Thermodynamics and Gases

Last time
- Kinetic Theory of Gases for simple (monatomic) gases
  - Atomic nature of matter
  - Demonstrate ideal gas law
  - Atomic kinetic energy = internal energy
  - Mean free path and velocity distributions
- From formula for $E_{\text{int}}$, can get specific heats
- Specific Heats of Simplest Gases
  - Constant Volume
  - Constant Pressure

Today
- Specific Heats for more complex gases
- Adiabatic Expansion
- Entropy
Internal Energy from Atomic Nature

- \( pV = nRT \) understood from atomic nature of matter
  - \( pV = NkT \) is equivalent form
  - Both are generally applicable (up to small van der Waals corrections) for all gases \( \ldots \) \( pV \approx \text{kinetic energy of atoms} \)

- Internal energy of the gas is a sum of all the energy forms (including kinetic energy) of the molecules
  - simplest is monatomic gas (one atom in the molecule, rotationally symmetric) \( \rightarrow \) energy all translational
  - real world: coefficient, \( 3/2 \), only applies to “noble gases”

\[
\begin{align*}
\text{monatomic gas} & \\
pV &= NkT = nRT \\
\langle K_{\text{atom}} \rangle &= \frac{3}{2} kT \\
E_{\text{int}} &= N \langle K_{\text{atom}} \rangle = \frac{3}{2} NK_T \\
E_{\text{int}} &= \frac{3}{2} nRT \\
\end{align*}
\]

\[
\begin{align*}
\text{ANY gas} & \\
pV &= NkT = nRT \\
\langle E_{\text{atom}} \rangle &= \frac{C_v}{R} kT \\
E_{\text{int}} &= N \langle E_{\text{atom}} \rangle = N \frac{C_v}{R} kT \\
E_{\text{int}} &= nC_vT \\
\end{align*}
\]
Specific Heat at Constant Volume (isochoric)

1st Law of Therm.
\[ dE_{\text{int}} = dQ - dW \]

- No change in volume implies no work done:
  - \( dW = 0 \)
- Heat introduced proportional to temperature change when no work:
  - \( Q \equiv n \, C_V \, \Delta T \)
- Since \( dW = 0 \), then the heat added must equal the change in internal energy:
  - \( \Delta E_{\text{int}} = Q = n \, C_V \, \Delta T \)

And we predict:
Monatomic (billiard ball) gases have \( C_V = \frac{3R}{2} \)

\[ E_{\text{int}} = \frac{3}{2} nRT \]

any gas
\[ E_{\text{int}} = nC_V T \]
Specific Heat at Constant Pressure (isobaric process)

- For process shown (n fixed)
  - $Q \equiv n \, C_p \, \Delta T$

- Here, as expansion occurs,
  - work is done and
  - internal energy increases

\[
Q = \Delta E_{\text{int}} + W
= nC_v \Delta T + p \Delta V
= nC_v \Delta T + nR \Delta T
\]

\[
Q = n \left( C_v + R \right) \Delta T
\]

\[
C_p = C_v + R
\]
How about molecules that are not “monatomic”?

- We found that “sphere-like” molecules (single inert atoms) had $C_V = \frac{3R}{2}$ … what about the rest?
  - Came from considerations of kinetic energy ($E_{\text{int}} = nC_VT$) deriving gas law
- Our single atoms had only one kind of available energy $\rightarrow$
  - Kinetic energy from translation in 3 dimensions
- More generally molecules can have other “degrees of freedom”
  - rotations
  - vibrations
  - …
- Maxwell: $E_{\text{molecule}}^{\text{int}} = f \left( \frac{1}{2} kT \right)$
  - $f = \# \text{deg of freedom}$
Molecular Specific Heats

\[ E_{\text{molecule}} = f \left( \frac{1}{2} kT \right) \]

\[ f = \# \text{ deg of freedom} \]

- \( f \) = different independent ways that molecule can contain and exchange energy
- Need enough thermal energy to "excite" the modes to be seen (Quantum Mechanics)
  - fig - \( H_2 \) gas \( C_V/R \)

\[ E_{\text{int}} = nf \left( \frac{1}{2} RT \right) \]

\[ E_{\text{int}} = nC_vT \]

\[ C_v = \frac{1}{2} Rf \]

\[ C_p = R \left( \frac{f}{2} + 1 \right) \]
Real Gas at low pressures

### Empirical check

- Any gas
  - \[ f = \# \text{ active d.f.} \]
  - \[ C_v = \frac{1}{2} R f \]
  - \[ C_p = R \left( \frac{f}{2} + 1 \right) \]
  - \[ \gamma \equiv \frac{C_p}{C_v} = 1 + \frac{2}{f} \]

#### Molar Heat Capacities of Gases at Low Pressure

<table>
<thead>
<tr>
<th>TYPE OF GAS</th>
<th>GAS</th>
<th>( C_v ) (J/mol \cdot K)</th>
<th>( C_p ) (J/mol \cdot K)</th>
<th>( C_p - C_v ) (J/mol \cdot K)</th>
<th>( \gamma = C_p / C_v )</th>
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<tbody>
<tr>
<td>Monatomic</td>
<td>He</td>
<td>12.47</td>
<td>20.78</td>
<td>8.31</td>
<td>1.67</td>
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<td></td>
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<td>12.47</td>
<td>20.78</td>
<td>8.31</td>
<td>1.67</td>
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<tr>
<td>Diatomic</td>
<td>H_2</td>
<td>20.42</td>
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<td>8.32</td>
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<td>29.07</td>
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<tr>
<td></td>
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<td>29.17</td>
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<tr>
<td></td>
<td>CO</td>
<td>20.85</td>
<td>29.16</td>
<td>8.31</td>
<td>1.40</td>
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<tr>
<td>Polyatomic</td>
<td>CO_2</td>
<td>28.46</td>
<td>36.94</td>
<td>8.48</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>SO_2</td>
<td>31.39</td>
<td>40.37</td>
<td>8.98</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>H_2S</td>
<td>25.95</td>
<td>34.60</td>
<td>8.65</td>
<td>1.33</td>
</tr>
</tbody>
</table>
Aside: How about Solids?

- Generally expect $C_v = fR/2$
- While gases are **unbound**, solids have atoms bound to adjacent atoms
  - no net translations in 3D space but
  - there **does** exist
    - Vibrational kinetic energy -- 3 deg of freedom
    - Potential energy (of binding) -- 3 deg of freedom
- Recall table 19-3: many solids tend to have molar heat capacity $C \sim 25 \text{ J/mol-K}$
- Naively expect $f=6$ and $C_v = 3R \sim 3(8.31 \text{ J/mol-K})$
- This value approached in most solids as temperatures rise
Adiabatic Expansion of Gas

- Adiabatic = no heat enters or leaves system (gas) ... Q=0
- But temperature changes as gas does work

\[ pV = nRT \]
\[ pdV + Vdp = nRdT \]
\[ ndT = \frac{pdV + Vdp}{R} = \frac{pdV + Vdp}{(C_p - C_V)} \]

\[ dE_{int} = dQ - dW \]
\[ dE_{int} = -dW \]
\[ nC_v dT = -pdV \]
\[ ndT = -\frac{pdV}{C_v} \]

\[ \frac{pdV + Vdp}{C_p - C_v} = -\frac{pdV}{C_v} \]
Adiabatic Expansion - algebra

\[
\frac{pdV + Vdp}{c_p - c_V} = -\frac{pdV}{c_V}
\]

\[
pdV \left[ \frac{1}{c_p - c_V} + \frac{1}{c_V} \right] = -\frac{Vdp}{c_p - c_V}
\]

\[
pdV \left[ \frac{c_p}{c_V (c_p - c_V)} \right] = -\frac{Vdp}{c_p - c_V}
\]

\[
Vdp + \frac{c_p}{c_V} pdV = 0
\]

\[
\frac{dp}{p} + \gamma \frac{dV}{V} = 0 \quad \gamma = \frac{c_p}{c_V}
\]

Differential equation states that fractional change in pressure plus \(\gamma\) times fractional change in volume must equal zero in any adiabatic expansion.
Adiabatic Expansion - calculus

\[ \frac{dp}{p} + \gamma \frac{dV}{V} = 0 \quad \gamma = \frac{C_p}{C_V} \]

\[ \ln p + \gamma \ln V = \text{const.} \]

\[ \ln(pV^\gamma) = \text{const.} \]

\[ pV^\gamma = \text{const} \]

\[ \left( \frac{nRT}{V} \right)^\gamma = \text{const} \]

\[ T_V^\gamma = T_2 V_2^\gamma - 1 \]

- Conclude that adiabatic change (no heat enter or leave) requires new relations among parameters
  - ratio (\( \gamma \)) spec. heats important
  - Ideal gas law also still true
Gases: Isothermal Expansion

\[ pV = nRT \]

- **Units**
  - \( R = 8.31 \text{ J/(mol-K)} = kN_A \)
- **Work (constant temperature)** done obtained from integral in \( p-V \) (see sample prob 20-1)

\[
W = \int_{V_i}^{V_f} p \, dV = \int_{V_i}^{V_f} \frac{nRT}{V} \, dV = nRT \ln \left( \frac{V_f}{V_i} \right)
\]
Reversibility

- All these (isothermal, isobaric, isochoric, adiabatic) are reversible processes
  - each point on $P,V$ diagram is a possible state ... state can be changed in any direction along a curve
  - Contrast free expansion of gas
    - not reversible
    - $T_f = T_i$
    - $p_f V_f = p_i V_i$
    - but $f$ state cannot return to $i$ state
Sample Problem 20-9a

- Recall sample problem 20-2, isothermal expansion of 1 mole $O_2$ at 310K & $p_i=2.0$ atm from 12 liters to 19 liters gave $P_f = 1.26$ atm & $W=Q=1180$ J.
- Now adiabatic expansion of same sample.
  - Final pressure?
  - How much work done?

\[ p_2 = p_1 \left( \frac{V_1}{V_2} \right)^\gamma \]
\[ T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma - 1} \]
\[ p_2 = 2.0 \left( \frac{12}{19} \right)^{1.40} \]
\[ T_2 = 310 \left( \frac{12}{19} \right)^{0.40} \]
\[ p_2 = 1.05 \text{ atm} \]
\[ T_2 = 258K \]
\[ \Delta T = -52.0K \]
\[ Q = 0 \]
\[ W = -\Delta E_{\text{int}} = -nC_v \Delta T = -(1)(20.85)(-52.0) \]
\[ W = 1085 \text{ Joules} \]
### Contrast Gas Expansions
(sample 20-2 & 20-9)

All involve expansion of gas at 2 atm, 310K, and 12 liters to a volume 19 liters in different ways.

#### Free Expansion

- **Variable**
- **Isothermal**
- **Adiabatic**
- **Free**

<table>
<thead>
<tr>
<th></th>
<th>Isothermal</th>
<th>Adiabatic</th>
<th>Free</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1$</td>
<td>2.0 atm</td>
<td>2.0 atm</td>
<td>2.0 atm</td>
</tr>
<tr>
<td>$V_1$</td>
<td>12 L</td>
<td>12 L</td>
<td>12 L</td>
</tr>
<tr>
<td>$T_1$</td>
<td>310 K</td>
<td>310 K</td>
<td>310 K</td>
</tr>
<tr>
<td>$P_2$</td>
<td>1.26 atm</td>
<td>1.05 atm</td>
<td>1.26 atm</td>
</tr>
<tr>
<td>$V_2$</td>
<td>19 L</td>
<td>19 L</td>
<td>19 L</td>
</tr>
<tr>
<td>$T_2$</td>
<td>310 K</td>
<td>258 K</td>
<td>310 K</td>
</tr>
<tr>
<td>$W$</td>
<td>1180 J</td>
<td>1085 J</td>
<td>0 J</td>
</tr>
</tbody>
</table>

- Check you get the answers for these
- Big difference for **irreversible**: ENTROPY
Entropy Definition

\[ \Delta S = S_f - S_i \equiv \int_{i}^{f} \frac{dQ}{T} \]

\[ = \frac{\Delta Q}{T} \text{ for } T \text{ fixed} \]

- precise quantitative definition measuring heat flow energy at specific temperature \((S=Q/T, \text{ units } J/K)\)
  - Sign convention: heat added \((\Delta Q>0)\), then entropy increases \((\Delta S>0)\)
- simplest underlying concept underlying thermodynamics:
  - *Closed system* ... total entropy change zero or positive
- Reversible process: an entropy increase is compensated by an entropy decrease in another part of system ... entropy recoverable
- Irreversible: entropy increases and cannot be recovered
- can calculate entropy change for irreversible process by connecting initial & final states with (series of) reversible processes
Second Law of Thermodynamics

- Simplest (and simplistic) expression: “Heat energy always flows from hotter bodies to cooler bodies”
  - intuitively obvious
- Take a more complete statement (though more abstract) with concept of entropy
  - “In any closed system, the entropy always increases for irreversible processes and is constant for reversible processes.” Entropy never decreases in closed systems, and typically increases in real processes!
  - Heat flow from hot to cold is a consequence.
  - Found to be provide experimentally correct predictions in wide array of circumstances
  - Has a physical interpretation in terms of the system’s order
  - Provides an understanding of where our sense of the “arrow of time” arises.
Reversibility: isothermal expansion of gas

\[ \Delta S = \frac{Q}{T} = \frac{W}{T} = \int \frac{pdV}{T} = \frac{nRT}{T} \int \frac{dV}{V} \]

\[ \Delta S_{\text{gas}}^{\text{expansion}} = +nR \ln \frac{V_f}{V_i} \]

- Entropy increase of the gas during expansion occurs as a consequence of heat (Q) into gas at temp T
- An equal and opposite decrease in the entropy of the reservoir occurs at the same time
- If the gas is isothermally compressed, the gas entropy decreases and the reservoir entropy increases

\[ \Delta S_{\text{compression}}^{\text{gas}} = -nR \ln \frac{V_f}{V_i} \]
Isochoric temperature change of gas

- Add heat with doing work by increasing reservoir temp
- Temperature change of gas in contact with temp reservoir is also reversible

\[ \Delta S = \frac{\Delta Q}{T} = \int \frac{\Delta E_{\text{int}}}{T} = nC_v \int_{T_i}^{T_f} \frac{dT}{T} \]

\[ \Delta S_{T_i \rightarrow T_f} = +nC_v \ln \frac{T_f}{T_i} \]

\[ \Delta S_{T_f \rightarrow T_i} = +nC_v \ln \frac{T_i}{T_f} = -\Delta S_{T_i \rightarrow T_f} \]
Entropy (more)

- Entropy is a physical measurable property of a system (like $T, V, p, \ldots$) that is calculable in terms of the others
  - “state function”
- How does one calculate entropy change when the net entropy increases? (in an irreversible process like free expansion of a gas)
- Answer: Calculate entropy change for irreversible process by connecting initial & final states with (imagined series of) reversible processes. Examples
  - Simple heat flow between two solids.
  - Free expansion.
Entropy Change in Irreversible Process

\[
\Delta S_{t=0} = \frac{\Delta Q_{t=0}}{350} - \frac{\Delta Q_{t=0}}{650} > 0
\]

- Note that entropy will increase so long as heat flows from hot body to cold body. The reverse (cold to hot) is not possible from 2nd Law.
- Simple heat flow from hot body to cold is irreversible.
- Calculate entropy change in irreversible process: connect initial & final states with series of pretend reversible processes.
Entropy change: solids

- Net entropy change of any process of a closed system is either zero (reversible) or greater than zero (irreversible)
  - Example sample problem 21-2: 2 equal mass (m) solids at different temps ... equilibrium when both at final temperature $T_f$ ... what is entropy chg?

\[
\Delta S = \int_{i}^{f} \frac{dQ}{T} = mc \int_{i}^{f} \frac{dT}{T} = mc \ln \frac{T_f}{T_i}
\]

\[
\Delta S_{\text{rev}} = \Delta S_L + \Delta S_R = mc \left[ \ln \frac{T_f}{T_{iL}} + \ln \frac{T_f}{T_{iR}} \right]
\]

\[
\Delta S_{\text{irrev}} = \Delta S_{\text{rev}}
\]

Physics 1401 - L 23

Frank Sciulli
Sample Problem 21-2

- \( m = 1.5 \text{ kg} \)
- \( c = 386 \text{ J/kg-K} \)

\[
\Delta S_{\text{rev}} = mc \ln \frac{T_f^2}{T_{iL} T_{iR}}
\]

\[
\Delta S_{\text{rev}} = \Delta S_{\text{irrev}}
\]

Equal masses:

\[
T_f = \frac{1}{2} \left[ T_{iL} + T_{iR} \right] = 40^0C
\]

\[
\Delta S = (1.5\text{kg})(386\text{J/kg\cdot K}) \ln \left( \frac{313^2}{(293)(333)} \right)
\]

\[
\Delta S = 2.37 \text{ J/K}
\]

- Same net entropy increase for the two masses
  - Lost in irreversible process
  - Stored in reservoir for reversible process
Entropy increase of free expansion of gas

\[ \Delta S = \frac{Q}{T} = \frac{W}{T} = \frac{nRT}{T} \ln \frac{V_f}{V_i} \]

- Derived previously for isothermal expansion of the gas
- Since, in the two processes (reversible and irreversible), the gases have same initial states and same final states
  - the entropy change of the gas is the same for both processes
- Note that free expansion process is irreversible
- Note that net entropy of closed system in isothermal expansion is zero
2nd Law of Thermodynamics: gases

- Net entropy change of any process of a closed system is either zero (reversible) or greater than zero (irreversible)
  - discussion section 21-2
- Entropy is a state function; depends only on parameters of the system: calculate general change for gas

\[ \Delta S \geq 0 \]

\[ dQ = dE_{\text{int}} + dW \]
\[ dQ = nC_v \, dT + pdV \]

\[ \Delta S_{i \rightarrow f} = S_f - S_i \]
\[ = \int_{i}^{f} \frac{dQ}{T} \]

\[ \Delta S_{\text{rev}} = \Delta S_{\text{irrev}} \]

\[ \Delta S = \int_{i}^{f} \frac{dQ}{T} = nC_v \int_{T_i}^{T_f} \frac{dT}{T} + nR \int_{V_i}^{V_f} \frac{dV}{V} \]

\[ \Delta S = nC_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i} \]
Thermodynamics and Gases

Today

- Specific Heats of Simplest Gases
  - Constant Volume (isochoric)
  - Constant Pressure (isobaric)
- Specific Heats more generally
- Adiabatic Expansion
- Reversible and Irreversible Processes
- Entropy

Next

- More on Entropy
- Uses in engines, heat pumps, refrigerators
- Origin of Entropy