ETA-Lab
Energy Transport Advances

ME-251: Thermodynamics and energetics I
Thermodynamic Properties II

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Photo Credit: Trougnouf

Last Time

- Enthalpy

$$H = U + pV \qquad h = u + pv \qquad \tilde{h} = \tilde{u} + p\tilde{v}$$

- Specific heat

$$c_v = \left(\frac{\delta Q}{\partial T}\right)\Big|_v = \left(\frac{\partial u}{\partial T}\right)\Big|_v \qquad c_p = \left(\frac{\delta Q}{\partial T}\right)\Big|_p = \left(\frac{\partial h}{\partial T}\right)\Big|_p$$

- Evaluating thermodynamic properties with CoolProp

ILOs Today

- Estimate thermodynamic properties in special cases
  - Incompressible substance
  - Ideal gas

○ Reading: Moran 3.10-3.15

Incompressible Substance

- Liquids and solids are often modeled as incompressible *v* = const

In general *u* is a function of *v and T* $\Rightarrow u = u(T)$ for incompressible substances

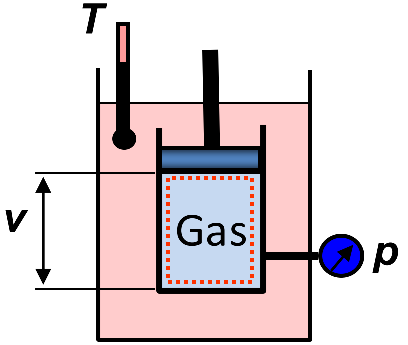
$$\Rightarrow c_v = \left(\frac{\partial u}{\partial T}\right)|_v = \frac{du}{dT} = c_v(T) \text{ for incompressible substances}$$

$$\Rightarrow c_p = \left(\frac{\partial h}{\partial T}\right)|_p = \left(\frac{\partial u + \partial pv}{\partial T}\right)|_p = \frac{du}{dT} + p\frac{\partial v}{\partial T} = c_v \text{ ignoring thermal expansion}$$

$$v = \text{const} \Rightarrow c_v = c_p = c(T)$$

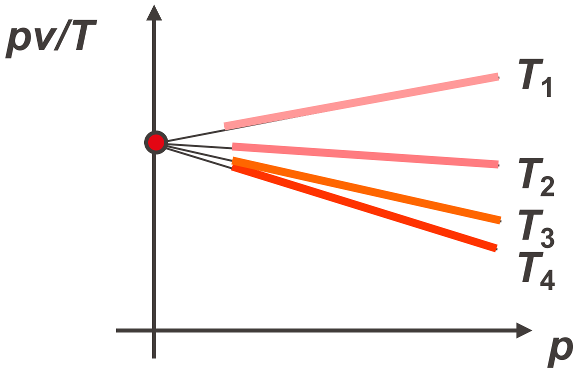
$$h = u(T) + pv \Rightarrow \text{at constant } T, dh = d(pv) = vdp$$

Gases



- Consider gas confined in a piston-cylinder assembly and held at a constant temperature.
- Gas pressure is varied through piston movement
- At a constant temperature, the pressure and specific volume are measured.

$$\lim_{p\to 0}\frac{pv}{T} = R = \frac{\tilde{R}}{M}$$



M: molar mass [kg/mol]
T : temperature [K]
$\tilde{R}$: universal gas constant
R: specific gas constant

Universal Gas Constant

- $\tilde{R} = 8.314$ J/K/mol
- $\tilde{R}$ is the same for different gases, the specific gas constant R is different for different gases
- $\tilde{R} = k_B N_A$
  - The Boltzmann constant $k_B = 1.38 \times 10^{-23}$ [J/K], converts temperature scale to thermal energy scale for individual particles
  - The Avogadro constant $N_A = 6.022 \times 10^{23}$ [1/mol], historically defined to make one mole of hydrogen atoms weigh 1 gram
  - $\tilde{R}$ converts temperature scale to thermal energy scale for one mole of particles

Pop Quiz

What is the SI unit for specific gas constant ***R***

A. [J]

B. [J/K]

C. [J/K/mol]

D. None of above

Scan the QR code with
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Compressibility Factor

- $Z = \frac{pv}{RT} = \frac{p\tilde{v}}{\tilde{R}T}, \quad \tilde{v} = vM = V/n$ molar volume
- $\lim_{p \to 0} Z = 1$
- In practice, Z is a function of temperature, pressure/specific volume, and gas species

Viral Equations of State

$$Z = 1 + \frac{B(T)}{\tilde{v}} + \frac{C(T)}{\tilde{v}^2} + \frac{D(T)}{\tilde{v}^3} + \cdots$$

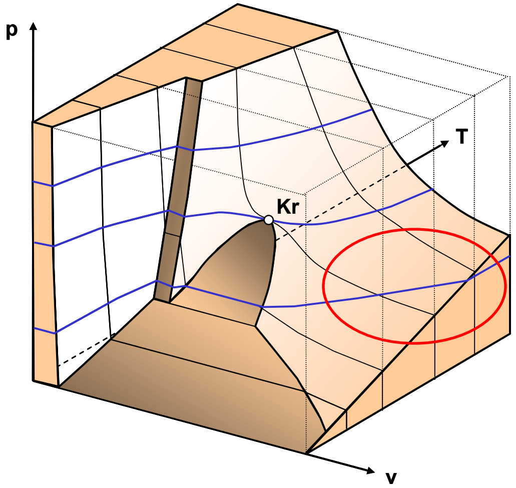
$$Z = 1 + \hat{B}(T)p + \hat{C}(T)p^2 + \widehat{D}(T)p^3 + \cdots$$

Viral coefficients B, C, D (or $\hat{B}, \hat{C}, \widehat{D}$) account for intermolecular interactions and can be derived from statistical mechanics

Ideal Gas Model

- Ideal gas model: $\frac{pv}{RT} = \frac{p\tilde{v}}{\tilde{R}T} = Z \equiv 1$, the dilute limit of real gases
  - No intermolecular interactions (other than elastic collision)
  - Volume of molecules ignored

- When we approximate real gases as ideal gas
  - In p-v diagram, $p \propto \frac{1}{v}$ for isotherms
  - In T-v diagram, $T \propto v$ for isobars



Ideal Gas Thermodynamic Properties

- Given a gas species, $u = u(T)$ (intermolecular interactions insignificant)
- $h = u + pv = u(T) + RT$, also just a function of temperature
- $c_v = \left(\frac{\partial u}{\partial T}\right)|_v = \frac{du}{dT} = c_v(T)$
- $c_p = \left(\frac{\partial h}{\partial T}\right)|_p = \frac{du}{dT} + R = c_v(T) + R$
- Specific heat ratio $k = \frac{c_p}{c_v} = 1 + \frac{R}{c_v}$
  - $c_v = \frac{R}{k-1}; c_p = \frac{kR}{k-1}$

Ideal Gas Polytropic Processes

- A process where $pv^n = \text{const}$
  - Isobaric process: $p = \text{const} \Rightarrow n = 0$
  - Isothermal process: $pv = RT = \text{const} \Rightarrow n = 1$
  - Isochoric processes: $v = \text{const} \Rightarrow n = +\infty \quad (p^{1/n}v = \text{const})$
  - Isentropic process (not covered yet): $pv^k = \text{const} \Rightarrow n = k = c_p/c_v$

Ideal Gas Polytropic Processes

- Compression/expansion work (intensive form)

$$w = \int_1^2 p dv = \begin{cases} p_1 v_1 \ln\left(\frac{v_2}{v_1}\right), n = 1 \\ \frac{p_2 v_2 - p_1 v_1}{1 - n}, n \neq 1 \end{cases}$$

- Applying ideal gas law

$$w = \int_1^2 p dv = \begin{cases} RT \ln\left(\frac{v_2}{v_1}\right), n = 1, \text{isothermal} \\ \frac{R(T_2 - T_1)}{1 - n}, n \neq 1 \end{cases}$$

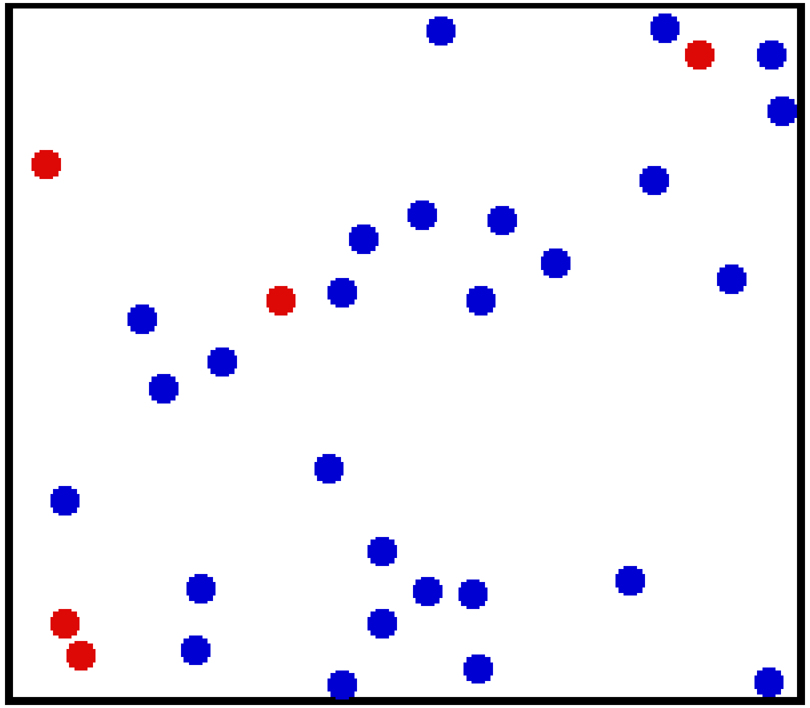
Perfect Gas

- Special case of ideal gas (also called calorically perfect)
  - Like an ideal gas and what’s more, the specific heats are approximated as **independent of temperature**
  - $c_v = \text{const}, \; c_p = c_v + R$

Monoatomic $c_v = 1.5R$
Diatomic $c_v = 2.5\,R$
Polyatomic: $c_v = 3R$

Crash Course on Kinetic Theory of Gases

- Consider gas as **a large number of randomly moving particles** that collide with one another every now and then
- Collisions are elastic: **kinetic energy is conserved** before and after
- Between collisions, particles are not affected by any force field



Credit: A. Greg

Temperature Revisited

- The kinetic theory defines temperature by considering the average kinetic energy of a particle in a system
- The average translational kinetic energy $e_{kt} = \frac{3}{2}kT$

Specific Heat From Kinetic Theory

- If an ideal gas system only contains monatomic molecules (Ar, He,..), one only needs to consider translational kinetic energy

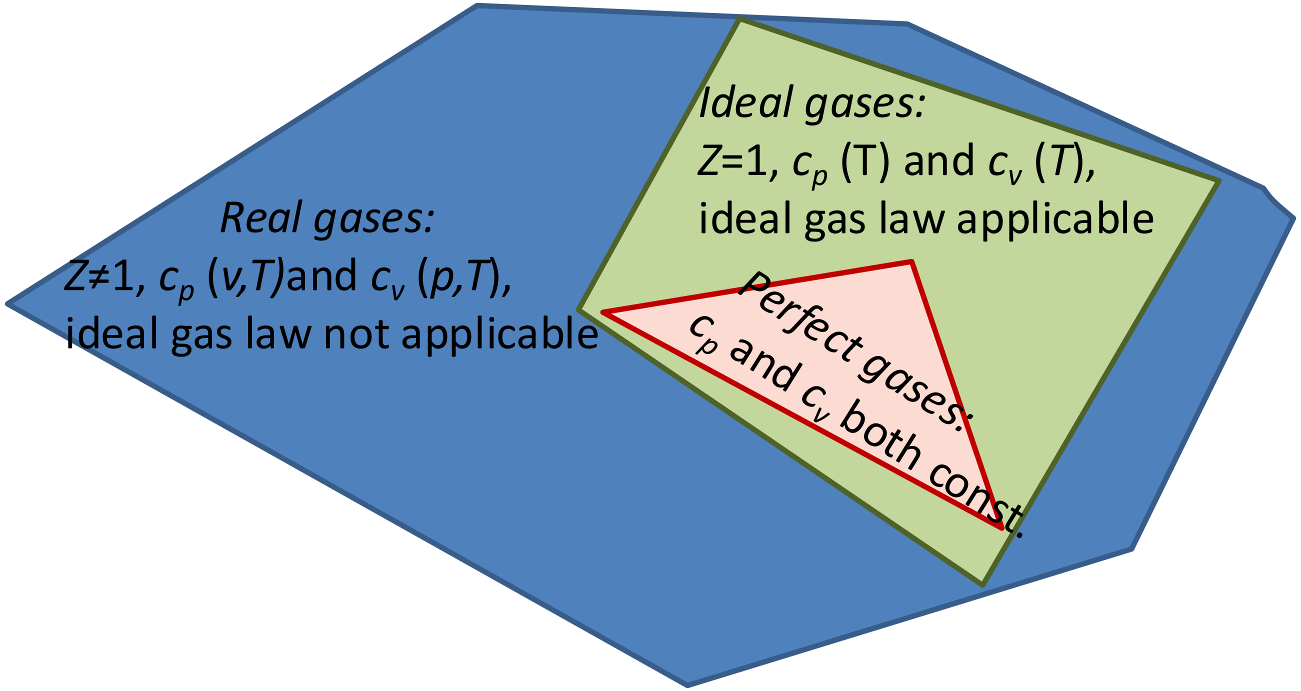
$$U = \frac{3}{2} N_{sys} kT$$

- For monatomic ideal gases

$$c_v = \frac{1}{m_{sys}} \frac{dU}{dT} = \frac{3}{2} \frac{N_{sys}}{Mn} \frac{\tilde{R}}{N_A} = \frac{3}{2} R$$

- For diatomic and polyatomic molecules, internal energy can also come from rotation and vibration, still proportional to temperature.

Gas Model Summary



Real gases:
Z≠1, c_p (*v*,*T*)and c_v (*p*,*T*),
ideal gas law not applicable

Ideal gases:
Z=1, c_p (T) and c_v (*T*),
ideal gas law applicable

Perfect gases:
c_p and c_v both const.