_{V} \Delta T \quad \text { constant volume }
$$

the $1^{\text {st }}$ law of thermodynamics gives

$$
\begin{aligned}
& \Delta E_{\mathrm{int}}=Q-W=n C_{V} \Delta T-W=n C_{V} \Delta T \\
& \Rightarrow \quad C_{V}=\frac{\Delta E_{\mathrm{int}}}{n \Delta T}=\frac{3 n R \Delta T / 2}{n \Delta T} \\
& \Rightarrow \quad C_{V}=\frac{3}{2} R=12.5 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K} \quad \text { monatomic gas }
\end{aligned}
$$

- the internal energy of any ideal gas can be rewritten


$$
E_{\mathrm{int}}=n C_{V} T \quad \text { any idea gas }
$$

- This equation applies to monatomic, diatomic, and polyatomic ideal gases, provided the appropriate value of $C_{V}$ is used.
- When an ideal gas that is confined to a container undergoes a temperature change $\Delta T$, then the change in its internal energy as is

$$
\Delta E_{\mathrm{int}}=n C_{V} \Delta T \quad \text { ideal gas, any process }
$$



A change in the internal energy $E_{\text {int }}$ of a confined ideal gas depends on the change in the gas temperature only; it does not depend on what type of process produces the change in the temperature.

- Although the values of heat $Q$ and work $W$ associated with these 3 paths differ, the values of $\Delta E_{\text {int }}$ associated with them are identical because they all involve the same temperature change $\Delta T$.


## Molar Specific Heat at Constant Pressure

- $Q$ is related to the temperature change $\Delta T$ by

$$
Q=n C_{p} \Delta T
$$

constant pressure

- This $C_{p}$ is greater than the molar specific heat at constant volume $C_{V}$, because energy must $\approx$ now be supplied not only to raise the temperature of the gas but also for the gas to do work.

- From the $1^{\text {st }}$ law of thermodynamics

$$
\begin{aligned}
& n C_{V} \Delta T \Leftarrow \Delta E_{\mathrm{int}}=Q-W=n C_{p} \Delta T-p \Delta V=n C_{p} \Delta T-n R \Delta T \quad \mathrm{He} \\
& \Rightarrow \quad C_{V}=C_{p}-R \Rightarrow C_{p}=C_{V}+R
\end{aligned}
$$

problem 19-7

## Degrees of Freedom and Molar Specific Heats

- to explain the discrepancy by considering the possibility that molecules with more than one atom can store internal ${ }^{\mathrm{O}}$ energy in forms other than translational kinetic energy.

(b) $\mathbf{O}_{\mathbf{2}}$
- assume that all 3 types (monatomic, diatomic, polyatomic) of H
- assume that the diatomic and polyatomic molecules can have oscillatory motions.
- the theorem of the equipartition of energy:

Every kind of molecule has a certain number $f$, degrees of freedom, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with it - on average - an energy of $k T / 2$ per molecule (or $R T / 2$ per mole).

- For the translational motion, the molecules have velocity components along $x y z$ axes. Thus, gas molecules of all types have 3 degrees of translational freedom and, on average, an associated energy of $3(k T / 2)$ per molecule.
- A monatomic gas molecule does not rotate and so has no rotational energy.
- A diatomic molecule can rotate only about axes perpendicular to the line connecting the atoms and have only 2 degrees of rotational freedom and a rotational energy of only $2(k T / 2)$ per molecule.
- Only the polyatomic molecules are able to rotate with an angular velocity component along each of the 3 axes, and have 3 degrees of rotational freedom, and an energy of $3(k T / 2$ )per molecule.
- Now the internal energy: $E_{\mathrm{int}}=\frac{f}{2} n R T \Rightarrow C_{V}=\frac{f}{2} R=4.16 \mathrm{f} / \mathrm{mol} \cdot \mathrm{K}$ where $f$ is the number of degrees of freedom.
- $f=3$ for monatomic gases, $f=5$ for diatomic gases, $f=6$ for polyatomic gases. Degrees of Freedom for Various Molecules

|  |  | Degree of Freedom |  |  |  | specific heat |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Molecule | Example | Translational | Rotational | Total $(f)$ | $C_{V}$ | $C_{p}$ |  |  |  |
| monatomic | He | 3 | 0 | 3 | $\frac{3}{2} R$ | $\frac{5}{2} R$ |  |  |  |
| diatomic | $\mathrm{O}_{2}$ | 3 | 2 | 5 | $\frac{5}{2} R$ | $\frac{7}{2} R$ |  |  |  |
| polyatomic | $\mathrm{CH}_{4}$ | 3 | 3 | 6 | $3 R$ | $4 R$ |  |  |  |

## A Hint of Quantum Theory

- improve the agreement of kinetic theory by including the oscillations of the atoms in a gas of diatomic or polyatomic molecules.
- experiment shows that such oscillations are "turned on" only when the gas molecules have relatively large energies.
- quantum theory shows that rotational motion of the molecules requires a certain minimum amount of energy; oscillatory motion of the
 molecules requires a certain (higher) minimum amount of energy.


## The Adiabatic Expansion of an Ideal Gas

- ensure that $Q=0$ either by carrying out the process very quickly (as in sound waves) or by doing it (at any rate) in a well-insulated container.
- the relation between the pressure and the volume during an adiabatic process is

$$
p V^{\gamma}=\text { a constant adiabatic process }
$$

in which $\gamma=C_{p} / C_{V}$, the ratio of the molar specific heats for the gas.


Volume

## Proof

- the $1^{\text {st }}$ law of thermodynamics:


$$
\begin{equation*}
n C_{V} \mathrm{~d} T \Leftarrow \mathrm{~d} E_{\mathrm{int}}=Q-p \mathrm{~d} V=-p \mathrm{~d} V \quad \Rightarrow \quad n \mathrm{~d} T=-\frac{p}{C_{V}} \mathrm{~d} V \tag{a}
\end{equation*}
$$

- Now from the ideal gas law ( $p V=n R T$ ) we have

$$
n R \mathrm{~d} T=p \mathrm{~d} V+V \mathrm{~d} p \Rightarrow n \mathrm{~d} T=\frac{p \mathrm{~d} V+V \mathrm{~d} p}{C_{p}-C_{V}} \quad(\mathrm{~b}) \quad \Leftarrow \quad R=C_{p}-C_{V}
$$

- Combining (a) \& (b) gives

$$
\frac{\mathrm{d} p}{p}+\frac{C_{p}}{C_{V}} \frac{\mathrm{~d} V}{V}=0 \Rightarrow \ln p+\gamma \ln V=\text { a const } \Rightarrow p V^{\gamma}=\mathrm{a} \text { constant }
$$

$$
\begin{aligned}
& {\left[-\frac{p}{C_{V}} \mathrm{~d} V=\frac{p \mathrm{~d} V+V \mathrm{~d} p}{C_{p}-C_{V}}\right] \times\left(C_{p}-C_{V}\right)} \\
& \Rightarrow \quad-\frac{C_{p}-C_{V}}{C_{V}} p \mathrm{~d} V=p \mathrm{~d} V+V \mathrm{~d} p \\
& \Rightarrow \quad(1-\gamma) p \mathrm{~d} V=p \mathrm{~d} V+V \mathrm{~d} p \\
& \Rightarrow \quad \gamma p \mathrm{~d} V+V \mathrm{~d} p=0 \\
& \Rightarrow \quad \int_{i}^{f}\left[\frac{\mathrm{~d} p}{p}+\gamma \frac{\mathrm{d} V}{V}=0\right] \\
& \Rightarrow \quad \ln p+\gamma \ln V=\mathrm{const}
\end{aligned}
$$

- Since the gas goes from an initial state $i$ to a final state $f$,

$$
p_{i} V_{i}^{\gamma}=p_{f} V_{f}^{\gamma} \quad \text { adiabatic process }
$$

- use the ideal gas equation ( $p V=n R T$ ) to eliminate $p$,

$$
\frac{n R T}{V} V^{\gamma}=\text { a constant } \quad \Rightarrow \quad T V^{\gamma-1}=\text { a constant adiabatic process }
$$

- When the gas goes from an initial state $i$ to a final state $f$, we can rewrite

$$
T_{i} V_{i}^{\gamma-1}=T_{f} V_{f}^{\gamma-1} \quad \text { adiabatic process }
$$

- Understanding adiabatic processes allows you to understand why popping the cork on a cold bottle of champagne or the tab on a cold can of soda causes a slight fog to form at the opening of the container.


## Free Expansions

- Since a free expansion is not in equilibrium, the equation of the adiabatic expansion can not apply to it.
- In a free expansion, because $\Delta E_{\text {int }}=0$, the temperature of the final int state must be that of the initial state, ie, $T_{i}=T_{f}$, and $p_{i} V_{i}=p_{f} V_{f}$.

Problem 19-9, 19-10


Insulation


## Four Special Processes

Volume

## Some Special Results

Path Constant Quantity Process Type $\Delta E_{\text {int }}=Q-W$ and

$$
\Delta E_{\text {int }}=n C_{V} \Delta T \text { for all paths }
$$

| 1 | $p$ | Isobaric | $Q=n C_{p} \Delta T ; W=p \Delta V$ |
| :--- | :---: | :--- | :--- |
| 2 | $T$ | Isothermal | $Q=W=n R T \ln \left(V_{f} / V_{i}\right) ; \Delta E_{\text {int }}=0$ |
| 3 | $p V^{\gamma}, T V^{\gamma-1}$ | Adiabatic | $Q=0 ; W=-\Delta E_{\text {int }}$ |
| 4 | $V$ | Isochoric | $Q=\Delta E_{\text {int }}=n C_{V} \Delta T ; W=0$ |

Selected problems: 6, 14, 23, 41

