Chem 1045 — Chemistry & Chemical Reactivity
Lecture Notes — Kotz/Treichel/Townsend, 8th Ed

These Notes are to SUPPLEMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test! The author is not responsible for typos in these notes.

Chapter 11 Gases and Their Properties

"Acute mountain sickness" AMS is due to the lack of oxygen at high altitude, also called Hypoxia. We will learn about the relationship of Pressure, Temperature, Volume, and the amount of material using examples of SCUBA and a car air bag. Airplane pilots, when flying in a non-pressurized airplane and above 12,500 ft, are required to be breathing supplemental oxygen so they don't pass out.

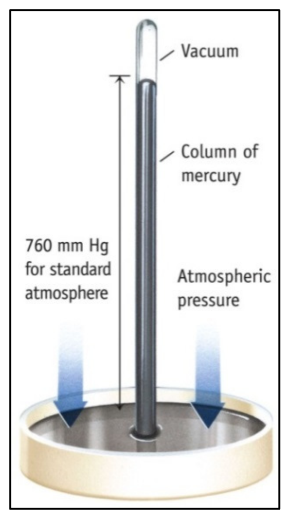
Pressure is the force exerted on an object divided by the area of the object
Standard atmosphere (atm) = 1 atm = 760 mm Hg = 1.01325 bar

Example 11.1 Convert 635 mm Hg into the other units?

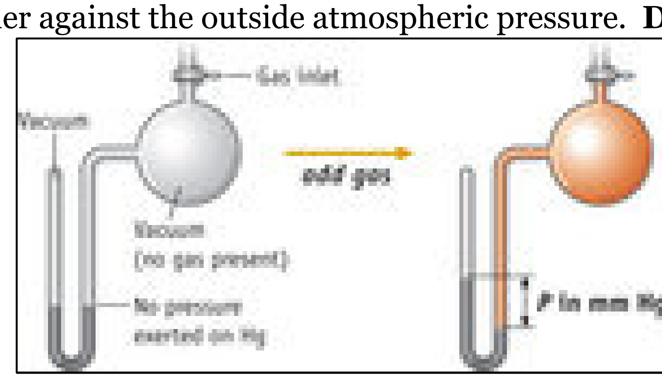
635 mm Hg * 1 atm / 760 mm Hg = 0.836 atm

635 mm Hg * 1.013 bar / 760 mm Hg = 0.846 bar

We measure atmospheric pressure with a **Barometer**:



We measure the pressure inside of a reaction vessel using a manometer. This measures the "Relative" pressure inside the container against the outside atmospheric pressure. **Discuss the difference!**



Discuss the differences between a barometer and a manometer!

<u>Boyle's Law</u> Pressure is indirectly related to volume. Take a bicycle pump, when you push the piston down, you decrease the volume, so you increase the pressure.

P1V1 = P2V2 at constant n and t

Example 11.2 A bicycle pump has a volume of 1400. cm^3 at a pressure of 730. mm Hg. What is the pressure when the handle is pushed down and the volume is now 170. cm^3? **Note I added decimal!**

P1V1 = P2V2 **P2** = P1V1 / V2 = 730 mm Hg * 1400 cm^3 / 170 cm^3 = 6011. = **6.01 x 10^3 mm Hg**

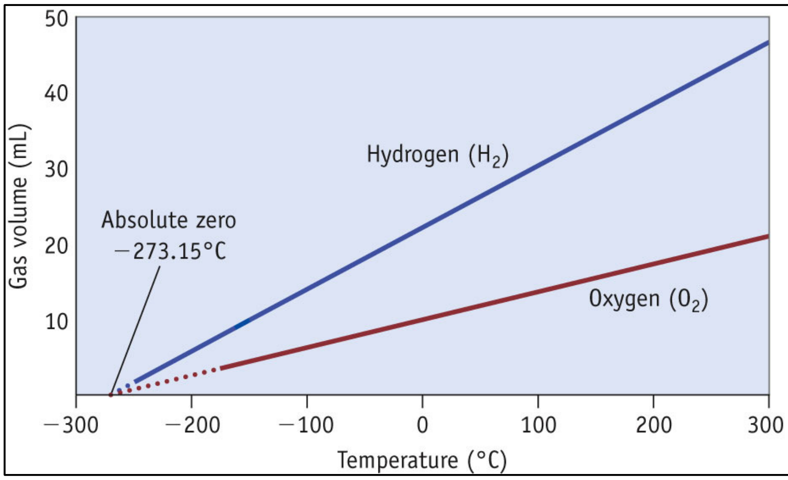
<u>Charle's Law</u> The volume of a gas is directly related to the temperature. Take a balloon and put it out in the hot sun, it will expand; put it in a freezer, it will shrink.

V1/ T1 = V2/T2 at constant n and P

Example 11.3 A sample of CO2 is a gas-tight syringe has a volume of 25.0 ml at room temperature (20.0 ^oC). What is it's volume at 37 ^oC?

V1/T1 = V2/T2 **V2** = V1 * T2/T1 = 25.0 ml * (20.0 + 273.2) K / (37. + 273) = **26.4 ml**

NOTE: Discuss Sig Digits with Temperature



T (°C)	T (K)	Vol. H_2 (mL)	Vol. O_2 (mL)
300	573	47.0	21.1
200	473	38.8	17.5
100	373	30.6	13.8
0	273	22.4	10.1
−100	173	14.2	6.39
−200	73	6.00	—

Determination of Abslolute Zero – 0 K

<u>Combined or General Gas Law</u> **P1V1 / T1 = P2V2 / T2**

Example 11.4 A Helium balloon is launched at T = 22.5 ^oC and a pressure of 754 mm Hg and a volume of 4.19 x 10^3 L. What is it's volume at an altitude of 20 miles where the pressure is 76.0 mm Hg and the temperature is -33 ^oC?

P1V1 / T1 = P2V2 / T2 Derive: V2 = P1 V1 T2 / T1 P2

T1 = 22.5 + 273.2 = 295.7 K T2 = - 33. + 273.2 = 240.0 = 240. K

V2 = 754 mm Hg * 4.19 x 10^3 L * 240.K/295.7 K * 76.0 mm Hg = 33.738 x 10^3 L = **3.37 x 10^4 L**

Car Tire Pressure: You fill your car tires on a hot summer day to 35.0 lb, the outside temperature is 99 ^oF. Overnight, the temperature drops to freezing, 32. ^oF. What is the tire pressure?

We need temperature in K and not F.

T1 C = (99 – 32)*5/9 = 37 ^oC T1 K = 37 + 273 = 310 K
T2 C = (32 – 32)*5/9 = 0 ^oC T2 K = 0 + 273 = 273 K

Note: we do not have the car tire volume! But the car tire is rigid, so its volume when the tire is hot or cold is the same. And the equation has V1 / V2, so the same value V1/V2 = 1

From: P1V1 / T1 = P2V2 / T2

Derive **P2** = P1 T2 / T1 = 35.0 lb * 273 K / 310 K = 30.8 = **31 lbs**

We lost @ 5 pounds of air, so the tire may start to look flat

Avogadro's Hypothesis:

equal volumes of a gas, under the same conditions, will have equal number of molecules. **V α [is proportional to] n** at constant T and P

Example 11.5 For the following reaction, what volume of N2 is needed to complete the reaction if you start with 15.0 L of hydrogen.

N_2 (g) + 3 H_2 (g) → 2 NH_3 (g)

Volume N_2 = 15.0 L H_2 * (1 L N_2 / 3 L H_2) = **5.00 L N_2**

Volume NH_3 = 15.0 L H_2 * (2 L NH_3 / 3 L H_2) = **10.0 L NH_3**

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The **Ideal Gas Law** **PV = nRT** R = the gas constant = 0.082057 L atm / Mole K

STP = Standard Temperature and Pressure = 0 $_oC$ and 1 atm.

One mole of a gas will occupy 22.4 L at STP

PV = nRT V = nRT/P 1 mole * 0.082 L atm / Mol K * 273 K / 1 atm = **22.4 L**

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Charles flew the first Hydrogen Balloon in 17?? Using 225 Kg of Sulfuric Acid and 450 Kg of Iron metal to generate the hydrogen. How many Liters of hydrogen did he make?

3 H_2SO_4 + 2 Fe → Fe2$(SO_4)_3$ + 3 H_2 ↑
225 Kg 450 Kg ?

Calculate Mw of H_2SO_4			
	3 H_2	6 * 1.008	6.048
	1 S	1 * 32.07	32.07
	4 O	4 * 16.00	64.00

MW = 102.118 = **102.12 g/mole of H_2SO_4**

$\frac{225.000 \text{ g } H_2SO_4}{3 * 102.12 \text{ g/mole}}$ = **734. Moles** $\frac{450.000 \text{ g Fe}}{2 * 55.85 \text{ g/mole}}$ = 4028 Moles

H_2SO_4 is the Limiting Reagent

$\frac{225.000 \text{ g } H_2SO_4}{3 * 102.12 \text{ g/mole}} = \frac{X \text{ g } H_2}{3 * 2 * 1.008 \text{ g/mole}}$ = 4442. g H_2

Volume H_2 = 22.4 L/mole * moles = (22.4 L/mole) * 4442. g H2 / 2 * 1.008 g/mole =

= 49,355.55 = 49,400 = **4.94 x 10^4 L of H_2 gas** = @ 158 cu ft H_2

Example 11.6 How many moles of N_2 is in an inflated car air bag if the volume is 65 L, pressure is 829 mm Hg, and the temperature is 25 ^oC.

Pressure in atm = 829 mm Hg/(760 mm Hg/ 1 atm) = 1.09 atm   T = 25 + 273 = 298 K

From: PV = nRT

Derive: n = PV/RT = 1.09 atm * 65 L / (0.082057 L atm / Mol K) * 298 K = 2.899 = **2.9 mole**

Density of a Gas

Density is Mass (wt)/Vol = g/V

PV = nRT ➔ PV = (g/Mw) * RT ➔ Density = g/V = P Mw / RT

So the density of a gas can be calculated, or by rearranging the equation

You can also solve it for Mw, and use this methodology to determine the molecular weight of a gas.
Mw = gRT / PV = (g/V) * RT/P
And, at constant P and T, the density of a gas is proportional to the Mw of the gas.

Example 11.7 What is the density of CO2 at STP? Is it more dense than air (1.29 g/L) **and WHY?**

Mw CO2 1 C = 12.01 g/mole + 2 O = 2 * 16.00 g/mole = 44.01 g/mole

Density = g/V = P Mw / RT = 1.00 atm * 44.01 g/mole / (0.082057 L atm /mole K) * 273 K
Density = 1.96 g / L

Dry air has an average molecular weight of 29 g/mole (80% N2 at 28.02, 20% O2 at 32.00)
It has a density around 1.29 g/L

If we have another gas with a molecular weight greater than dry air, its density will be larger
So, most cases such as gas vapour or smelly SO2 or H2S, or Chlorine as used in WWI, will sink to the ground!

Example 11.8 Determine the molecular weight and molecular formulae for a chlorofluorocarbon (CHF2) from: 0.100 g sample had a pressure of 70.5 mm Hg in a 256 ml container at 22.3 ^oC.

From: PV = (g/Mw) * RT   **Derive:** Mw = g R T / PV

g = 0.100g   T = 22.3 ^oC + 273.*2* = *295.5 K*   *V* = *256* ml * 1 L / 1000. ml = 0.256 L

P = 70.5 mm Hg * 1 atm / 760.0 mm Hg = 0.09276 = 0.0928 atm

$$\textbf{Mw} = g\,R\,T / PV = \frac{0.100\text{ g} * (0.082057\text{ L atm /mole K}) * 295.5\text{ K}}{0.0928\text{ atm} * 0.256\text{ L}} = \textbf{102 g/mole}$$

Mw CHF2	1 C	1 * 12.01	12.01
	1 H	1 * 1.008	1.008
	2 F	2 * 19.00	<u>38.00</u>
		Mw =	51.018 = 51.02 g/mole

102 g/mole / 51 g/mole = **2**

Molecular Formulae = 2 * Empirical Formulae = 2 * CHF_2 = $\mathbf{C_2H_2F_4}$

Example 11.9 **Car Air Bag** How much sodium azide is required to fill a car air bag at 829 mm Hg, 22.0 ^oC, volume = 45.5 L $2\,NaN_{3\,(s)} \rightarrow 2\,Na_{(s)} + 3\,N_{2\,(g)}$

- First determine the moles of nitrogen it will take,
- Then calculate the moles of sodium azide, then the grams.

From: PV = n * RT   **Derive**: n = P V / R T

P = 829 mm Hg * 1 atm / 760 mm Hg = 1.09 atm   T = 22.0 ^oC + 273.2 = 295.2 K

n = 1.09 atm * 45.5 L / (0.082057 L atm /mole K) * 295.2 K = 2.05 mole N2

1 Na	1 * 22.99	22.99
3 N	3 * 14.01	42.03
	Mw =	65.02

Calculate the moles of NaN_3 using the stoichiometric coefficient and Mw of NaN_3

2.05 mole N_2 * (2 mole $NaN_{3\,(s)}$ / 3 $N_{2\,(g)}$) * 65.02 g / mole NaN_3 = 88.860 = **88.9 g NaN_3**

Example 11.10 Students do this example 2 Li↓ + 2 $D2O_{(l)}$ → 2 $LiOD_{(aq)}$ + D2↑
How much D2 can be prepared from 0.125 Li and 15.0 ml of D2O (d = 1.11 g/ml)? If the gas is in a 1450 ml flask at 22.0 °C, what is the pressure? Mw D = 2.0147 g/mole.

11.5 Gas mixtures and Partial Pressure

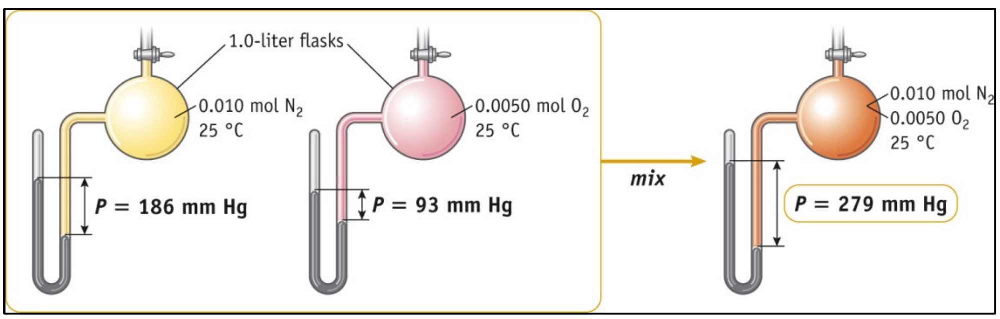
Dalton's Law of Partial Pressure: the pressure of a mixture of ideal gases is the sum of the partial pressures of the different gases in the mixture.

$\mathbf{P_{total} = P_1 + P_2 + P_3}$ .. = n_a (RT/V) + n_b (RT/V) + n_c (RT/V) + = $\mathbf{n_{total}}$ **(RT/V)**

Mole Fraction of a Gas "A" $X_a = n_a / (n_a + n_b + n_c) = n_a / n_{total}$

From which we can derive $\mathbf{P_a = X_a P_{total}}$

The pressure of a gas in a mixture is the product of its mole fraction to the total pressure of the mixture.



Example 11.11 What is the partial pressure of each gas in a mixture of 15.0 g of halothane C_2 H Br Cl F_3, mixed with 23.5 g of oxygen gas and the total pressure is 855 mm Hg.

Haloethane	2 C	2 * 12.01	24.02
	1 H	1 * 1.008	1.008
	1 Br	1 * 79.90	79.90
	1 Cl	1 * 35.45	35.45
	3 F	3 * 19.00	57.00
		Mw =	196.378 = 196.38 g/mole

Moles Haloethane = g / Mw = 15.0 g / 196.38 g/mole = 0.07638 = 0.0764 moles haloetheane

Moles Oxygen = g / Mw = 23.5 g / 32.00 g/mole = 0.73437 = 0.734 moles oxygen

MF Haloethane = $X_{haloetheane}$ = 0.0764 moles / (0.0764 moles + 0.734 moles) = 0.09427 = 0.0943 MF

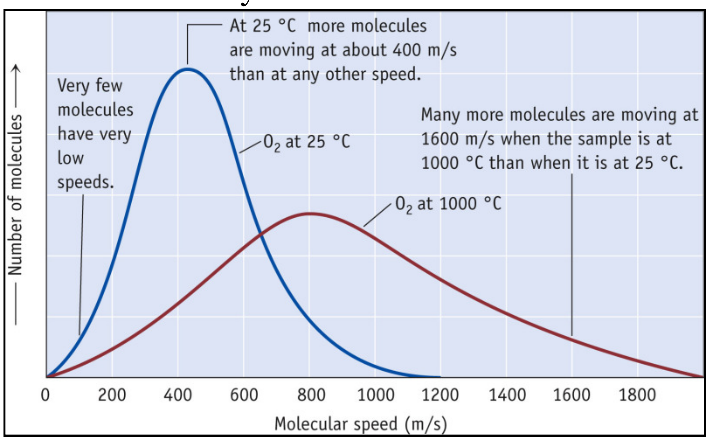
$X_{haloetheane} + X_{oxygen}$ = 1.0000 X_{oxygen} = 1.0000 - $X_{haloetheane}$ = 0.90572 = 0.906 MF
$\mathbf{P_{oxygen}}$ = X_{oxygen} * P_{total} = 0.906 MF * 855 mm Hg = 774.63 = **775. mm Hg**
$\mathbf{P_{haloethane}}$ = $X_{haloetheane}$ * P_{total} = 0.0943 MF * 855 mm Hg = 80.626 = **80.6. mm Hg**

11.6 Kinetic-Molecular Theory of Gases

- A gas is a collection of a very large number of particles that are in constant random motion
- The pressure of a gas is due to the collisions with the container walls
- The particles are much smaller than the distance between them
- The particles move in straight lines between collisions with other particles and with the container wall
- The average kinetic energy (½ mv^2) of a collection of gas particles is proportional to its T_{Kelvin}
- Gas particles collide with the walls of the container and one another without a loss of energy

Molecular Speed and Kinetic Energy

- Molecules of a gas are always in motion and the speed of the molecules depends on the Kelvin temperature.
- All of the gas molecules do not have the same speed or energy. They have a distribution of energy; this distribution is defined by the **Maxwell – Boltzmann curve**.



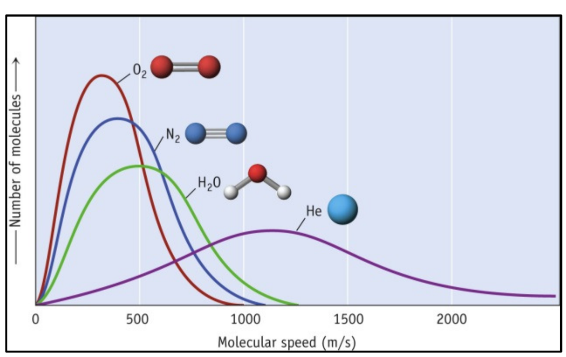
Looking at the curve, we can see that at a certain temperature there is an area (max number of molecules) where we are going to find a higher portion of molecules moving at a certain speed. At a higher temperature, this peak area shifts to the right so the higher portion of molecules are moving at a higher speed. For oxygen at 25 °C, the peak is around 400 m/s, at 1000 °C it shifts to around 800 m/s. 400 m/s corresponds to 900 miles per hour!

The Root-Mean-Square-Speed or rms is defined as $(\mu^2)^{1/2}$ which equals

$$(\mu^2)^{1/2} = (3\,R\,T / M)^{1/2}$$

R is the gas constant 8.3145 J/mole K   T is K temperature   M the molar mass in kg/mole

- All gases have the same average kinetic energy at the same temperature
- Different gasses at the same temperature may have different rms speed
- The smaller the gas, larger M, the greater the speed



Example 11.12 Calculate the rms speed of oxygen at 25 ^oC.

$(\mu^2)^{1/2} = (3 R T / M)^{1/2} = (3 * (8.3145 J/mole K) * 298 K / 32.0 x 10^{-3} kg/mole)^{1/2} =$

$(\mu^2)^{1/2} = (2.32 x 10^5 m2/s^2)^{1/2} = 482 m/s$ which equals about 1100 miles per hour

Pressure of a gas = force of collusions / area

This is directly related to the number of collisions of the gas molecules with the walls

Increasing the temperature, increases the speed of the molecules which increases the number of collisions with the walls thus increasing the pressure

Increasing the number of molecules also at a fixed temperature has all the molecules with the same speed as before adding the molecules thus increasing the number of collisions with the walls thus increasing the pressure

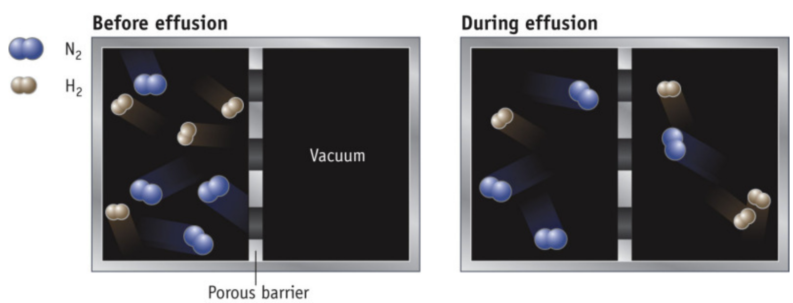
11.7 Diffusion and Effusion

Diffusion is the mixing of molecules of two or more gases due to their random molecular motions

- Someone with perfume on walks into a room, you smell the perfume at the other end
- McDonalds is cooking a new batch of French fries, you smell it as your drive by

Effusion is the movement of a gas through a tiny opening in a container into another container where the pressure is very low. Graham's Law is the rate of effusion is inversely proportional to the square root of the gas molar mass:

$$\frac{\textbf{Rate of effusion of gas 1}}{\textbf{Rate of effusion of gas 2}} = \left| \frac{\textbf{molar mass of gas 2}}{\textbf{molar mass of gas 1}} \right|^{1/2}$$



Example 11.13 TFE (Tetrafluoroethyene) C_2F_4 effuses at a rate of $4.6 x 10^{-6}$ mol/h. An unknown gas containing boron and hydrogen effuses at $5.8 x 10^{-6}$ mol/h. What is the mass of the unknown gas?

Mw of C_2F_4
2 C 2 * 12.01 24.02
4 F 4 * 19.00 76.00
Mw = 100.02 g/mole

$$\frac{5.8 x 10^{-6} mol/h}{4.6 x 10^{-6} mol/h} = \left| \frac{100.02 g/mole}{\text{molar mass of gas 2}} \right|^{1/2}$$

$$\frac{5.8 x 10^{-6} mol/h}{4.6 x 10^{-6} mol/h} = 1.3 = \left| \frac{100.02 g/mole}{M = \text{molar mass of gas 2}} \right|^{1/2}$$

Square both sides

1.6 = 100.02 g/mole / molar mass of gas 2

M = 63 g/mole

11.8 Nonideal Behavior of Gases

The ideal gas law (PV=nRT) holds at and around room temperature and 1 atm or less. At higher pressure or lower temperature there are deviations. These occur as the molecules are now closer together. The **van der Waals Equation** compensates for these differences:

$$[\ P\ \alpha\ (n/V)^2\ ]\ (\ V - \beta\ n) = n\ RT$$

Table 11.2 van der Waals Constants

Gas	*a* Values (atm · L²/mol²)	*b* Values (L/mol)
He	0.034	0.0237
Ar	1.34	0.0322
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
Cl_2	6.49	0.0562
H_2O	5.46	0.0305

4.00 mole of Chlorine gas in a 4.00 L tank at 100.0 ^oC would have a pressure of 30.6 atm via PV=nRT. But using van der Waals Equation you get 26.0 atm.

CO2 and Green Chemistry

Students DISCUSS pumping CO2 from our power generation stations into storage underground!

Mandy-Tae Cruickshank holds a world record free dive depth record of 446 ft which took 6 min 25 seconds. Assuming the sea level temperature as a warm 95 deg F and the water temp at 446 ft was 45 deg F and her lung capacity at sea level was 1.5 L, what was her lung capacity at 446 ft? Assume pressure increases 1.0 atm for each 33 ft of depth.

Filling dive tanks. A dive tank will hold 120 cu ft of air at 3500 psi and room temperature (20 ^oC). From this you can calculate the volume of the tank at 1 atm (14.69 psi) and room temperature When the tank is refilled, it gets hot as compressed air is added. One dive shop fills the tank and returns it to you still hot. On one occasion my hot tank was 70 oC and a check with a pressure gauge showed the tank at 3500 psi. But the next morning, when the tank cooled off to room temperature, I noticed the tank did not have 3500 psi. What was it's pressure? What percent of compressed air was I cheated out of?