More Thermodynamics

- Specific Heats of a Gas
- Equipartition of Energy
- Reversible and Irreversible Processes
    - Carnot Cycle
    - Efficiency of Engines
    - Entropy

Specific Heat of Gases

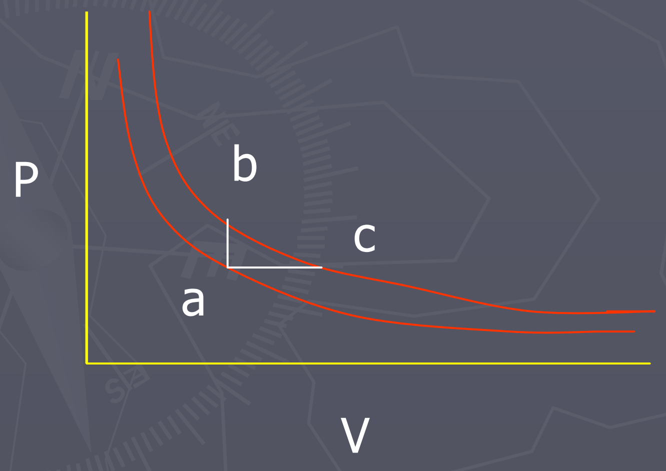
- Consider the gas as elastic spheres
  - No forces during collisions
  - All energy internal to the gas must be kinetic
  - Per mole average translational KE is 3/2 kT per particle
  - The internal energy U of an ideal gas containing N particles is $U = 3/2\ N\ kT = 3/2\ \mu\ RT$
- This means the internal energy of an ideal gas is merely proportional to the absolute temperature of a gas

Heat Capacity

- Molar heat capacity C is a specific heat
  - It is the heat (energy) per unit mass (mole) per unit temperature change
  - It has two components: C_p and C_V
    - C_p is the heat capacity at constant pressure
    - C_v is the heat capacity at constant volume.

Heat Capacities

- Consider a piston arrangement in which heat can be added/subtracted at will.
  - The piston can be altered for constant volume if desired.



- Consider a ☟ b : a constant volume process
  - T ☟ T + ⌖T
  - P ☟ P + ⌖P
  - V ☟ V
- First Law: dU = dQ – dW
  - ⌖Q = ⌖U + ⌖W
  - ⌖Q = μC_v⌖T (definition of a heat capacity)
  - ⌖W = p ⌖V = 0
  - ⌖Q = μC_v⌖T = ⌖U
- NB: this can be arranged so that ⌖T is the same in both cases a ☟ b and a ☟ c !

Now an Isobaric Change: a → c

- Consider a → c : a constant pressure process
    - $T \rightarrow T + \Delta T$
    - $P \rightarrow P$
    - $V \rightarrow V + \Delta V$
- $\Delta Q = \mu C_p \Delta T$ (definition of heat capacity)
- $\Delta W = p\,\Delta V$
- $\Delta Q = \mu C_p \Delta T = \Delta U' + p\,\Delta V$
- For an ideal gas ΔU depends only on temperature and ΔT was the same (!) so $\Delta U = \Delta U'$
- $\mu C_p \Delta T = \mu C_v \Delta T + p\,\Delta V$
    - Apply the perfect gas law to the constant pressure change: $p\Delta V = \mu R \Delta T$
- $\mu C_p \Delta T = \mu C_v \Delta T + \mu R \Delta T$

Heat Capacities

- $\mu C_p \Delta T = \mu C_v \Delta T + \mu R \Delta T$
  - $C_p = C_v + R$
  - $C_p - C_v = R$
- Now we know $U = 3/2\ \mu RT$
  - $dU / dT = 3/2\ \mu R$
- $\Delta U = \mu C_v \Delta T$
  - $\Delta U / \Delta T = \mu C_v$
  - $3/2\ \mu R = \mu C_v$
- $C_v = 3/2\ R$
  - Good for monatomic gases, terrible for diatomic and polyatomic gases.

PV^{γ}

- We shall now prove that PV^{γ} is a constant for an ideal gas undergoing an adiabatic process
  - $\gamma = C_p / C_v$
  - Adiabatic process: $\Delta Q = 0$ (No heat exchange)
- $\Delta Q = \Delta U + \Delta W$
- $0 = \mu C_v \Delta T + p \, \Delta V$
- $\Delta T = -p \, \Delta V / \mu C_v$

Continuing

- For an ideal gas: $pV = \mu RT$
  - $p\delta V + V\delta p = \mu R\delta T$
  - $\delta T = (p\delta V + V\delta p) / \mu R = -p\,\delta V / \mu C_v$
  - $-R\,p\,\delta V = C_v\,p\delta V + C_v\,V\delta p$
  - $-(C_p - C_v)\,p\,\delta V = C_v\,p\delta V + C_v\,V\delta p$
  - $-C_p\,p\,\delta V - C_v\,V\delta p = 0$
  - $C_p\,p\,\delta V + C_v\,V\delta p = 0$
  - Divide by $p\,V\,C_v$:
  - $C_p / C_v\,\delta V/V + \delta p/p = 0$
  - $\gamma\,dV/V + dp/p = 0$ (take to limits)
  - $\ln p + \gamma \ln V = \text{const.}$
- $PV^{\gamma} = \text{const}$

Equipartition

- Kinetic Energy of translation per mole is 3/2 RT

$$\frac{1}{2}M\overline{v_x^2}+\frac{1}{2}M\overline{v_y^2}+\frac{1}{2}M\overline{v_z^2}=\frac{3}{2}RT$$

- All terms are equal or each is ½ RT
- The gas is monatomic so
  - $U = 3/2nRT$
  - $C_v = 3/2\ R$
    - $C_p - C_v = R$
    - $C_p = 5/2\ R$
  - $\gamma = C_p/C_v = 5/3 = 1.67$

Diatomic Molecule

- Consider a diatomic molecule: It can rotate and vibrate!
  - $I\omega_y^2 = I\omega_z^2 = ½ RT$
  - $U = 5/2\ nRT$
  - $dU/dT = 5/2\ Rn$
- $C_v = dU/ndT = 5/2\ R$
  - $C_p = C_v + R = 7/2\ R$
  - $\gamma = C_p/C_v = 7/5 = 1.4$
- For polyatomics we must add another ½ RT as there is one more axis of rotation.
  - $\gamma = C_p/C_v = 1.33$

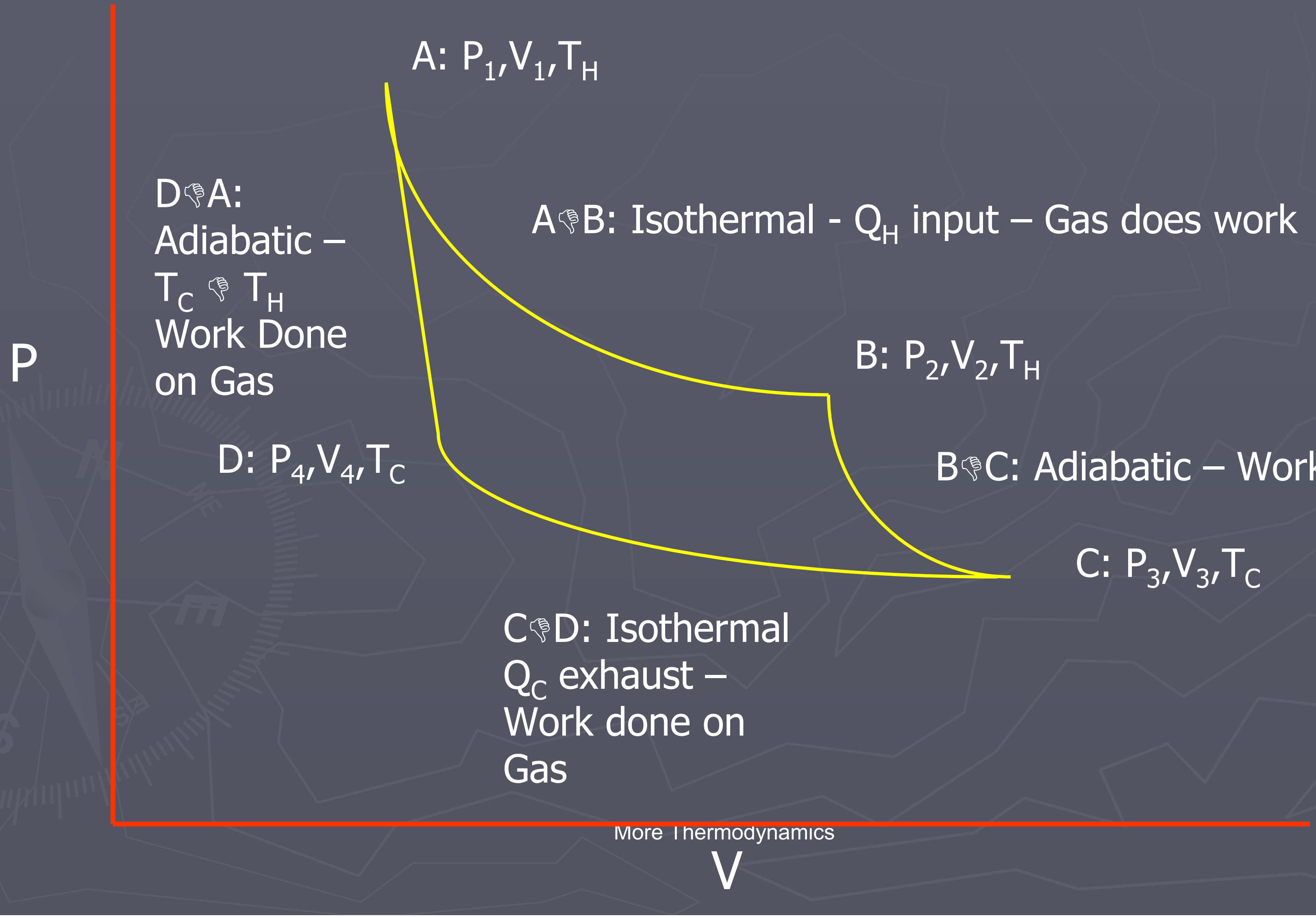
Thermodynamic Values

Particle	KE	U	C_v	C_p	γ
Monatomic	3/2kT	3/2kT	3/2R 2.98	5/2R 4.97	5/3
Diatomic	3/2kT	5/2kT	5/2R 4.97	7/2R 6.95	7/5
Polyatomic	3/2kT	3kT	3R 5.96	4R 7.94	4/3

Thermodynamic Processes

- Irreversible: Rapid change (P_i, V_i) 👎 (P_f, V_f)
  - The path cannot be mapped due to turbulence; ie, the pressure in particular is not well defined.
- Reversible: Incremental changes leading to “quasi steady state” changes from (P_i, V_i) 👎 (P_f, V_f)
- Irreversible is the way of nature but reversible can be approached arbitrarily closely.

Carnot Cycle: Reversible



A: P_1,V_1,T_H

D👎A:
Adiabatic –
T_C 👎 T_H
Work Done
on Gas

A👎B: Isothermal - Q_H input – Gas does work

B: P_2,V_2,T_H

D: P_4,V_4,T_C

B👎C: Adiabatic – Work Done

C: P_3,V_3,T_C

C👎D: Isothermal
Q_C exhaust –
Work done on
Gas

Carnot Process

- Step 1: Equilibrium State (p_1, V_1, T_H)
  - Place on a temperature reservoir at T_H and <u>expand</u> to (p_2, V_2, T_H) absorbing Q_H. The process is isothermal and the gas does work.
- Step 2: Place on a non-conducting stand.
  - Reduce load on piston and go to (p_3, V_3, T_C). This is an adiabatic expansion and the gas does work.
- Step 3: Place on a heat reservoir at T_C and compress slowly.
  - The gas goes to (p_4, V_4, T_C). Q_C is removed from the piston isothermally.
- Step 4: Place on a non-conducting stand and compress slowly.
  - The gas goes to (p_1, V_1, T_H). This is an adiabatic compression with work being done on the gas.

Carnot Cycle

- Net Work: Area enclosed by the pV lines.
- Net Heat Absorbed: $Q_H - Q_C$
- Net Change in U is 0 (initial = final)
- $W = Q_H - Q_C$ so heat is converted to work!
  - Q_H energy input
  - Q_C is exhaust energy
- Efficiency is $e = W / Q_H = 1 - Q_C / Q_H$
  - $e = 1 - T_C/T_H$

Proof

$$\textit{Consider the ab path:}$$

$$\Delta U = 0 \qquad (\textit{isothermal})$$

$$Q_H = W_H = nRT_H \ln(\frac{V_2}{V_1})$$

$$\textit{Similarly for the cd path:}$$

$$Q_C = W_C = nRT_C \ln(\frac{V_3}{V_4})$$

$$\frac{Q_H}{Q_C} = \frac{T_H \ln(\frac{V_2}{V_1})}{T_C \ln(\frac{V_3}{V_4})}$$

$$\textit{For ab and cd (both isothermal)}$$

$$p_1V_1 = p_2V_2$$

$$p_3V_3 = p_4V_4$$

$$\textit{and } pV^\gamma = C \qquad (\textit{adiabatic})$$

$$p_2V_2^\gamma = p_3V_3^\gamma$$

$$p_4V_4^\gamma = p_1V_1^\gamma$$

More Fun Stuff

$$p_1V_1\,p_3V_3\,p_2V_2^{\gamma}\,p_4V_4^{\gamma} = p_2V_2\,p_4V_4\,p_3V_3^{\gamma}\,p_1V_1^{\gamma}$$

$$V_1V_3V_2^{\gamma}V_4^{\gamma} = V_2V_4V_3^{\gamma}V_1^{\gamma}$$

$$V_2^{\gamma-1}V_4^{\gamma-1} = V_3^{\gamma-1}V_1^{\gamma-1}$$

$$(V_2V_4)^{\gamma-1} = (V_3V_1)^{\gamma-1}$$

$$V_2V_4 = V_3V_1$$

$$V_4/V_3 = V_1/V_2$$

The Second Law

- Clausius: It is not possible for any cyclical engine to convey heat continuously from one body to another at a higher temperature without, at the same time, producing some other (compensating) effect.
- Kelvin-Planck: A transformation whose only final result is to transform into work heat extracted from a source that is at the same temperature throughout is impossible.

Entropy

- Consider a Carnot Cycle.
  - $Q_H/T_H = Q_C/T_C$
  - But WRT to Q_H Q_C is negative and
    - $Q_H/T_H + Q_C/T_C = 0$
- Any arbitrary cycle can be thought of as the sum of many Carnot cycles spaced arbitrarily close together.
  - ✦Q/T = 0 for the arbitrary cycle
  - For an infinitesimal ΔT from isotherm to isotherm:

$$\oint \frac{dQ}{T} = 0$$

Entropy II

- $\oint$ is the line integral about the complete cycle
- If $\oint$ is 0 then the quantity is called a state variable
    - T, p, U are all state variables
- We define $dS = dQ/T$ as the change in the entropy (S) and $\oint dS = 0$ which means that entropy does not change around a closed cycle.
- For a reversible cycle the entropy change between two states is independent of path.

Entropy For a Reversible Process

$$\oint dS = 0$$

$$\int_{1\,a}^{b} ds + \int_{2\,a}^{b} ds = 0$$

$$\int_{1\,a}^{b} ds - \int_{2\,a}^{b} ds = 0$$

$$\therefore \int_{1\,a}^{b} = \int_{2\,a}^{b}$$

The change in entropy from reversible state a to b is thus:

$$S_b - S_a = \int_{a}^{b} dS = \int_{a}^{b} \frac{dQ}{T}$$

Entropy and Irreversible Processes

- Free Expansion: $W = 0$, $Q = 0$ (adiabatic), so $\Delta U = 0$ or $U_f = U_i$ so $T_f = T_i$ as U depends only on T)
- How do we calculate $S_f - S_i$ – we do not know the path!
  - First find a reversible path between i and f and the entropy change for that.
    - Isothermal Expansion from V_i to V_f
    - $S_f - S_i = \int dQ/T = nR\ln(V_f/V_i)$
    - The above is always positive!

2^{nd} Law and Entropy

- Reversible: $dS = 0$ or $S_f = S_i$
- Irreversible: $S_f > S_i$

Isothermal Expansion

$$\Delta W = \int p dV = \Delta Q$$

$$\int dQ = \int dW = \int p dV$$

$$\int dS = \frac{1}{T}\int dQ = \frac{1}{T}\int p dV$$

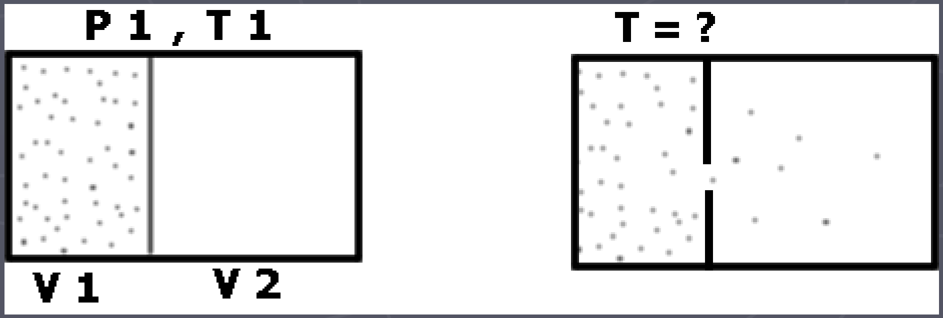
$$= \frac{1}{T}\int \frac{nRT}{V} dV$$

$$= nR\int \frac{1}{V} dV$$

$$= nR \ln\left(\frac{V_f}{V_i}\right)$$

A Better Treatment of Free Expansion

- Imagine a gas confined within an insulated container as shown in the figure below. The gas is initially confined to a volume V1 at pressure P1 and temperature T1. The gas then is allowed to expand into another insulated chamber with volume V2 that is initially evacuated. What happens? Let's apply the first law.



Free Expansion

- We know from the first law for a closed system that the change in internal energy of the gas will be equal to the heat transferred plus the amount of work the gas does, or . Since the gas expands freely (the volume change of the system is zero), we know that no work will be done, so W=0. Since both chambers are insulated, we also know that Q=0. Thus, ***the internal energy of the gas does not change during this process***.

Free Expansion

- We would like to know what happens to the temperature of the gas during such an expansion. To proceed, we imagine constructing a reversible path that connects the initial and final states of the gas. The *actual* free expansion is *not* a reversible process, and we can’t apply thermodynamics to the gas during the expansion. However, once the system has settled down and reached equilibrium after the expansion, we can apply thermodynamics to the final state.

Free Expansion

- We know that the internal energy depends upon both temperature and volume, so we write

$$dU = 0 = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV \quad (1)$$

where we have kept the number of molecules in the gas (N) constant. The first term on the right side in equation (1) simply captures how U changes with T at constant V, and the second term relates how U changes with V and constant T. We can simplify this using Euler's reciprocity relation, equation (2), where x,y,z are U,V,T

$$\left(\frac{\partial x}{\partial y}\right)_{z}\left(\frac{\partial y}{\partial z}\right)_{x}\left(\frac{\partial z}{\partial x}\right)_{y} = -1 \qquad (2)$$

obtain an expression for the change in gas temperature $dT = -\frac{\left(\frac{\partial U}{\partial V}\right)_{T,N}}{\left(\frac{\partial U}{\partial T}\right)_{V,N}} dV = \left(\frac{\partial T}{\partial V}\right)_{U,N} dV \quad (3)$

Free Expansion

- The term $(\partial T/\partial V)_{U,N}$ is a property of the gas, and is called the differential Joule coefficient. This name is in honor of James Prescott Joule, who performed experiments on the expansion of gases in the mid-nineteenth century. If we can either measure or compute the differential Joule coefficient, we can then sayhow temperature changes (dT) with changes in volume (dV). Let's see how we might compute the Joule coefficient from an equation of state. The simplest possible equation of state is the ideal gas, where $PV = nRT$. The easiest way to find the Joule coefficient is to compute $(\partial U/\partial V)_T$ and $(\partial U/\partial T)_V$. Note that we have left off the subscript "N" for brevity, but we still require that the number of molecules in our system is constant.

Free Expansion

- We can use the following identity

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (4)$$

to show that $(\partial U / \partial V)_T = 0$

so that $(\partial T / \partial V)_U = 0$

Free Expansion

- If the gas is described by the van der Waals equation of state

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad (5)$$

you can show that the term in the numerator of equation (3) is given by

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2} \qquad (6)$$

Van der Waals

- Think about what equation (6) is telling us. Recall that the parameter “a” in the van der Waals equation of state accounts for attractive interactions between molecules. Equation (6) therefore states that the internal energy of a system expanded at constant temperature *will* change, and this change is due to *attractive interactions between molecules*. Since the ideal gas equation of state neglects these interactions, it predicts no change in the internal energy upon expansion at constant temperature, but the van der Waals equation of state does account for this. The term in the denominator of equation (3) is nothing more than the constant volume heat capacity $(\partial U/\partial T)_V = C_V$. It can be shown that C_V is never negative and only depends upon temperature for the van der Waals equation of state. Since the parameter *a* is also never negative, equations (3) and (6) tell us that ***the temperature of a real gas will always decrease upon undergoing a free expansion***. How much the temperature decreases depends upon the state point and the parameter *a*. Molecules having strong attractive interactions (a large *a*) should show the largest temperature decrease upon expansion. We can understand this behavior in a qualitative sense by imagining what happens to the molecules in the system when the expansion occurs. On average, the distance between any two molecules will increase as the volume increases. If the intermolecular forces are attractive, then we expect that the potential energy of the system will increase during the expansion. This potential energy increase will come at the expense of the kinetic or thermal energy of the molecules. Therefore the raising of the potential energy through expansion causes the temperature of the gas to decrease.

Real Gases

- We can compute how much the temperature is expected to decrease during a free expansion using the van der Waals equation of state. If one performs this calculation for the expansion of oxygen from 10 bar at 300 K into a vacuum, the temperature is found to be reduced by roughly 4.4 K.