

Chapter 12 Models

- What we have done so far is generally applicable to all substances, whether solid, liquid or gases.
- We need to add physical properties - the interrelationship between the various parameters.
- These are called "Equations of State".

A. Ideal Gas

Let's derive the ideal gas law ($PV = nRT$)

a monatomic "ideal" gas has 3 d.o.f. (x, y, z).
Translation only, no rotation.

$$\text{i.e. } \nu = 3, \quad \mathcal{R} = 3N \leftarrow \text{number of molecules.}$$

$$\therefore \mathcal{R}_{\text{ideal gas}} \propto E^{\mathcal{R}/2} = E^{3N/2} \quad \text{from before}$$

Buried in the constant of proportionality is the factor V^N . So we have:

$$\mathcal{R}_{\text{ideal gas}} = \text{const } V^N E^{3N/2} \quad (\text{see pg 192 for more details})$$

$$\begin{aligned} \text{Thus } S_{\text{ideal gas}} &= k \ln \Omega_{\text{ideal gas}} \\ &= NK \ln V + \frac{3}{2} NK \ln E + \text{const} \end{aligned} \quad \textcircled{1}$$

But what do we know about how S is related to E, P, V, \dots ?

$$\text{1st Law: } dE = dQ - dW + \mu dN$$

$$\begin{array}{ccc} & \uparrow & \uparrow \\ & T ds & p dV \end{array}$$

$$\text{ie } \left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{1}{T}, \quad \left. \frac{\partial S}{\partial V} \right|_{E, N} = \frac{P}{T}$$

Apply this to $\textcircled{1}$:

$$\frac{1}{T} = \frac{3}{2} \frac{NK}{E}$$

↓

$$\underline{E = \frac{3}{2} NKT}$$

↑

no surprise, we had this before

$$\frac{P}{T} = \frac{NK}{V}$$

↓

$$\underline{PV = NKT}$$

↑

Tada! The ideal gas Law!

$$NK \equiv nR$$

↑ # of moles

$$\text{ie } PV = nRT$$

$$\text{or } P \underline{v} = RT$$

↑ $v/n = \text{molar volume}$

B. Real Gases

The ideal gas law assumes molecules of zero size + neglects forces of attraction.

So we modify the law:

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT$$

vander Waals
equation of state

↑ attractive force $\propto \frac{1}{r^6} = \frac{1}{v^2}$

See coursepack for a table of $a+b$ for some substances (experimentally determined).

C. Liquids

We don't have a good model for liquids!

D. Solids

Ditto!

E. Other common systems

We get to a bit of this in chapter 15. See also later chapters in Stowe.

F. Sample Applications

F.1 Heat Capacities

Let's revisit $C_v + C_p$ to see what we can find.

We have: $dE = dQ - pdv + \mu dN$

Let's hold N const.

Now $E = \frac{1}{2} NKT + N\mu$ (see 6-6
9-3)

$\therefore dE = \frac{1}{2} NKdT + Nd\mu$ (N const)

$\therefore dQ = dE + pdv$
 $= \frac{1}{2} NKdT + N d\mu + pdv$

(Man! There is no end to the number of ways to rewrite the 1st Law!)

$Nd\mu$ is small compared to the other terms unless there is a phase change or something special going on to alter the potential.

\therefore on a molar basis:

$$dq = \frac{1}{2} R dT + pdv$$

New recall $C_v \equiv \left. \frac{\partial q}{\partial T} \right|_v = \frac{v}{2} R$

$$C_p \equiv \left. \frac{\partial q}{\partial T} \right|_p = \frac{v}{2} R + p \left. \frac{\partial v}{\partial T} \right|_p$$

$$\text{ie } C_p = C_v + p \left. \frac{\partial v}{\partial T} \right|_p$$

- Great result! C_v is a function of v .

- So if we study C_v we can learn about v

macroscopic world meets microscopic world.

$$\text{also } C_p - C_v = p \left. \frac{\partial v}{\partial T} \right|_p$$

↑ large for gases

↑ small for solids & liquids.

Example (see Table 12.1)

$$(C_p - C_v)/R$$

Air 1.00

Water vapour 1.14

Water 0.045

Ice 0.027

Example

What is $C_p - C_v$ for an ideal gas.

$$C_p - C_v = p \left(\frac{\partial v}{\partial T} \right)_p$$

$$pv = RT \Rightarrow p dv + v dp = R dT$$

$$\therefore \left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p}$$

$$\therefore C_p - C_v = R$$

Example

What is $C_p - C_v$ for a van der Waals gas?

$$\left(p + \frac{a}{v^2} \right) (v - b) = RT$$

$$\therefore \left(dp - \frac{2a}{v^3} dv \right) (v - b) + \left(p + \frac{a}{v^2} \right) dv = R dT$$

$$\therefore \left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{\left(p + \frac{a}{v^2} \right) - \frac{2a(v-b)}{v^3}}$$

$$\begin{aligned} \therefore C_p - C_v &= p \left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{1 + \frac{a}{pv^2} - \frac{2a(v-b)}{pv^3}} \\ &= \frac{R}{1 - \frac{a}{pv^2} + \frac{2ab}{pv^3}} \end{aligned}$$

Note: When gas molecules are well separated: $p \gg a/v^2 + v \gg b$

$$\therefore C_p - C_v \rightarrow \frac{R}{1 - \frac{a}{pv^2} + \frac{2ab}{pv^3}} \rightarrow R$$

↓ when density is great (ie approaching a liquid)
 $p \ll a/v^2$, $v \approx b$

$$\therefore C_p - C_v \rightarrow \frac{R}{\frac{a}{pv^2}} \rightarrow 0$$

← large

This agrees with our expectations.

F.2 Isothermal Compressibilities

$$K \equiv -\frac{1}{v} \left. \frac{\partial v}{\partial p} \right|_T = -\frac{1}{v} \left. \frac{\partial v}{\partial p} \right|_T$$

We know gases are compressible, liquids & solids are not.

Ideal gas

$$pv = RT \Rightarrow p dv + v dp = R dT$$

$$\therefore \left. \frac{\partial v}{\partial p} \right|_T = -\frac{v}{p}$$

$$\therefore K = \frac{1}{p} \quad \leftarrow \text{as } p \uparrow, K \downarrow \text{ makes sense.}$$