Chap. 2

Equation of State
(Ideal Gas Law)

Quiz: True or False?
(Some have caveats)

1. Atmospheric pressure is just the weight of the atmosphere above us.
2. Absolute zero is the temperature at which all motion ceases.
3. As temperature increases, so does pressure, and vice versa.
4. Cold air is denser that hot air.

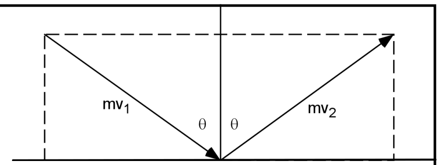
Quiz: True or False? (Some have caveats)

1. Atmospheric pressure is just the weight of the atmosphere above us. True, if dw/dt = 0
2. Absolute zero is the temperature at which all motion ceases. http://en.wikipedia.org/wiki/Absolute_zero
3. As temperature increases, so does pressure, and vice versa. Must assume that V = const.
4. Cold air is denser that hot air. Depends on pressure.

From elementary kinetic theory . . .

- Assume an **ideal gas** has the following properties:
  - The molecules are in random motion and obey Newton's laws of motion.
  - The total number of molecules is large.
  - The volume of molecules is negligible relative to the volume occupied by the gas.
  - No appreciable (molecular) forces act on the molecule during a collision.
  - Collisions among molecules are elastic and of negligible duration.
  - In addition, the following assumptions are made regarding the interaction between molecules and a surface membrane or wall, which contains the molecules.
  - The collision with the wall is elastic.
  - There is no loss in momentum, in the direction parallel to the wall, during the collision with the wall (i.e., no friction).

Derivation of the equation of state from kinetic theory – in abbreviated form



- $mv\cos\theta - (-mv\cos\theta) = 2mv\cos\theta$ change in momentum (wall collision)
- $mv^2 dn\text{-}v\sin\theta\cos^2\theta d\theta$ incremental change from all collisions
- $(mv^2/3)dn_v$ integration over all angles
- $dF = (m/3)(\int v^2 dn_v)dA$ differential force from molecules
- $p \equiv dF/dA = (m/3)\int v^2 dn_v$ definition of pressure + algebra
- $p = mn\langle v^2\rangle/3$ simplification using v_{bar}
- $pV = (1/3)Nm\langle v^2\rangle$ assume dN = ndV (uniform distribution)
- $p\alpha_m = (1/3)N_0\langle v^2\rangle$ definition of molar specific volume
- $(3/2)kT = (1/2)\langle mv^2\rangle$ definition of temperature
- $p\alpha_m = kN_0T = R^*T$ substitution
  $\alpha = \alpha_m / M$, definition
- $p\alpha = (R^*/M)T = RT$, *This is the final result* substitution

Equation of State from experimental results

- *Boyles Law: $V \propto p^{-1}$ for an <u>isothermal</u> (T = const) process.*
- *First Law of Gay-Lussac: $V \propto T$ for an <u>isobaric</u> (p = const) process*
- *Second Law of Gay-Lussac: $p \propto T$ for an <u>isochoric</u> (volume = const) process*

Boyles Law: $V \propto p^{-1}$ for an <u>isothermal</u> process

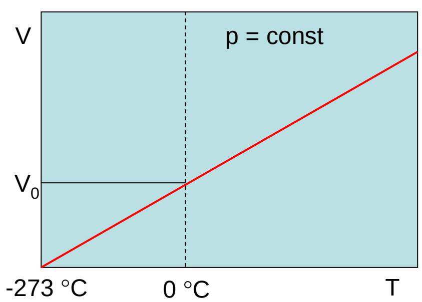
- $p_1V_1 = p_2V_2$ (T = const)
- http://www.grc.nasa.gov/WWW/K-12/airplane/aboyle.html (from google on "Boyle's Law")

First Law of Gay-Lussac (Charles' Law): $V \propto T$ for an <u>isobaric</u> process

- $dV = aV_0dT$

  "a" is the coefficient of thermal expansion at constant pressure, $a = 1 / 273\ deg^{-1}$, V_0 is the volume at 0 °C

  Integrated form: $V – V_0 = aV_0T$



Extrapolation to T = -273 C suggests that V = 0.

This temperature is *absolute zero*

Discussion? (theoretical)

http://en.wikipedia.org/wiki/Gay-Lussac's_law

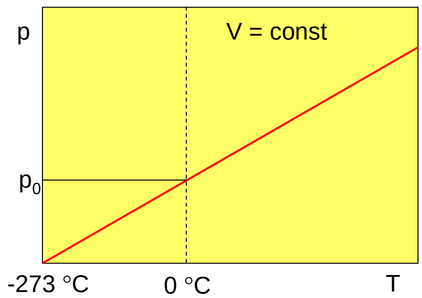
http://www.chem.csus.edu/gaslaws/gay-lus.html

Second Law of Gay-Lussac: $p \propto T$ for an isochoric process

- $dp = bp_0dT$

  "b" is the pressure coefficient of thermal expansion at constant volume (= 1 / 273 deg^{-1})

  Integrated form: $p = p_0(1 + bT)$



See Application at the bottom of page 12 (Tsonis).

Does such a pressure difference really exist?

http://en.wikipedia.org/wiki/Gay-Lussac's_law
http://www.chem.csus.edu/gaslaws/gay-lus.html

Equation of state by inference

- *Combination of the laws of Boyle and Gay-Lussac:*
- *$pV/T = p'V'/T' = A$*
- *$pV = AT$, where A is a constant, which can be equated to nR^* (or mR) as follows.*

  $pV = nR^*T = m(R^*/M)T = mRT$
- $p = \rho RT$
- $p\alpha = RT$ $(\alpha = \rho^{-1})$

In summary

- The equation of state ($p\alpha = RT$) is general
  - Boyle's Law is a special case of the equation of state: *$V \propto p^{-1}$ (T=const)*
  - *First Law of Gay-Lussac (Charles' Law) is a special case of the equation of state: $V \propto T$ (p = const)*
  - *Second Law of Gay-Lussac is a special case of the equation of state: $p \propto T$ (V = const or α = const)*

Dalton's Law of partial pressures

- The equation of state is valid for individual gases, as well as for a mixture of gases that comprise the atmosphere. For the i^{th} gas, the equation of state is:

  $p_i\alpha_i = R_iT.$
- Dalton's Law of partial pressures
  - $p = \sum p_i(T,V)$ (p_i is the partial pressure of gas i),
  - The pressure of a gas mixture is equal to the sum of the partial pressures of each component gas
  - See bottom of p. 17 (Tsonis)

Eq. of State for the atmosphere

- The value of R for the *dry* atmosphere in Eqs. (2.12a,b of the notes) is

  $R_d = 287.05 \text{ J kg}^{-1} \text{ K}^{-1}$
- For the dry atmosphere,
  - $p\alpha = R_d T$

Usage of the equation of state

- Used to derive the individual ideal gas laws (working backwards from our derivation)
- Use of Ideal Gas Law Equation to determine the density of a gas; ρ is difficult to measure directly. [The only instrument that can do this is the “direct detection” lidar which measures backscatter from molecules.]
- Solve for Partial Pressure of a known amount of gas in a gas mixture ($p_1 = n_1RT/V$ and $p_2 = n_2RT/V$)

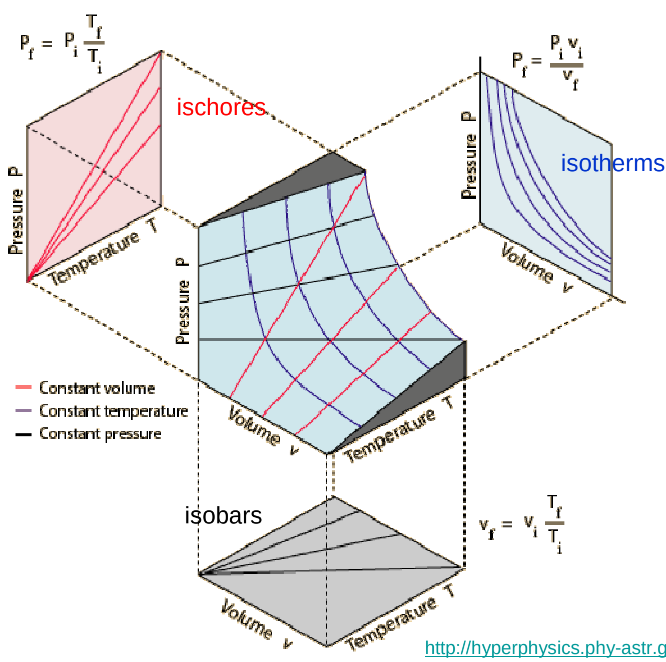
Applications of the eq. of state

- A 1 liter (L) sample of air at room temperature (25 ℃) and pressure (1 atm) is compressed to a volume of 3.3 mL at a pressure of 1000 atm. What is the temperature of the air sample?
- Use pV/T = const

$$\frac{1atm*1L}{(273+25)^\circ K} = \frac{1000atm*0.0033L}{T_2}$$

$$T_2 = 298^\circ K*3.3 = 983^\circ K$$

Eq. of state in graphical form



http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/idegas.html

Equation of state for moist air

- commonly used in atmospheric thermodynamics:
  - *water vapor pressure (e)*: the partial pressure due to water vapor molecules. (How could this be measured? We will see later that it can be determined theoretically/analytically with the Clausius-Clapeyron equation.)
  - *mixing ratio*: $r_v = m_v/m_d$
  - *specific humidity*: $q_v = (m_v/(m_v+m_d)) = r_v/(1+r_v)$

- As an aside, we note that the eq. of state applies to water vapor: $e = \rho_v R_v T$
- $p = \rho_m T[(m_d R_d + m_v R_v)/(m_d + m_v)]$ (mass weighted), $R_v = R^*/M_{H2O}$
- $\rho_m = (m_d+m_v)/V = \rho_d + \rho_v$
- Eventually, we derive the eq. of state for moist air, using the new variable T_v:

$$p = \rho_m R_d T_v$$

Forms of the equation of state for dry air

- $pV = NR^*T$ ($R^* = 8314.5$ J K^{-1} $kmol^{-1}$)
- $pV = mR_dT$ ($R_d = 287.05$ J K^{-1} kg^{-1})
- $p\alpha = RT$

- Notes: $R_d = R^*/m_d$

Empirical eq. of state with corrections to account for non-ideal gas

- Vander Waals' equation
  - $(p + aV^{-2})(V - b) = R^*T$
  - http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch4/deviation5.html
- Kammerlingh-Omnes (HW problem on this one)
  - $pV = A(1 + B'p + C'p^2 + \ldots)$
  - $A=R^*T$; B' from Table 2.1 (p^2 term can be ignored to good approximation

T (°C)	B' (10-8 m2N-1)	pV/R*T	
		P = 500 mb	P = 1000 mb
-100	-4.0	0.9980	0.9996
-50	-1.56	0.9992	0.9984
0	-0.59	0.9997	0.9994
50	-0.13	0.9999	0.9999

A linearized equation of state

- Linearize the equation about a dry reference state
- The reference state obeys the gas law $p_0\alpha_0=R_dT_0$
- Substitue the following into the eq. of state

  $\alpha=\alpha_o+\alpha'$, $p=p'+p_o$, $T=T'+T_o$, and $r_v=r_v'$
- Then:

  $$p_o(1+p'/p_o)\ \alpha_o(1+\alpha'/\alpha_o) = R_d(1+0.61r_v')T_o(1+T'/T_o)$$
- Take natural log of both sides, expand the log in a Taylor's series, and ignore the higher order terms. The result is

  $$\alpha'/\alpha_o = T'/T_o + 0.61\ r_v' - p'/p_o$$

Example

Typical perturbations within a cloud are:

T' ~ 1 K (up to 15 K)

r_v' ~ 2 g kg^{-1} (up to 8 g kg^{-1})

p' ~ 0.2 mb (up to 1-2 mb)

Thus, $T'/T_o = 1/273 = 0.0037$, $r_v' = 0.002$, and $p'/p_o = 0.2/800 = 0.00025$.

Discussion

Temperature and moisture perturbations are comparable and thus provide the most important contributions to density fluctuations in the cloud (or cloud-free) environment. Only in limited regions of cloud systems does p' exceed 0.2-0.4 mb. [It is the density fluctuations that control cloud dynamical processes.]

2.5 Measurements of temperature, pressure, and water vapor

Temperature: thermometer, thermister, thermocouples, IR emission, microwave emission (O_2 band)

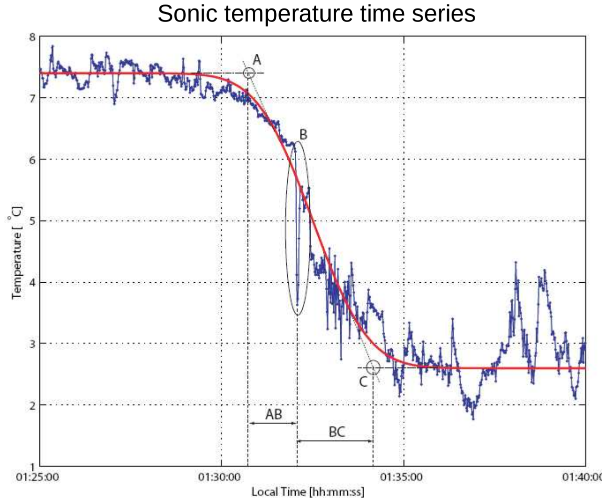
Density: lidar

Pressure: barometer (mercury, aneroid), transducer

Water vapor: wet bulb temperature, RH directly, lidar differential absorption, microwave emission

Virtual temperature: radio acoustic sounding system (RASS – speed of sound $\propto$ Tv)

Sonic temperature time series



Review of variables

Variable symbol	Variable	Measurable?
p	Pressure	Barometer, pressure transducer
T	Temperature	Thermometer, thermister, etc.
V	Volume	Special cases only
α	Specific volume	$\alpha = \rho^{-1}$
ρ	Density	Lidar; eq. of state calculation
T_v	Virtual temp.	Need T and r_v to calculate; Radio Acoustic Sounding System -- RASS
ρ_v	Water vapor density	Radiometer (indirectly); eq. of state calculation
R	Gas constant	Given (but it can be estimated)

Useful web links:

- Wikipedia discussion of the ideal gas law: http://en.wikipedia.org/wiki/Ideal_gas_law
- Hyperphysics, Georgia State Univ.: http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/idegas.html
- Gas Law animation http://intro.chem.okstate.edu/1314F00/Laboratory/GLP.htm

  http://www.phy.ntnu.edu.tw/java/idealGas/idealGas.html?CFID=6636104&CFTOKEN=35135960

Review, from http://www.grc.nasa.gov/WWW/K-12/airplane/eqstat.html

Equation of State (Ideal Gas)

Glenn Research Center

Properties

Density = r   Pressure = p   Temperature = T   Volume = V   Mass = M

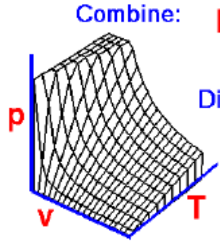
Observations

Boyle: For a given mass, at constant temperature, the pressure times the volume is a constant. $p V = C_1$

Charles and Gay–Lussac: For a given mass, at constant pressure, the volume is directly proportional to the temperature. $V = C_2 T$

Combine: $p V / T = n R$ R = 8.31 J / mole / K^o (Universal)

$p V = n R T$ n = number of moles



Divide by mass: Specific Volume = v = $\frac{volume}{mass} = \frac{1}{r}$

$p v = \frac{n R T}{M}$ or $p v = R T$ or $p = R r T$

R = Constant value for each gas
.286 kJ/ kg / K^o (for air)

Back to the quiz

Atmospheric pressure is just the weight of the atmosphere above us.

Yes, but one needs to be careful with this (dw/dt=0)

Absolute zero is the temperature at which all motion ceases.

One cannot assume that the ideal gas law is valid at T = 0 K.

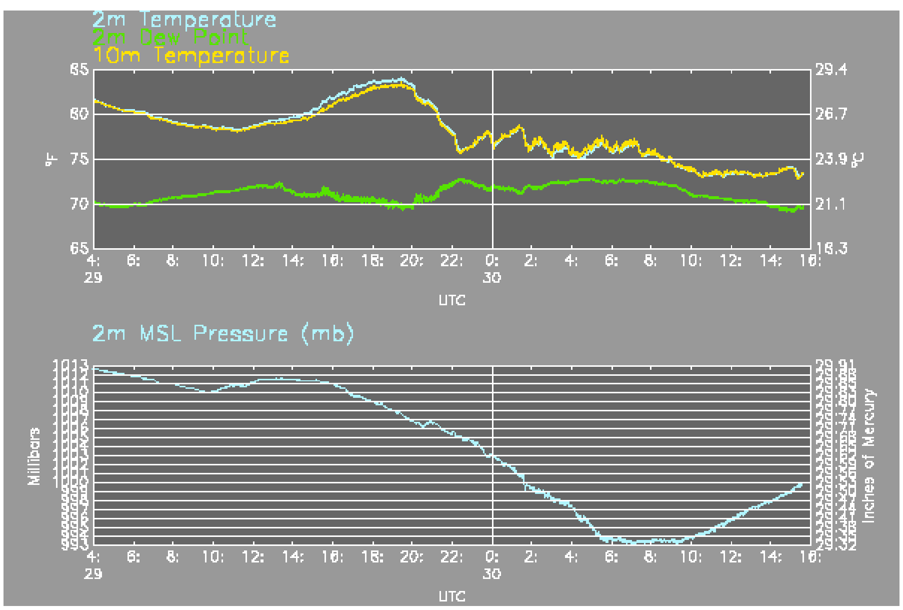
As temperature increases, so does pressure, and vice versa.

This assumes that V = const. (Does not generally apply in the atmosphere)

Cold air is denser that hot air.

This assumes that p = const. (Generally true in the atmosphere, but be careful!)

Relation between T and p?



Example:

If at 0 ℃ the density of dry air alone is 1.275 kg m^{-3} and the density of water vapor alone is 4.770 x 10^3 kg m^{-3}, what is the total pressure exerted by a mixture of the dry air and water vapor at 0 ℃?

Solution: From Dalton's law of partial pressures, the total pressure exerted by the mixture of dry air and water vapor is equal to the sum of their partial pressures. The partial pressure exerted by the dry air is

$$p_d = \rho_d R_d T$$

where rd is the density of the dry air (1.275 kg m^{-3} at 273 K), R_d is the gas constant for 1 kg of dry air (287.0 J K^{-1} kg^{-1}), and T is 273.2 K. Therefore,

p_d = 9.997 x 10^4 Pa = 999.7 hPa

Similarly, the partial pressure exerted by the water vapor is

$$e = \rho_v R_v T$$

where ρ_v is the density of the water vapor (4.770 x 10^3 kg m^{-3} at 273 K), R_v is the gas constant for 1 kg

of water vapor (461.5 J K-1 kg-1), and T is 273.2 K.

Therefore,

$$e = 601.4\ Pa = 6.014 \text{ hPa}$$

Hence, the total pressure exerted by the mixture of dry air and water vapor is

$$p = p_d + e = 999.7 + 6.014 = 1005.7 \text{ hPa.}$$

HW problems

1. Petty 3.1
2. Petty 3.5
3. Petty 3.10
4. Now, show that the density of moist air is less than that for dry air at the same temperature and pressure. Interpret your results. Does this difference have any relevant atmospheric applications? (Hint: Refer to Petty and the previous problem)
5. Determine the number of molecules in a 1 cm^3 volume of air having a pressure of 1 atm. Make any other reasonable assumption if required. [Ans: about 3×10^{19} cm^{-3} – your answer will be more precise]. (Note, this is similar to problem 3.5 in Tsonis.) (b) What is the mean free path for the average molecule in this volume? Mean free path is determined from $\Delta x_{mfp} = (n\sigma)^{-1}$, where n is the number of molecules per unit volume, $\sigma = \pi d_o^2$ is the collision cross section (σ is about 3 x 10^{-15} cm^2 for an air molecule), and d_o is the diameter of an average molecule. You can check your answer with Fig. 1.1b.
6. At what pressure is the ideal gas law in error by 1%, for air with T = 0 °C? [Ans: 17 atm; Hint: Use Table 1.3]
7. (a) Calculate some extremes in air density at the surface for different scenarios. For example, consider (a) International Falls in the winter under high pressure (anticyclone) conditions: T = -40 °F, p=1050 mb, r_v=0.1 g kg^{-1}; (b) Denver in the summer with T = 95 ° F, p=850 mb (actual station pressure) and r_v=10 g kg^{-1}. (c) What are some practical implications (e.g., aircraft lift, wind drag on a vehicle)?
8. [Fleagle and Businger Prob. 1, ch. 2.] If 10^6 molecules are required in order to ensure a statistically uniform distribution of velocities in all directions, what is the minimum volume in which the state can be defined at standard atmospheric conditions (p=1013 mb, T=0 °C)? [Ans. 37.21×10^{-21} m^3, which corresponds to a linear distance of 3.34×10^{-7} m for a cube. Hint: use the definition dN = ndV].

ATS/ES 441 students: You may eliminate two problems (choose from 4-8) of your choice, or if you turn in all problems, I will ignore the lowest scores on two problems.