A (non-rigid) diving bell has an air space of 3.0 m$^3$ when on the deck of a small boat. What is the volume of the air space when the bell has been lowered to a depth of 50 m? The density of sea water is 1.025 g cm$^{-3}$.

What do we need to assume? Ideal gas behavior for air

Constant T, so use Boyle: PV=cons't

Water temperature is unchanged at 50 m

Why is “rigid” important information?

Boyle’s law in the form $p_f V_f = p_i V_i$ is solved for $V_f$: $V_f = \frac{p_i}{p_f} \times V_i$.

$p_i = 1.0\ \text{atm},$

$p_f = p_i + \rho gh = 1.0\ \text{atm} + \rho gh$

$\rho gh = (1.025 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (50 \text{ m}) = 5.03 \times 10^5 \text{ Pa}.$

Hence, $p_f = (1.01 \times 10^5 \text{ Pa}) + (5.03 \times 10^5 \text{ Pa}) = 6.04 \times 10^5 \text{ Pa}.$

$V_f = \frac{1.01 \times 10^5 \text{ Pa}}{6.04 \times 10^5 \text{ Pa}} \times 3.0 \text{ m}^3 = \boxed{0.50 \text{ m}^3}.$
Real Gases

* Compressibility, $Z$

$$Z = \frac{PV}{nRT} = \frac{PV}{RT}$$

$Z = 1$ Ideal Gas behavior

$Z < 1$ PV less than expected Attractive forces

$Z > 1$ PV greater than expected Repulsive forces
Real Gases – data!

Compressibility \[ Z = \frac{PV}{nRT} = \frac{PV}{mRT} \]

\( Z = 1 \) at all \( P, T \) → Ideal Gas Behavior

Look at a broader 0 - 800 atm region

We need new eq of state for each gas
These data are many gases at one \( T \)
So next look at one gas at many \( T \)
Boyle Temperature, $T_B$

$Z = Z(P,T)$

$T_B$ is the temperature corresponding to the greatest extent of near-ideal behavior.

We can determine $T_B$ analytically.

$$\frac{\partial Z(T,P)}{\partial P} \bigg|_{\lim p \to 0^+} = f(T)$$

$$\frac{df}{dT} = 0 \text{ at } T = T_B,$$ the Boyle temperature
van der Waals equation of state

- Physically-motivated corrections to Ideal Gas EoS.
- For a real gas, both attractive and repulsive intermolecular forces are present. Empirical terms were developed to help account for both.

1. Repulsive forces: make pressure higher than ideal gas

   Excluded volume concept (nb)

   \[ P = \frac{nRT}{V - nb} \]

Volume of one molecule of radius \( r \) is \( V_{\text{mol}} = \frac{4}{3} \pi r^3 \)

Closest approach of two molecules with radius \( r \) is 2r.
Excluded volume

\[ P = \frac{nRT}{V - nb} \]

The volume of one molecule of radius \( r \) is \( V_{\text{mol}} = \frac{4}{3} \pi r^3 \)

The closest approach of two molecules with radius \( r \) is \( 2r \). What is the excluded volume for the two molecules?

A. \( 2V_{\text{mol}} \)
B. \( 4V_{\text{mol}} \)
C. \( 8V_{\text{mol}} \)
D. \( 16V_{\text{mol}} \)
van der Waals equation of state

- Physically-motivated corrections to Ideal Gas EoS.
- For a real gas, both attractive and repulsive intermolecular forces are present. Empirical terms were developed to help account for both.

1. Repulsive forces: make pressure higher than ideal gas (or, equivalently, make the volume smaller)

Do the latter: Excluded volume

\[ P = \frac{nRT}{V - nb} \]

Volume of one molecule of radius \( r \) is \( V_{\text{mol}} = \frac{4}{3} \pi r^3 \)
Closest approach of two molecules with radius \( r \) is \( 2r \).
The excluded volume \( V_{\text{exc}} \) is \( 2^3 V_{\text{mol}} = 8V_{\text{mol}} \) for two molecules.

So we might estimate that \( b \approx 4V_{\text{mol}}N_A \)

This assumes binary collisions only. Always true? NO!
van der Waals equation of state

- Physically-motivated corrections to Ideal Gas EoS.
- For a real gas, both attractive and repulsive intermolecular forces are present. Empirical terms were developed to help account for both.

2. Attractive forces: make pressure lower than ideal gas

Pressure depends on wall collisions, both on frequency and their force.

Not easy to show, but we expect a pressure correction of the form $-a(n/V)^2$, giving the van der Waals Equation of State

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{RT}{V - b} - \frac{a}{V^2}$$
3D van der Waals eqn of state

\[ T = \frac{T}{T_c} \]
Look at 50 °C isotherm. Behavior is near ideal gas

Look at 20 °C isotherm.
A→B→C Compression
At C, liquid condensation begins
D - liquid-vapor mixture at $P_{\text{vap}}(20 \, ^\circ C)$
E - last vapor condenses
F - Steep rise in pressure
A liquid or solid is much less compressible than a gas

For $T > T_c$, there is a single phase, with no liquid formed.
van der Waals Isotherms near $T_c$

$v d W$ “loops” are not physical. Why?

Patch up with Maxwell construction

van der Waals Isotherms, $T/T_c$
van der Waals Isotherms near $T_c$

Look at one of the van der Waals isotherms at a temperature of 0.9 $T_c$

- $A \to D$ compress the gas at constant $T$, (steep and not very compressible)
- $F \to G$ compress the liquid phase  
- $D \to F$ vapor condensing (gas and liquid coexist)

These are **stable** states

$F \to C$ supercooled liquid
$D \to B$ superheated gas
These are **metastable** states

$C \to B$ a non-physical artifact of vdW  
(patched up with Maxwell construction)

**Metastable example:**
Use a very clean glass. Add water and heat for a while with a microwave oven (superheat)  
Add a drop of sand or perhaps touch with a spoon.