

EAS 370: Applied Atmospheric Physics

Lecture Notes

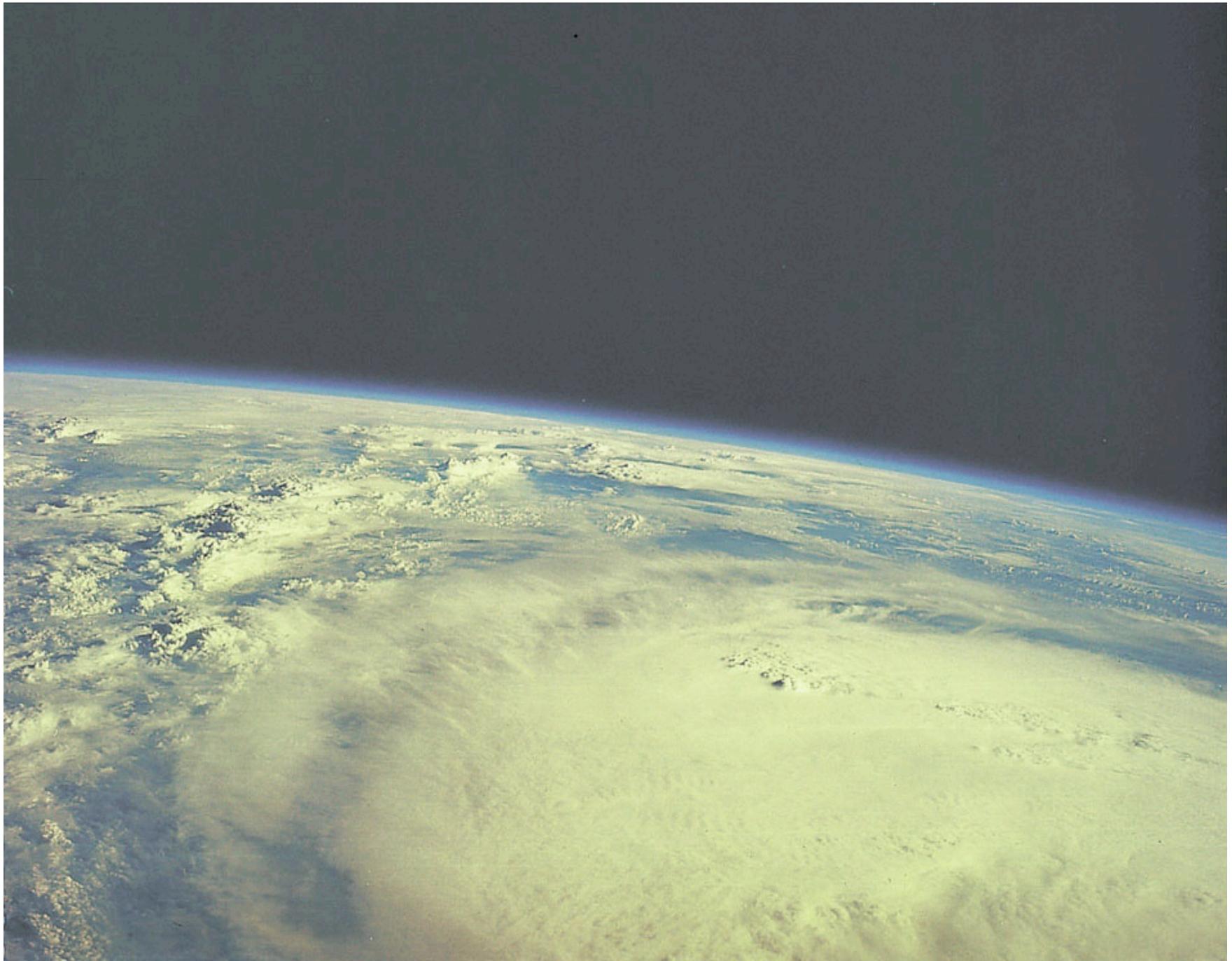
Andrew B.G. Bush

Department of Earth and Atmospheric Sciences
University of Alberta

1. BASIC THERMODYNAMIC CONCEPTS

- Why study atmospheric thermodynamics?
- Pressure
- Volume
- The concept of a gas in equilibrium
- Zeroeth law of thermodynamics
- Temperature
- Work of expansion/compression
- The ideal gas law
- First law of thermodynamics and differential changes

Note: colour figures in the following notes are from Meteorology today, 6th edition by C. Donald Ahrens, Brooks/Cole publishing, 2000.



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Why study atmospheric thermodynamics?

Our atmosphere is a mixture of gases. How this mixture behaves under spatially varying temperatures and pressures is critical to predicting weather and climate.

We therefore need to know the laws that govern gases in detail.

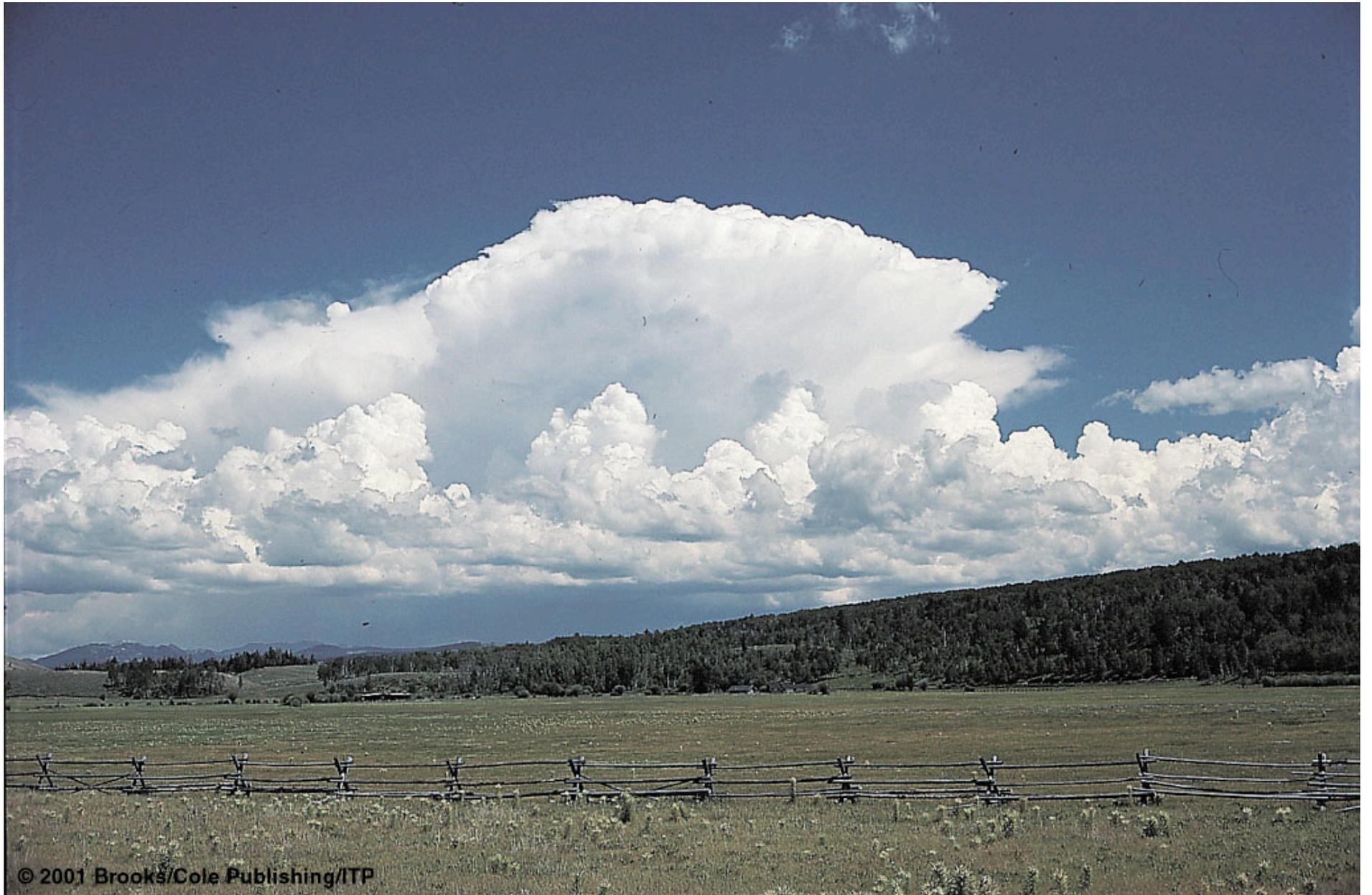
Solar radiation is the ultimate source of all the energy that drives our climate system.

The interaction of radiation with the multiple gases that constitute our atmosphere creates a temperature profile in accord with the laws of thermodynamics.

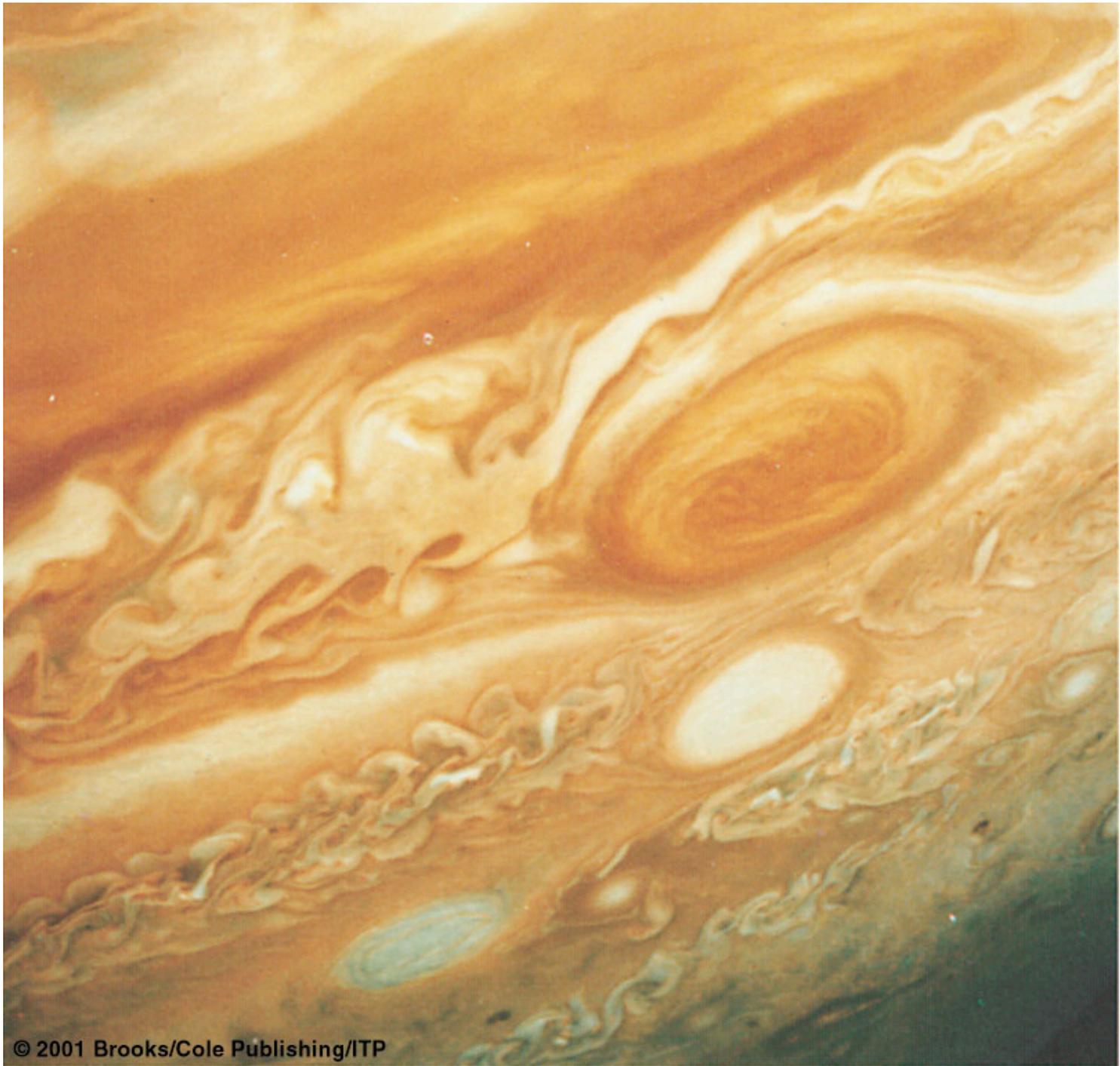
The spatial structure of the temperature field is related to the spatial structures of pressure and density in accord with the equation of state.

Spatial variations of pressure drive atmospheric winds.

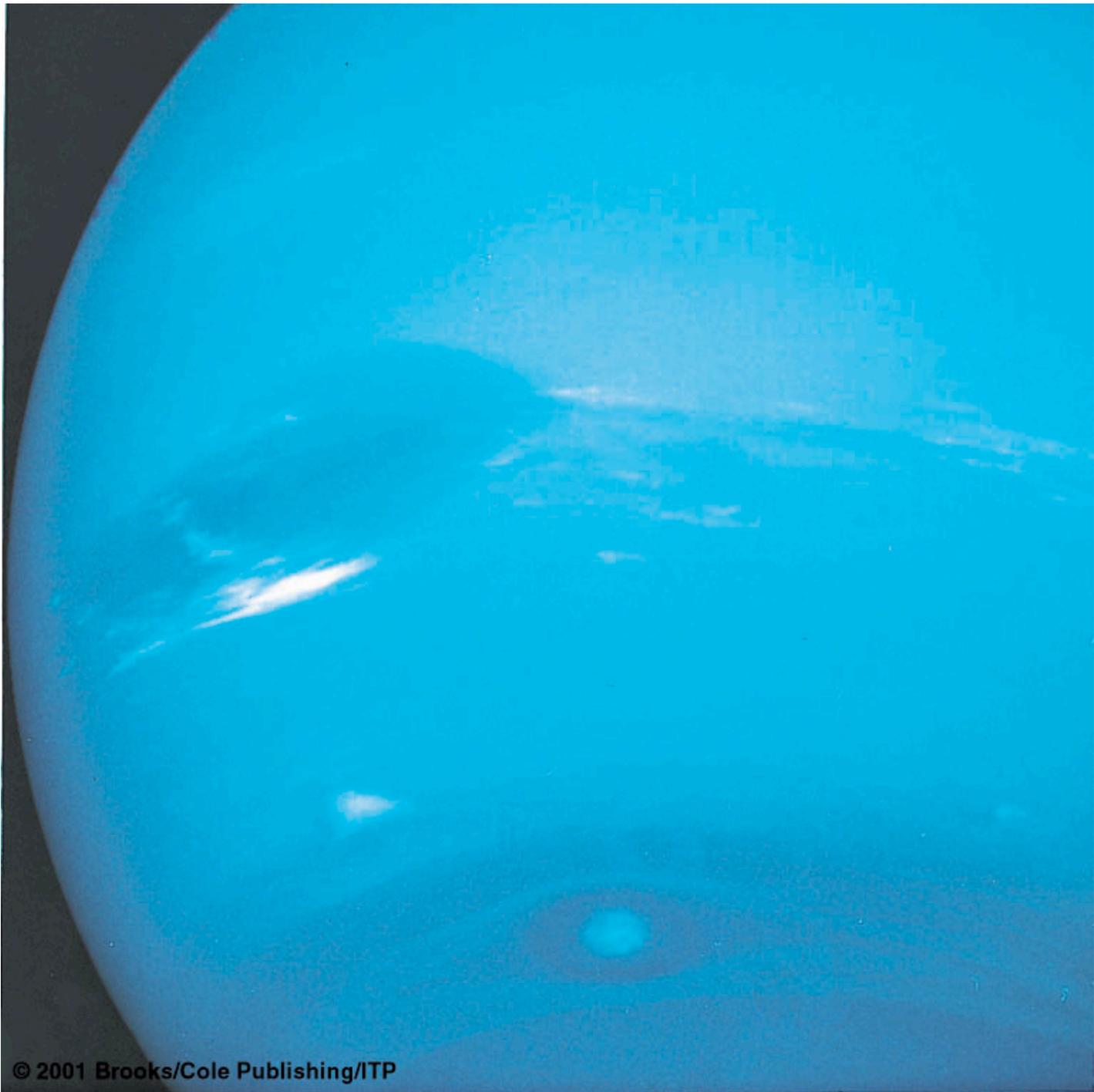
The phase changes of water play an enormous role in our climate system (clouds, precipitation, ice, etc.). Phase changes of a substance are governed by thermodynamics.



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PRESSURE

A gas is composed of molecules that are free to move in any direction. There are therefore numerous collisions between molecules, redirection of path trajectories, etc. Pressure in a gas is the normal force per unit area exerted by the gas.

Pressure is a MACROSCOPIC variable. It is observable (i.e., measurable). However, it is actually a time average of the momentum transfer per collision, averaged over many collisions and over a long time (with respect to the microscopic processes of particle collisions).

RECALL: Pressure=Force per unit area.

$$Pressure = \frac{Force}{Area}$$

UNITS: 1 atmosphere=101.325 kPa [N.B. 1 Pa=1 N/m²] where Pa is a Pascal.

1 barye = 1 dyne/cm² = 10⁻¹ Pa

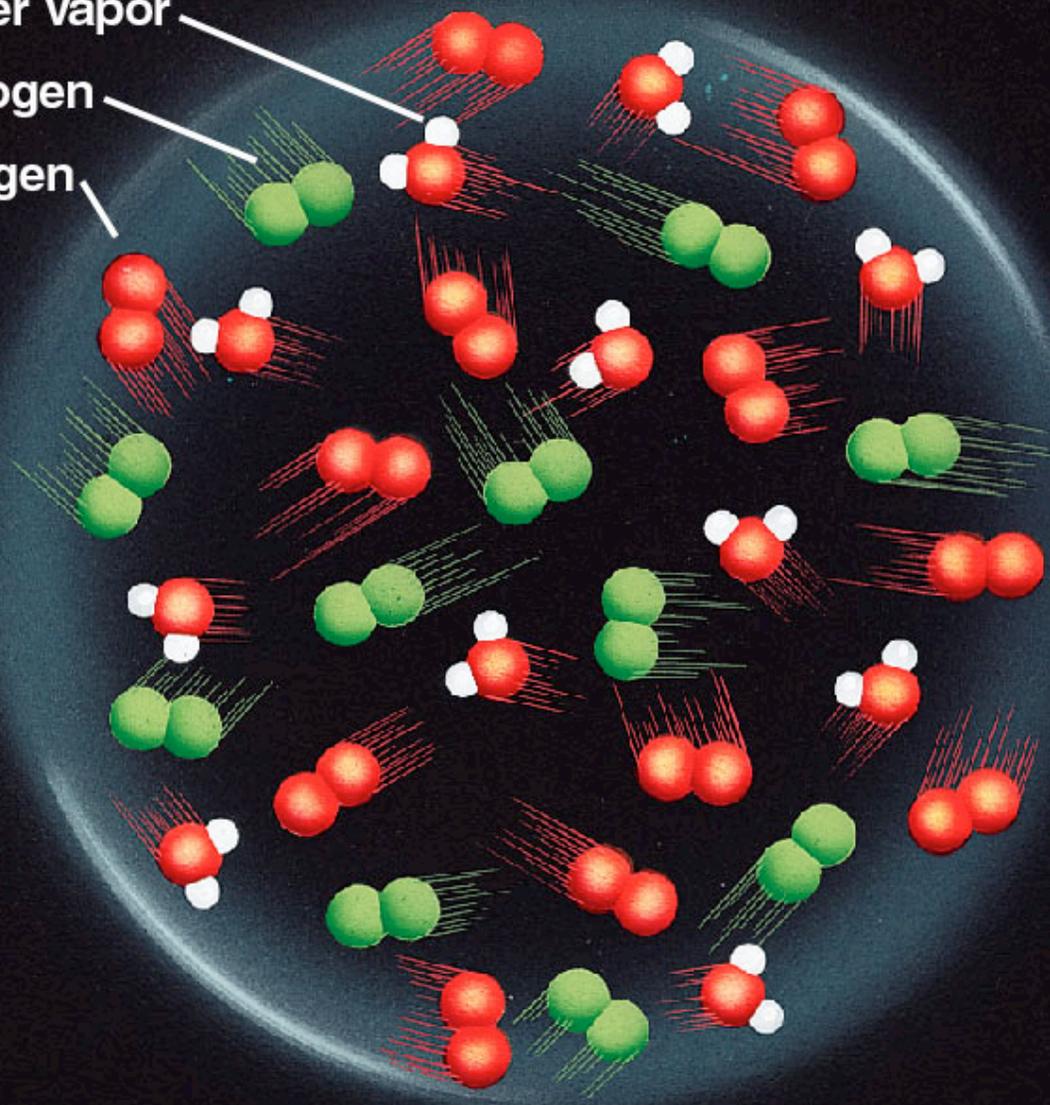
1 bar = 10⁶ barye = 100 Pa

1 mm Hg = 0.133322 kPa = 1 torr

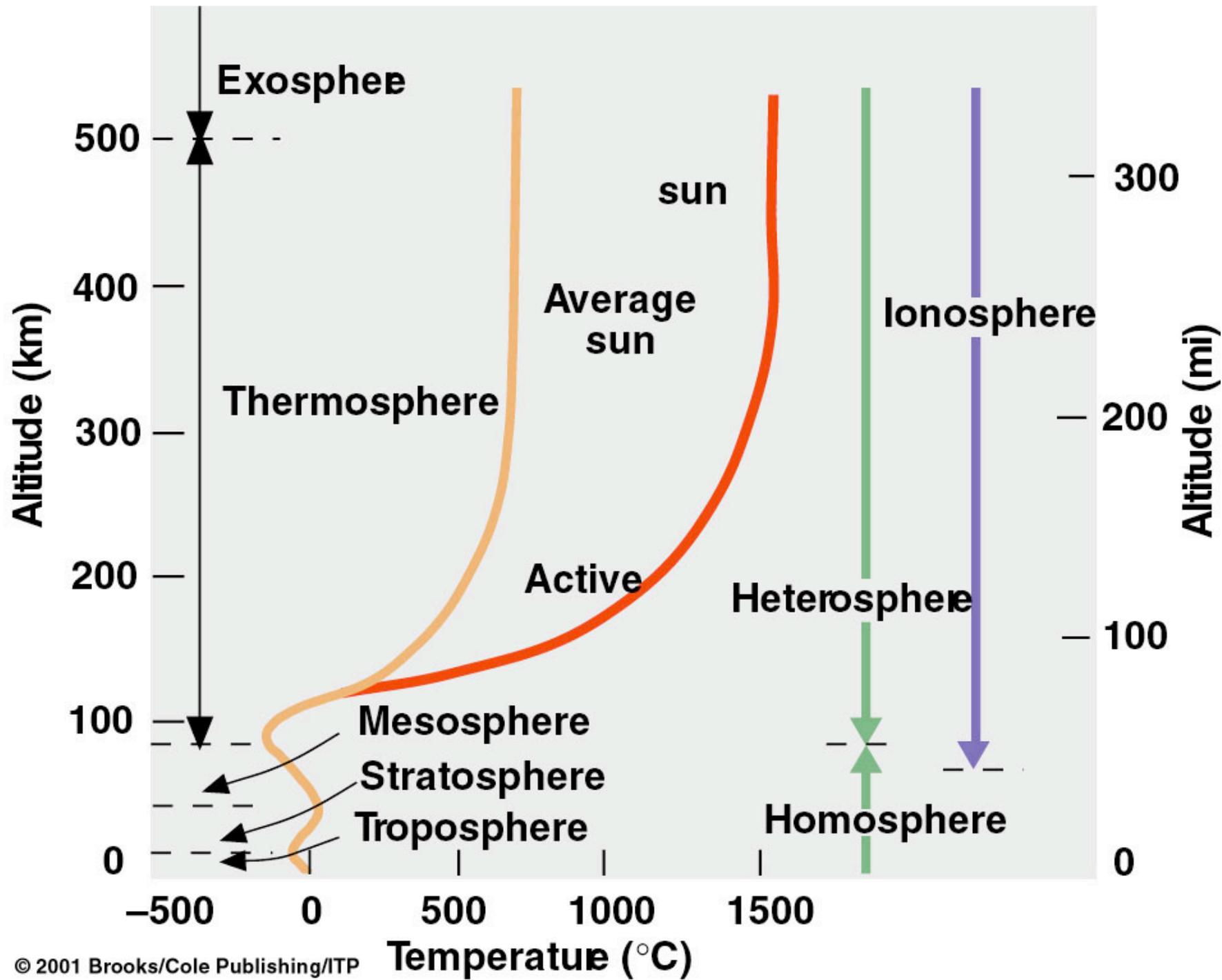
Water vapor

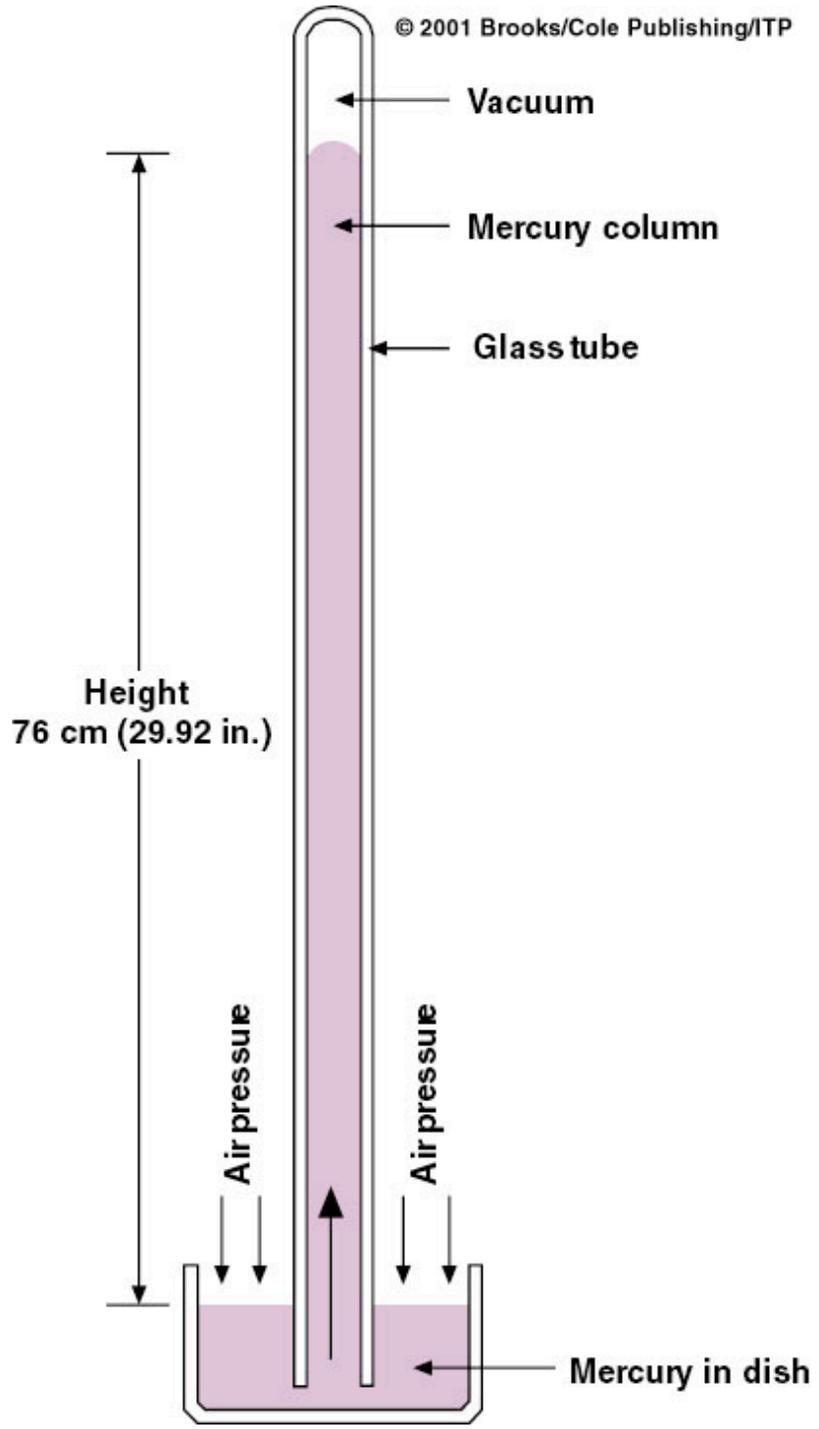
Nitrogen

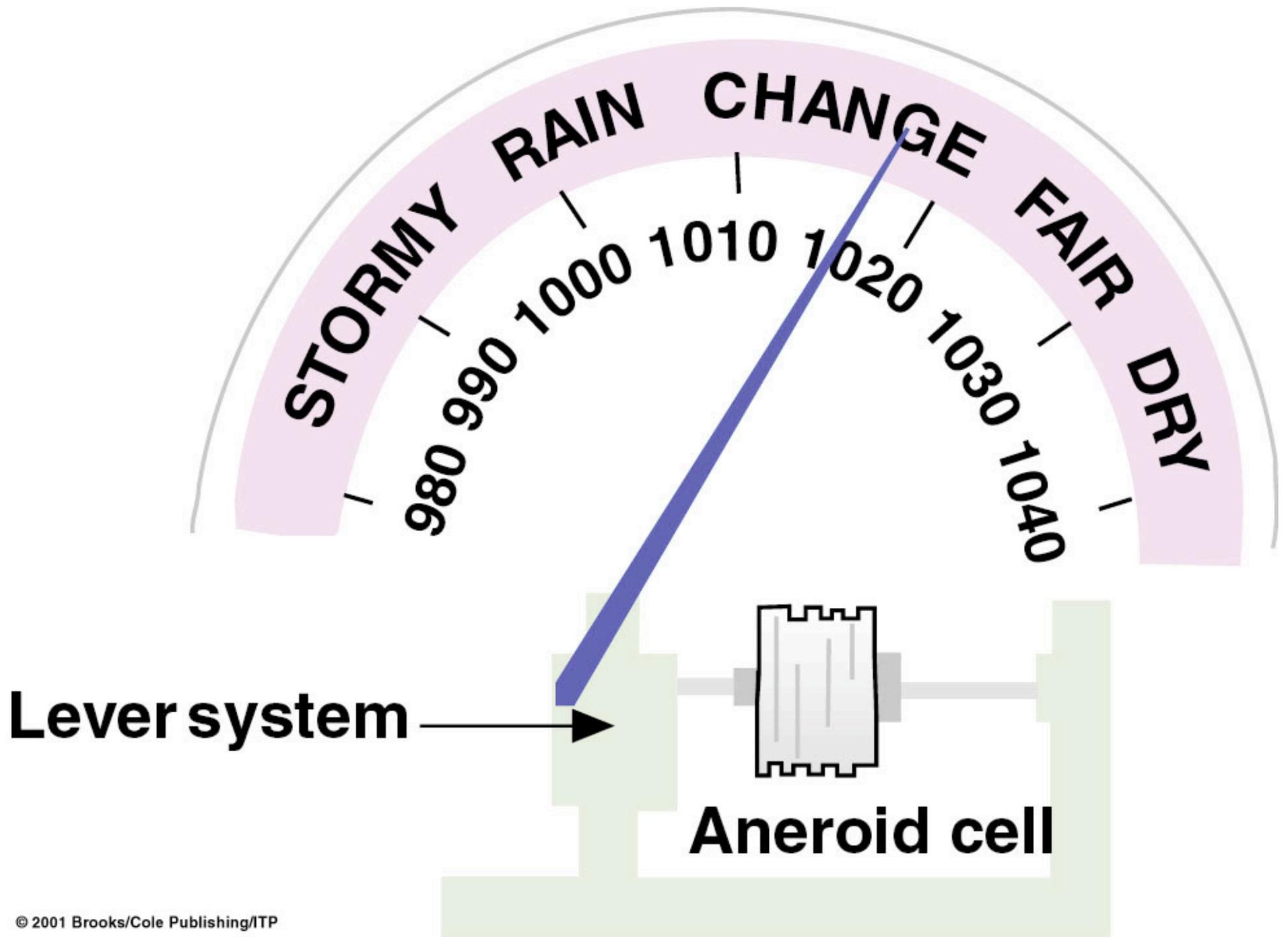
Oxygen



Air parcel







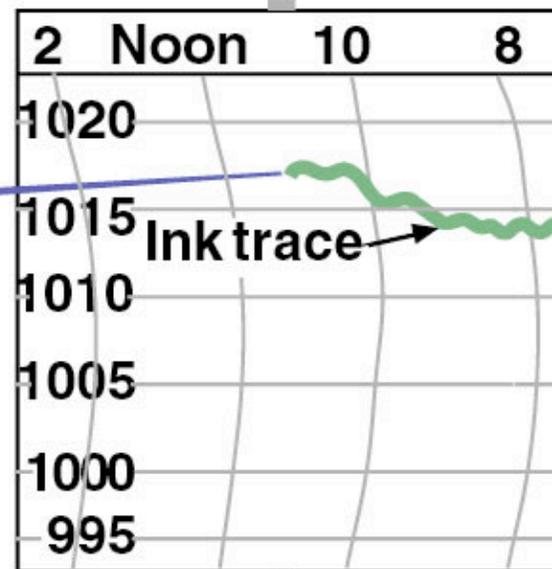
Protective case

Record paper on cylinder

Amplifying levers

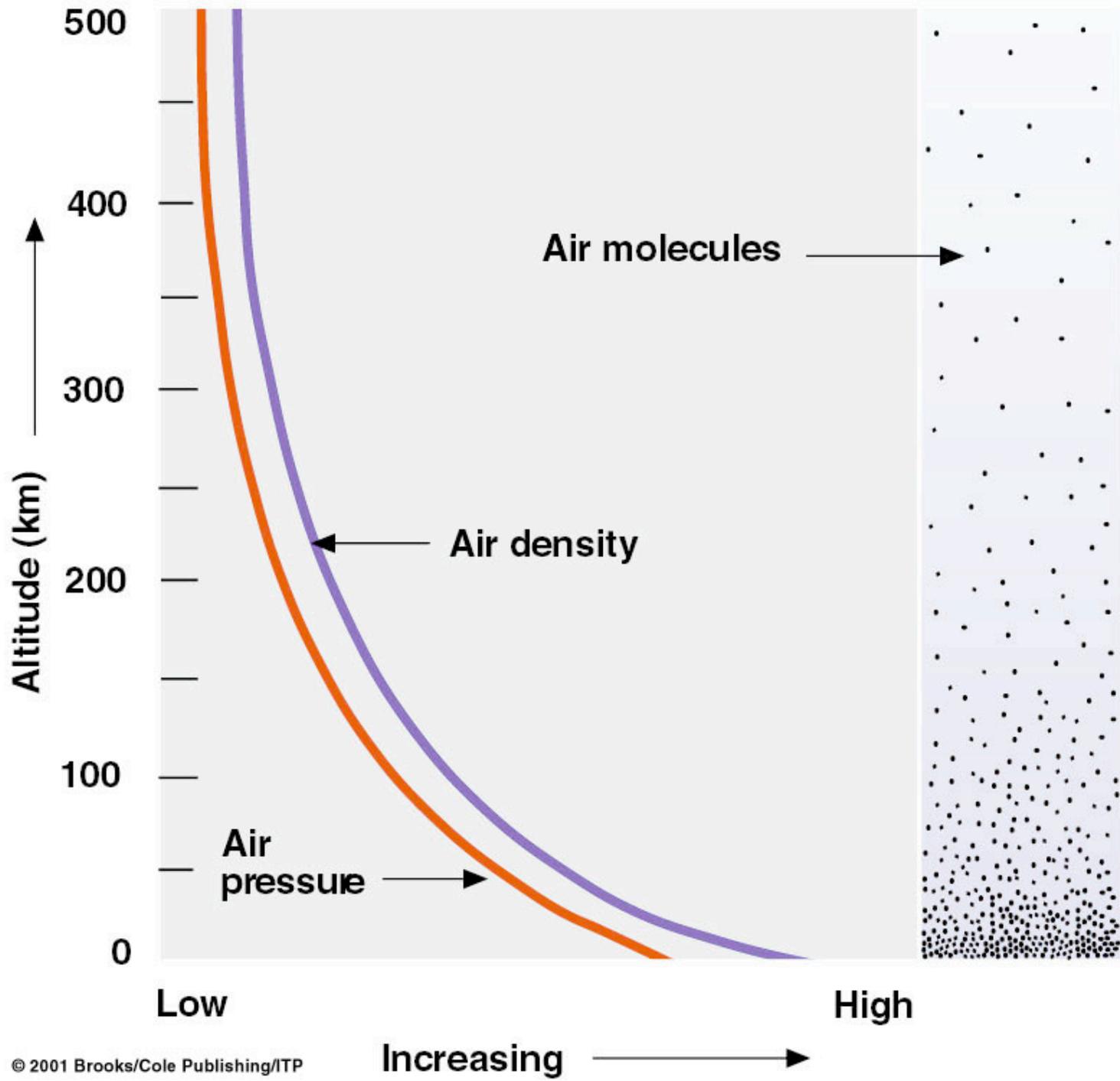
Aneroid cell

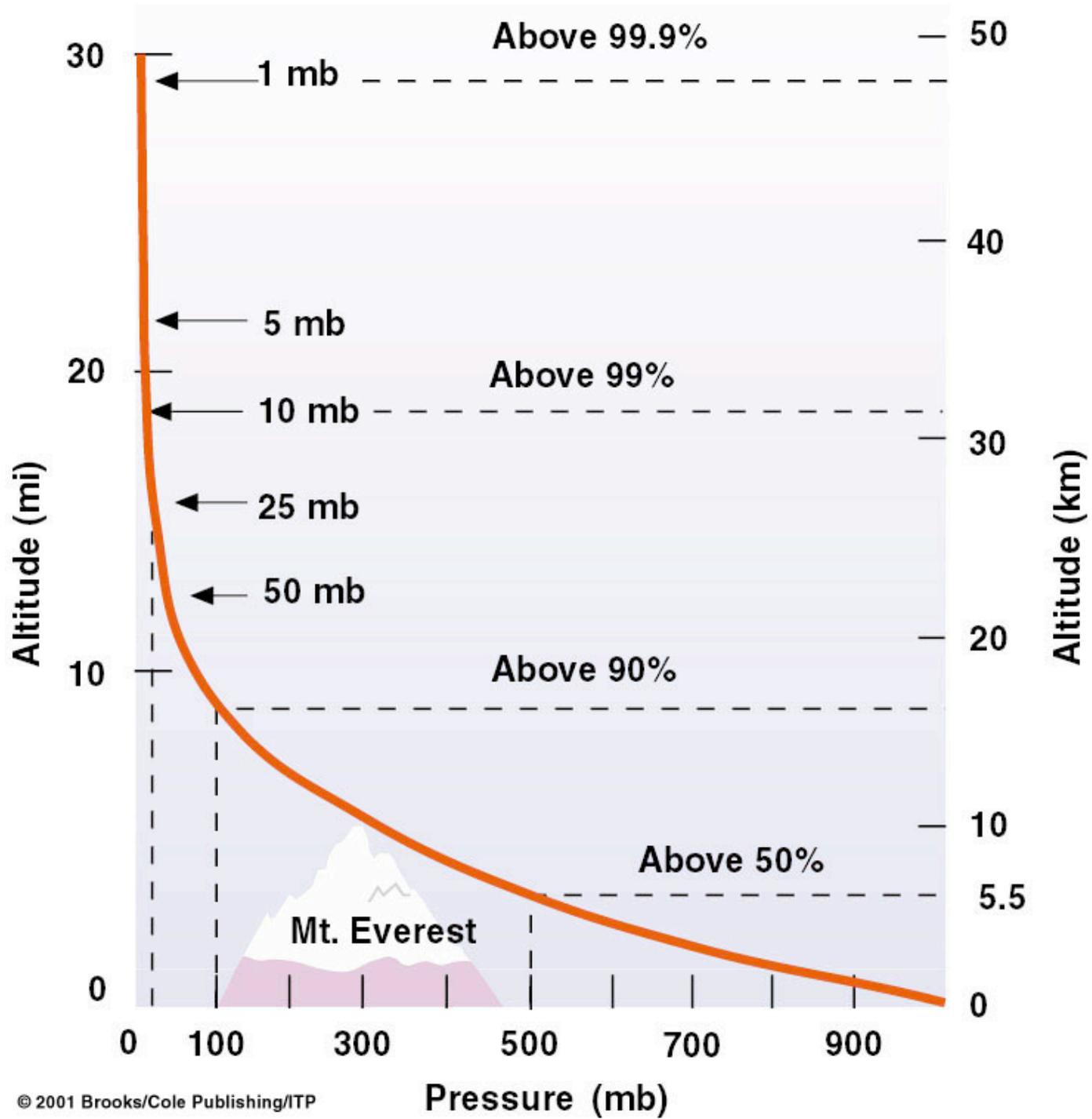
Ink trace

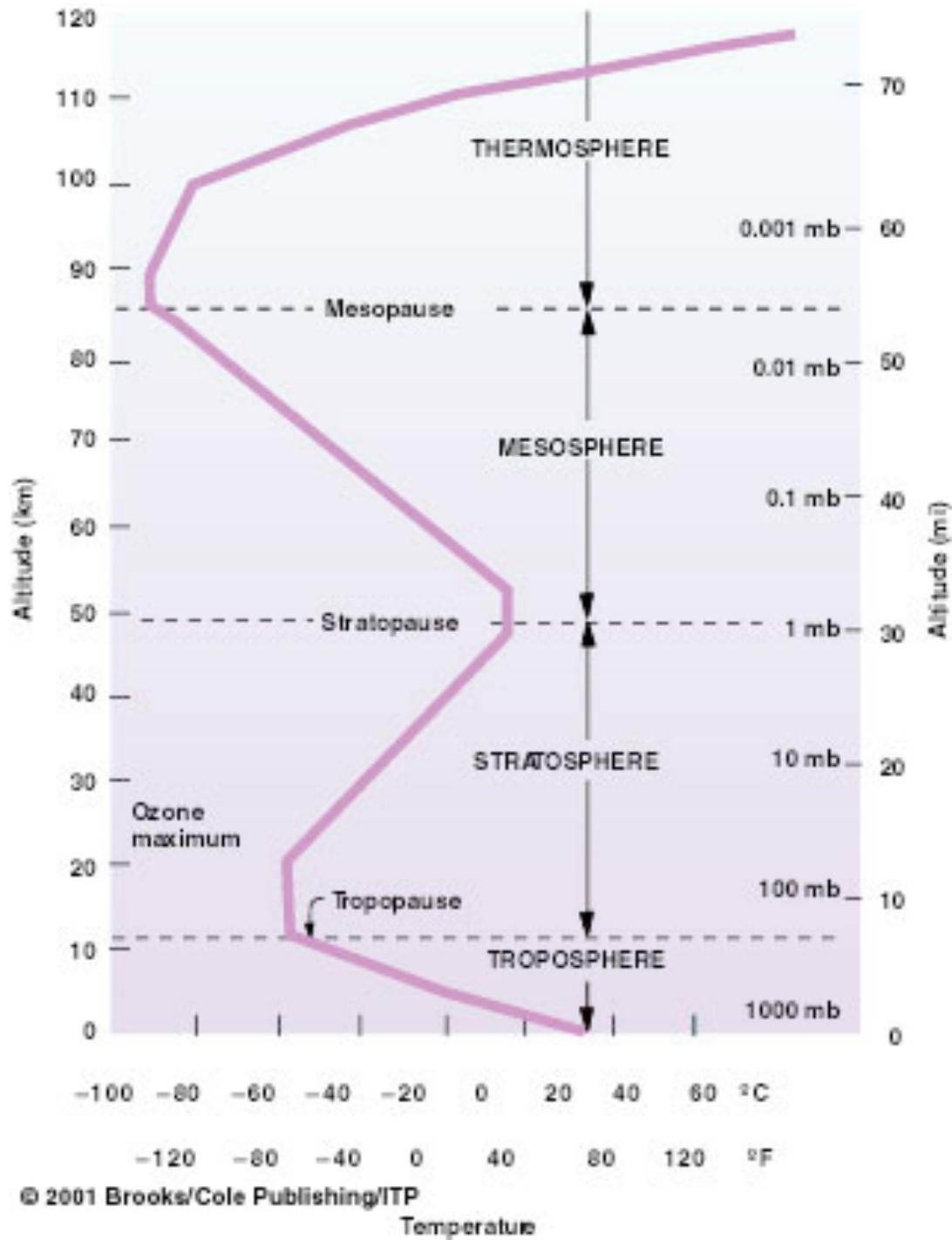


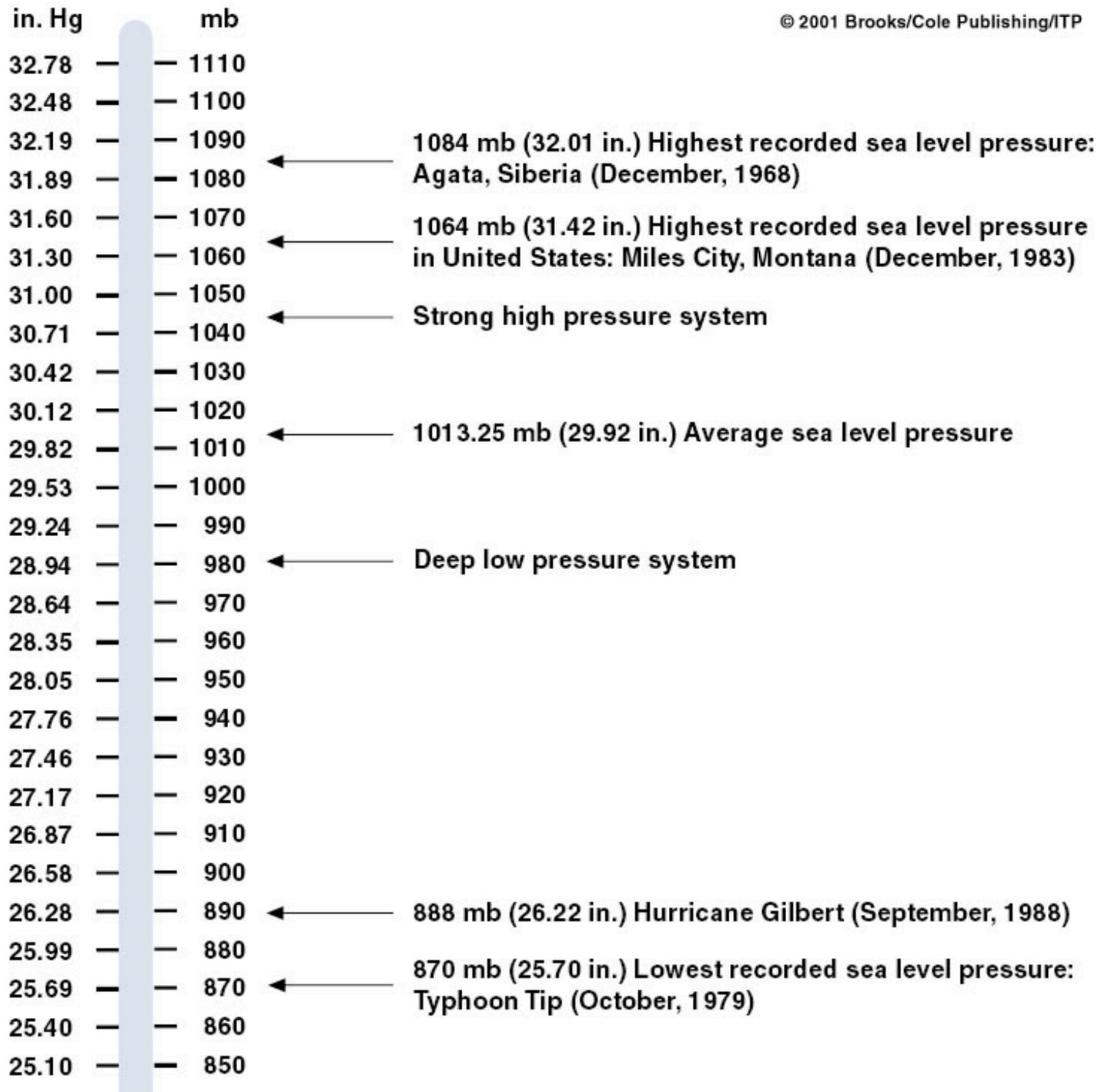


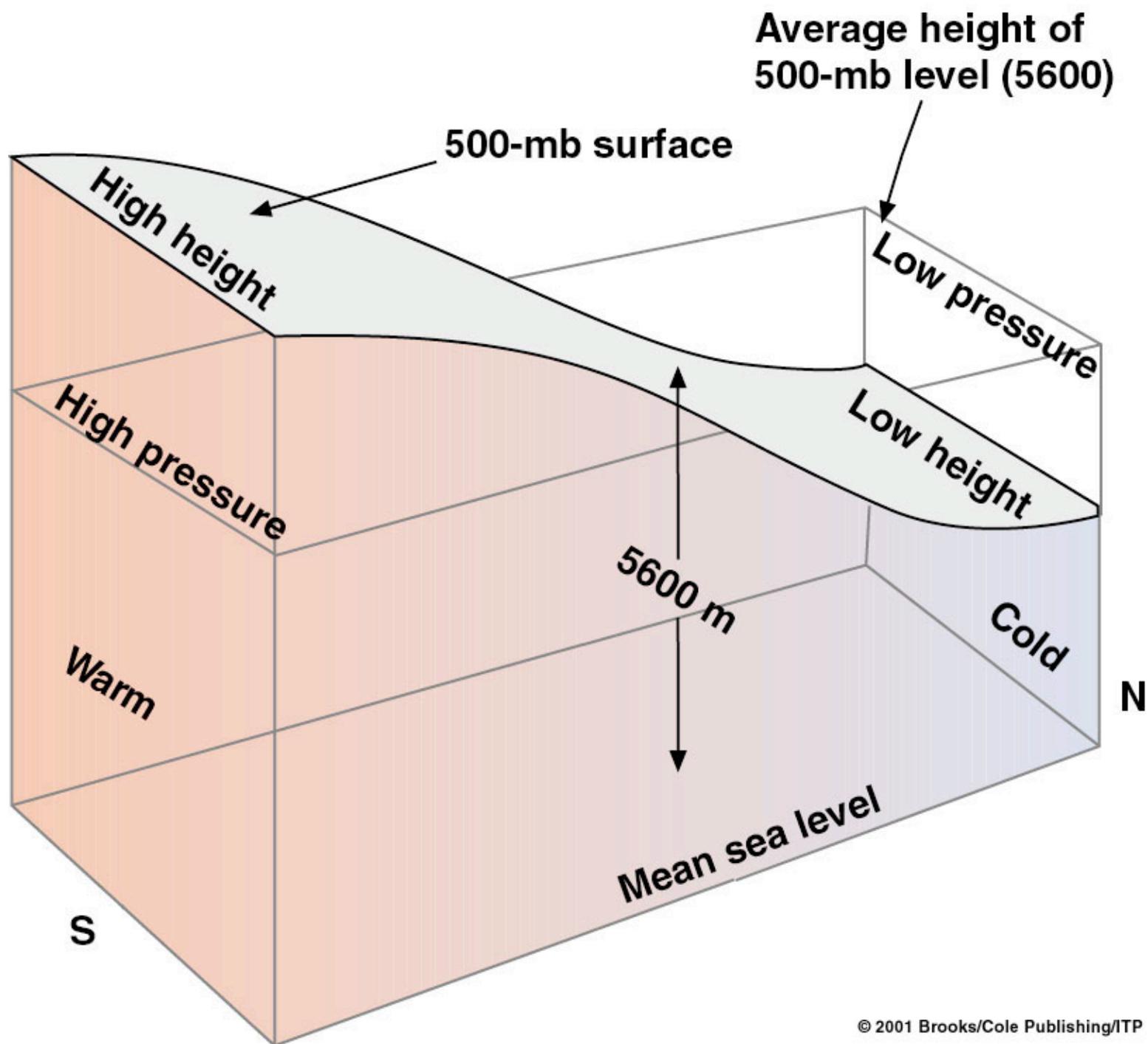
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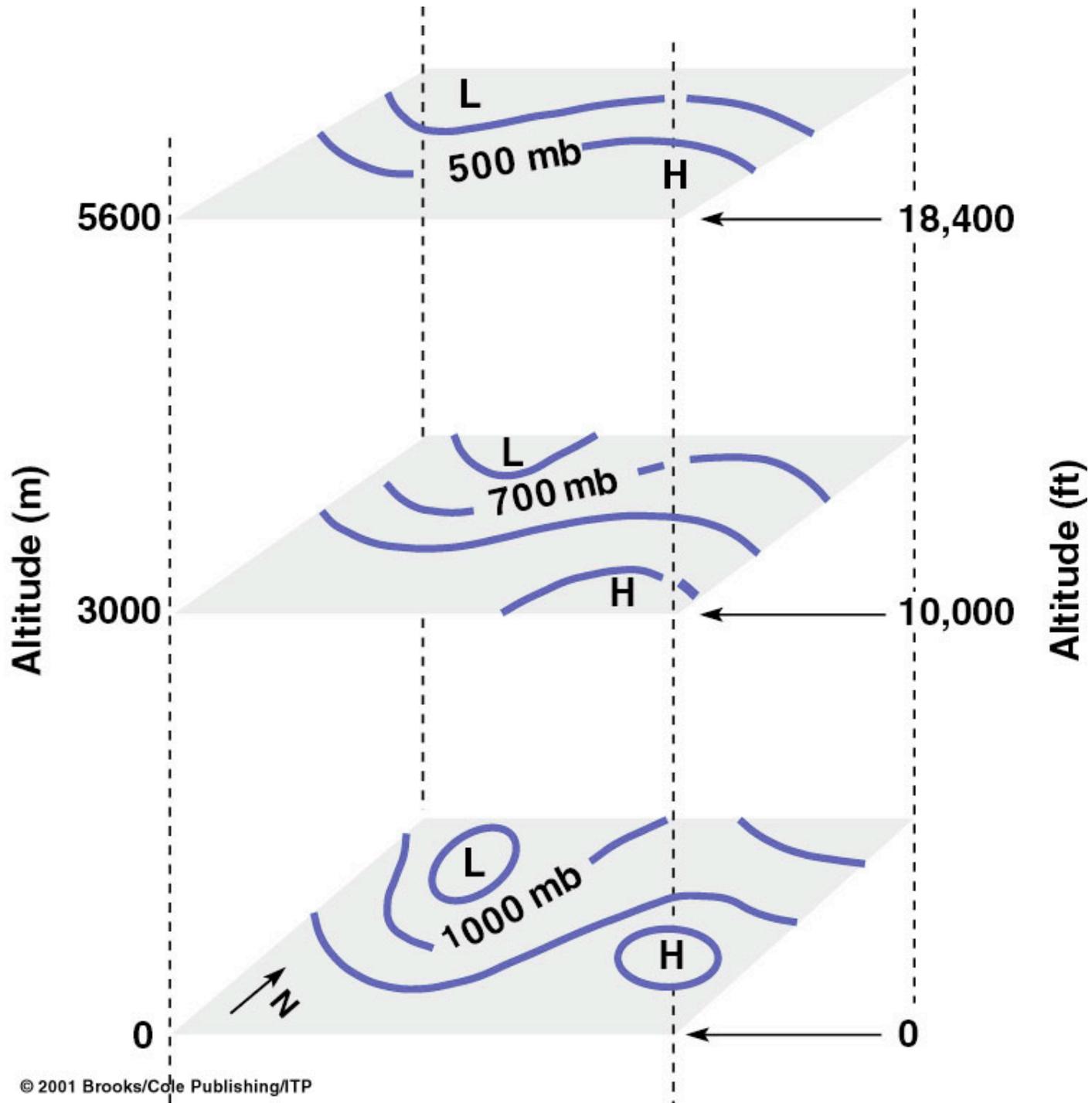












VOLUME

The volume that a given number of gas molecules occupies can vary. (Think of individual atoms or molecules colliding and the mean free path length between collisions; the larger that length is, the larger the volume of the gas will be.)

Volume and density are intimately linked thermodynamically because a given number of gas molecules implies a given MASS of gas (see our discussion of the equation of state of a gas and molecular weights). Since

$$Density = \frac{Mass}{Volume}$$

then if the volume of a gas changes, so does its density. Can you think of an example of how this can be easily demonstrated? (balloons; internal combustion engines; your lungs while underwater or at altitude)

CONCEPT OF A GAS IN EQUILIBRIUM

Always remember that any system (gas, liquid, solid, etc.) is composed of interacting atoms/molecules. In gases and liquids, those atoms/molecules are not bound into a rigid matrix and are free to move, rotate, gyrate, collide, vibrate, etc.

This ultimately leads to the higher COMPRESSIBILITIES of gases and liquids compared to solids. (More on this point later in the course, with its implications for sound wave propagation.)

Think of a gas composed of N particles, each of which has a variety of energetic states associated with translational, vibrational, rotational degrees of freedom, and all of which are interacting locally and remotely through collisions and central electromagnetic forces.

Now allow N to, for all practical purposes, approach infinity. Then we arrive at the Statistical Mechanics perspective of Physics, in which

AN EQUILIBRIUM STATE IS THE STATE OF HIGHEST PROBABILITY.

Our macroscopic perspective cannot measure individual molecules. Macroscopic observation of, e.g., pressure is a time average of all these microscopic interactions. A gas in equilibrium means that the distribution of molecules across all available energy states is not changing in time.

Gases can obviously go from one equilibrium state to another. E.g., a gas undergoes compression or expansion.

A gas/gases can be considered to be in equilibrium if the microscopic energetics of the molecules are always in equilibrium in the statistical sense. We will always assume this to be the case for our atmosphere, and this concept leads to our definition of temperature and the equation of state for a gas.

Can you think of any process, natural or anthropogenic, that might cause nonequilibrium in the atmosphere? What is a central criterion for nonequilibrium?

ZEROETH LAW OF THERMODYNAMICS (leads to the definition of temperature)

The state of most homogeneous substances is completely described by two independent variables. E.g., gases and liquids: pressure, volume; thin films: surface tension, area; etc.

Let's suppose we know absolutely nothing except for this fact.

From our definition of equilibrium, we can say that a gas is in equilibrium if P and V are independent of time. A function, call it F , can therefore be constructed such that $F(P,V)=0$. This is commonly called THERMAL EQUILIBRIUM.

If we have two gases, A and B , that can interact thermally but not mix (e.g. separated by a wall that can transmit heat) then the condition for thermal equilibrium is that $F_{ab}(P_a, V_a, P_b, V_b)=0$. (Note, F_{ab} is not necessarily the same function as F above.)

ZEROETH LAW: If A is in equilibrium with B and B is in equilibrium with C , then A is in equilibrium with C .

(Just like algebra! If $A=B$ and $B=C$ then $A=C$)

Temperature is a new property of a gas whose existence follows from the zeroeth law of TD.

FORMAL DEFINITION OF TEMPERATURE

If A and B are in equilibrium then $F_{ab}(P_a, V_a, P_b, V_b)=0$. Formally, we can solve for $P_b=f_1(P_a, V_a, V_b)$.

If B and C are in equilibrium then $F_{bc}(P_b, V_b, P_c, V_c)=0$. Formally, we can solve for $P_b=f_2(P_c, V_c, V_b)$.

Thus, in order that A and C are separately in equilibrium with B, we must have that

$$f_1(P_a, V_a, V_b) = f_2(P_c, V_c, V_b) \dots \dots \dots (1)$$

However, according to the Zeroeth Law, A and C must be in equilibrium with each other if they're both in equilibrium with B. Thus

$$F_{ac}(P_a, V_a, P_c, V_c) = 0 \dots \dots \dots (2)$$

Now, V_b appears in (1) but not in (2). In order for (1) and (2) to be equivalent, V_b must cancel from (1).

e.g., $f_1(P_a, V_a, V_b) = \phi_1(P_a, V_a)\xi(V_b) + \eta(V_b)$ and $f_2(P_c, V_c, V_b) = \phi_2(P_c, V_c)\xi(V_b) + \eta(V_b)$

Then from (1) we have that $\phi_1(P_a, V_a) = \phi_2(P_c, V_c) = \phi_3(P_b, V_b)$.

THUS: For every fluid (gas, liquid) there exists a function $\phi(P, V)$ such that the numerical value of $\phi(P, V)$ is the same for all systems in equilibrium.

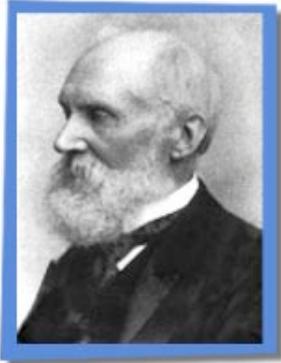
By definition, this value is TEMPERATURE.

The equation $\phi(P, V) = T$ is the *equation of state*.

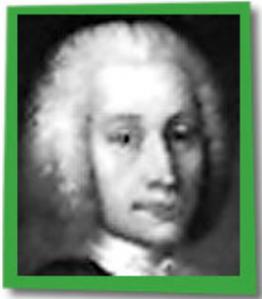
Note: in these arguments the number of molecules, N , of gas/liquid is assumed to be constant so that the volume, V , may equivalently be replaced by the density, ρ .

This temperature is in degrees Kelvin. The Celsius temperature scale is a more common one, with the conversion between the two of the form

$$T(^{\circ}\text{C}) = T(^{\circ}\text{K}) - 273.15$$



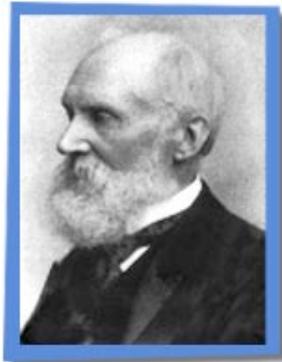
William Thomson (later Lord Kelvin)
(1824-1907)



Anders Celsius
(1701-1744)

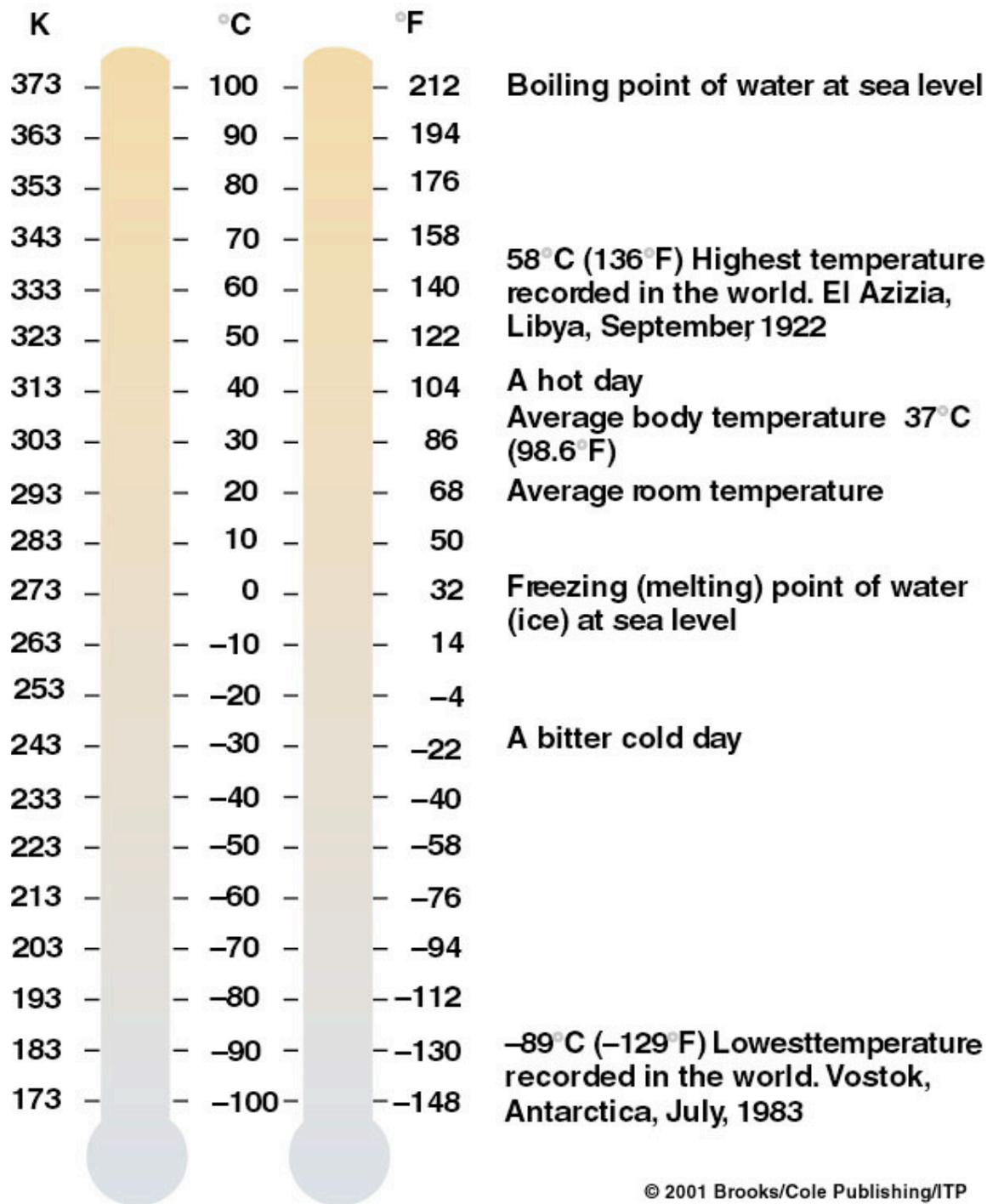


=



- 273.15

Also, $T(^{\circ}\text{C}) = (5/9) * (T(^{\circ}\text{F}) - 32)$



WORK OF EXPANSION/COMPRESSION

The expansion or compression of a gas requires work to be done by the gas or on the gas, respectively. (Examples?)

If a gas expands, it is doing work on its surroundings. If a gas is compressed, work is being done on it by its surroundings. In many circumstances, we wish to know how much energy is released/required in such expansion/compressions.

We can easily calculate how much work is required because we know from Physics that

$$Work = Force \times Distance$$

$$Force = Pressure \times Area$$

Example: Consider the gas in a cylindrical piston of cross-sectional area A , which expands by an amount dX . The work of expansion performed by the gas, δW , is

$$\delta W = pAdX = pdV$$

where p is the pressure exerted *by the surroundings* on the gas, and dV is the increase in volume.

DEFINITION OF ADIABATIC WORK: Work done by a system without simultaneous transfer of heat between it and its surroundings.

THE IDEAL GAS LAW FOR DRY AIR

- Equation of state for an ideal gas
- Atmospheric composition
- Equation of state for gaseous mixtures

Equation of state for an ideal gas

Following our discussion of the Zeroeth Law of TD, we can say that the state of a gas is represented as a point in p, V, T space. Knowledge of the function $\phi(P, V)$, however, means that we only need to know 2 of p, V, T in order to fully describe the gas. (I.e., given 2 of these variables, you can always figure out the third.)

The equation of state of an ideal gas is $pV = nR^* T$

where p is pressure, V is volume, n is the number of moles, R^* is the universal gas constant ($R^*=8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (in Kelvin). This may also be written as

$$p\nu = RT \quad (2.1)$$

or

$$p = \rho RT \quad (2.2)$$

where $\nu = \frac{1}{\rho}$ is the specific volume (sometimes also denoted by α).

NOTES ON THE EQUATION OF STATE FOR AN IDEAL GAS (THE IDEAL GAS LAW)

The ideal gas law can be interpreted to imply that gases behave elastically--when you “push” them to compress them, they resist or “push back.”

The ideal gas law was first determined empirically following work by Boyle (who showed that pressure was proportional to density when temperature was constant) and Charles (who showed that V is proportional to T when pressure is constant, and that pressure is proportional to temperature when volume is constant). It is also a consequence of Avogadro's (1811) principle, which can be stated as follows. The mean distance between the molecules of all gases at the same p , T is the same. Another way of stating this is that the molar volume, $v=V/n$, is the same for all gases at the same p , T .

One of the consequences of Avogadro's principle is that *the density of air diminishes when water vapour is added to it*. This occurs because heavier molecules like N_2 are being replaced by lighter molecules such as H_2O .

Avogadro's number, N_A , is the number of molecules in one mole of a gas. It follows from Avogadro's principle that this number is a constant for all gases, 6.022×10^{23} .

Boltzmann's constant, k , can be thought of as the universal gas constant per molecule:
 $k=R^*/N_A$.

The ideal gas law assumes that molecules occupy no space and that their only interaction is by collision. Real molecules occupy a finite volume and exert forces at a distance on each other. Van der Waal's equation of state takes these effects into account:

$$\left(p + \frac{a}{V^2}\right)(V - b) = nR * T \quad (2.3)$$

where a and b are constants specific to each gas.

LINEAR LIQUID: The equation of state for liquids differs in form from that of ideal gases. The linear form of the state equation is commonly used, although higher order polynomials are constructed for liquids whose state must be known with some accuracy (e.g., seawater):

$$\rho = \rho_0 \left[1 - \alpha(T - T_0) + \chi(p - p_0) \right] \quad (2.4)$$

(Note, it is more common to see the above equation using salinity, S, rather than pressure, when applied to seawater.)

ATMOSPHERIC COMPOSITION

Our atmosphere is, of course, a mixture of gases. The exact composition is of extreme consequence to life on the planet. For example, current global warming scenarios are triggered by a very small increase in a compositionally minor gas (CO₂) in the atmosphere.

The 4 major gases in the atmosphere are:

Major Gas	Molecular Weight (M _i)	Mole (or Volume) Fraction (n _i)	Mass Fraction (m _i)
N ₂	28.013 g/mol	0.7809	0.7552
O ₂	31.999	0.2095	0.2315
Ar	39.948	0.0093	0.0128
CO ₂	44.010	0.0003	0.0005

Other minor stable gases include: Ne, He, Kr, H₂ and N₂O. Minor variable gases include H₂O, O₂, O₃, CH₄, halocarbons, SO₂ and NO₂. The first 5 of the minor gases directly influence the radiation budget in ways that have global climatic consequences.

In addition, the atmosphere has a variable flux of aerosols (dust, soot, smoke, salt, volcanic ash, etc.) that affect radiation through scattering/absorption and act as condensation/freezing nuclei.

EQUATION OF STATE FOR GASEOUS MIXTURES

QUESTION: Since our atmosphere is composed of a variety of gases, can we still use an ideal gas law to describe it?

The partial pressure of a particular gas in a mixture, p_i , is the pressure which gas “i” would exert if the same mass of gas existed alone at the same temperature and volume as the mixture. DALTON’S LAW of partial pressures states that the total pressure in a mixture of gases is the sum of all the partial pressures.

$$p = \sum_i p_i$$

The ideal gas law applies to each gas (comments on this?) and can be written as

$$p_i V = n_i R * T = m_i \bar{R}_i T$$

Note that the volume, V, is the same for all gases in a mixture.

Summing over all gases, i, and applying Dalton’s Law we get:

$$pV = nR * T = m\bar{R}T$$

where

$$n = \sum_i n_i$$

$$m = \sum_i m_i$$

$$\bar{R} = \frac{\sum_i m_i R_i}{m}$$

If we define: $\bar{M} = \frac{m}{n}$ then $\bar{R} = \frac{R^*}{\bar{M}}$

Show for yourself that for dry air: $\bar{R} = R_d = 287.05 \text{ J kg}^{-1} \text{ K}^{-1}$

$$\bar{M} = M_d = 28.964 \text{ g} \cdot \text{mol}^{-1}$$

Then we finally have an equation of state for dry air:

$$p\nu = R_d T$$

or

$$p = \rho R_d T$$

(2.5)

Does dry air behave as an ideal gas under atmospheric conditions? The table below gives the ratio pV/R_dT as a function of temperature and pressure. If air were ideal, the ratio would be unity.

	500 mb	1000 mb
-100 C	0.998	0.996
-50 C	0.9992	0.9984
0 C	0.9997	0.9994
50 C	0.9999	0.9999

Notice that the ideal gas behaviour is approached (i.e., closer to 1) as the temperature rises and the pressure falls. That is, as the mean molecular spacing increases.

WHAT CAN'T BE INFERRED USING THE IDEAL GAS LAW

1. The ideal gas law by itself cannot be used to infer that the temperature in the atmosphere should diminish as height increases and pressure diminishes, even though this result might appear, at first sight, to be consistent with the ideal gas law. Can you explain why? In any event, the increase in temperature with height in the stratosphere would then appear to contradict the ideal gas law.
2. The fact that in winter the coldest surface temperatures are frequently associated with high pressure regimes would, again superficially, appear to contradict the ideal gas law.
3. The ideal gas law by itself cannot be used to infer that Chinook winds should be warm because “temperature increases as pressure increases.” Such an inference must take into account the increase in density that occurs as descending air is compressed. This change in density cannot be deduced from the ideal gas law alone. We will see later that the Chinook effect can be explained by combining the ideal gas law with the first law of thermodynamics.

SOME EXAMPLES OF THE APPROPRIATE USE OF THE IDEAL GAS LAW

1. What is the density of dry air at 84 kPa and 20°C (top of Tunnel Mountain)?

2. What is the total mass of air in this classroom?

3. What is the density of the atmosphere at the surface of Venus?

The Venusian atmosphere consists mainly of CO₂ with a molecular weight of 44 g/mol. The Measured surface pressure and temperature are 90 atmospheres and 750 K, respectively.

4. What power is required for a car to displace the air it moves through?

Let us assume that this power is the power, P_{\max} , required to accelerate all the displaced air to the velocity, v , of the car.

FIRST LAW

- **First law of thermodynamics**
- **Internal energy**
- **Specific heat capacities**
- **Enthalpy**
- **Thermal expansivity, isothermal compressibility**

FIRST LAW OF THERMODYNAMICS

FIRST LAW OF TD: If a system changes state by adiabatic means only then the work done is not a function of the path. (Where “path” here is, e.g., a trajectory in p,V space.)

For example: the work in going adiabatically from state A (p_a, V_a) to state B (p_b, V_b) does not depend on the path traversed in p,V space.

The first law is basically an expression of energy conservation.

The first law of thermodynamics expresses the observation that energy is conserved, and that its different forms are equivalent. Three forms of energy are relevant for the thermodynamics of ideal gases:

Internal energy, Heat, and mechanical Work.

Thus for unit mass of a gas, the first law may be expressed as an energy balance:

$$du = \delta q - \delta w \quad (3.1)$$

where du , δq and δw represent, respectively, infinitesimal changes in the internal energy of the gas, the heat **added to** the gas, and the work done **by the gas** in expanding its surroundings.

Note: we will call properties that refer to unit mass of gas **specific** properties (e.g., specific internal energy; specific heat; etc.) and they will be denoted by lower case letters.

Properties that are mass-dependent are called **extensive** properties and are denoted by upper case letters.

The reason for the difference in notation on the left- and right- hand sides of (3.1) is that u is a function of state while q and w are not functions of state. Thus, du is an exact differential (it depends only on the initial and final points and not on the path taken), whereas δq and δw are not functions of state because they do depend on the path taken.

Recall from our earlier discussion of work that infinitesimal changes of work are related to infinitesimal changes of volume by:

$$\delta w = p dv$$

(Recall that volume v is a state variable and so is a perfect differential. p here is the external pressure exerted upon the gas, which is equal to the internal pressure in equilibrium.)

Upon substituting into (3.1), we have the **first version of the first law**:

$$du = \delta q - p dv \quad (3.2)$$

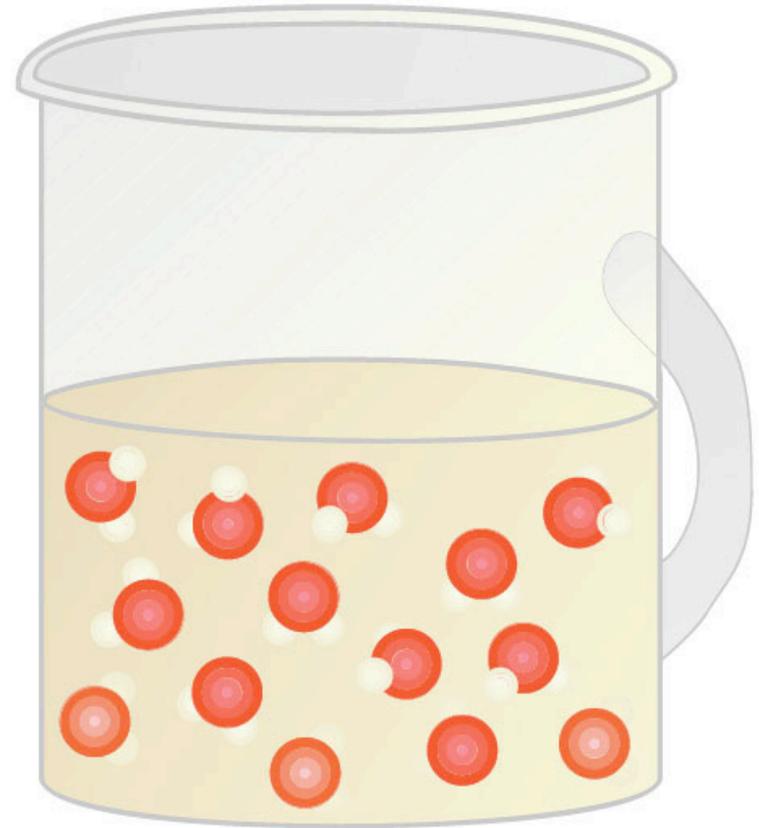
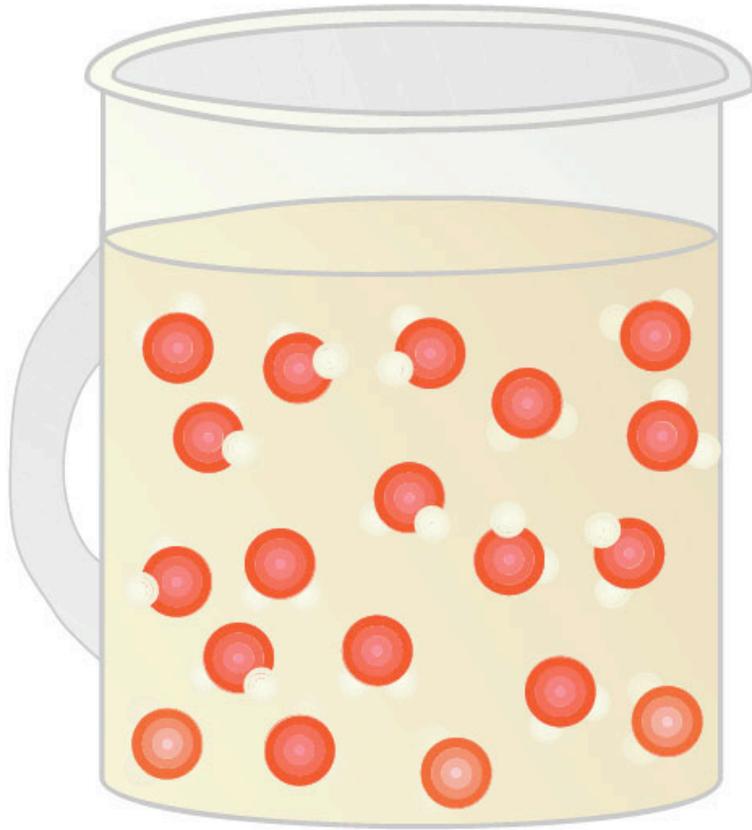
(3.2) implies that heat and mechanical work are equivalent. We can therefore, in principle, determine the mechanical equivalent of heat. Experimentally, it is found that $1 \text{ cal} = 4.1855 \text{ J}$.

INTERNAL ENERGY, u

If there is no work done (i.e., the gas does not expand), so that $dv=0$, and if there are no phase changes or chemical reactions which are evolving heat, then it is found experimentally that:

$$du_v = \delta q_v = c_v dT \quad (3.3)$$

where the subscript, v , denotes the fact that the specific volumes of the gas is held constant (such processes are called **isosteric**).



Isobaric thermal expansion

SPECIFIC HEAT CAPACITIES

Equation (3.3) may be re-arranged to define c_v , the **specific heat capacity at constant volume**:

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v \quad (3.4)$$

Equation (3.3) may also be integrated to provide a method for determining the specific internal energy, u :

$$u = \int_v c_v dT \quad (3.5)$$

where the subscript v on the integral implies an integration over an isosteric process.

In the atmosphere many processes are isobaric; i.e., they occur at constant pressure so that $dp=0$. Experimentally, one finds that if heat is added to a gas isobarically the heat is related to the temperature change by a relation similar in form to (3.2):

$$\delta q_p = c_p dT \quad (3.6)$$

where c_p is known as the specific heat capacity at constant pressure. For solids and liquids, c_p and c_v are essentially identical while for gases they are not.

ENTHALPY

Equation (3.2) may be rearranged as follows:

$$\begin{aligned} du &= \delta q - pdv = \delta q - d(pv) + vdp \\ d(u + pv) &= \delta q + vdp \end{aligned} \quad (3.7)$$

We call $u+pv$ the **specific enthalpy** of the gas and denote it by the symbol h (i.e., $h=u+pv$). Substituting for h in Eq. (3.7) yields the **second version of the first law of TD**:

$$\boxed{dh = \delta q + vdp} \quad (3.8)$$

In view of Eqs. (3.6) and (3.8), for isobaric processes we have:

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p \quad \text{or} \quad h = \int_p c_p dT \quad (3.9)$$

where the subscript p denotes a constant pressure (isobaric) process.

Values for c_p and c_v for air may be found in the Smithsonian Meteorological Tables. These and other atmospheric science references may be found at the University of Alberta by following this link: <http://www.library.ualberta.ca/subject/earthatmospheric/atguide/index.cfm>

Values of the specific heats are essentially constant for air over the meteorological range of conditions.

JOULE'S EXPANSION EXPERIMENT



James Prescott
Joule (1818-1889)

Since u and h are functions of state (i.e., perfect differentials), we expect that in general For gases $u=u(T,p)$ and $h=h(T,p)$. However, a simplification may be made for ideal gases. This simplification arises out of the consequences of Joule's expansion experiment, in which Joule allowed a gas to expand adiabatically (i.e., $\delta q=0$) into a vacuum. The principal experimental result was that Joule could not measure any change in temperature during the expansion. [ASIDE: Subsequent more careful experiments found a small cooling caused by what is known as the Joule-Thomson effect. This effect can be quantified if we were to use

van der Waals equation of state, since the change in temperature depends on a change in the interactions between molecules (as represented by “a” in our notes for van der Waals equation).]

Since the experimental apparatus was insulated, $\delta q=0$, and since there can be no work performed in expanding against a vacuum, $\delta w=0$. Hence by the first law, $du=0$, so there is no change in the internal energy of the gas. But, because of the expansion, the pressure in the gas was reduced while its temperature remained constant. Thus we deduce that for ideal gases, the internal energy cannot be a function of pressure, with the results that $u=u(T)$ and hence also that $h=h(T)$. So for ideal gases we may write:

$$c_v = \frac{du}{dT} \qquad c_p = \frac{dh}{dT} \qquad (3.10)$$

Finally, substituting the definition of enthalpy, h , into the right hand side of (3.10), subtracting the left equation, and using the ideal gas law (2.1), we have:

$$c_p - c_v = R \qquad (3.11)$$

In summary, then, the first two versions of the first law of thermodynamics may be written:

$$\delta q = c_v dT + p dv \quad (3.12)$$

and

$$\delta q = c_p dT - v dp \quad (3.13)$$

Note: Using the hydrostatic equation (later in the notes), Eq. (3.13) may be written as $\delta q = c_p dT + g dz$ which in turn may be written as $\delta q = dh + d\Phi$ where Φ is called the geopotential, equal to g times height z . Hence the first law becomes $\delta q = d(h + \Phi)$. When the kinetic energy of the air is taken into account, we need to add an extra term to the right hand side of the equation, viz: $\delta q = d(h + \Phi + \frac{1}{2} v^2)$

In this case, v is the velocity of the air parcel, and the quantity in parenthesis is known as the **dry static energy**. When latent heating is also included, the quantity Ldq is added into the right hand side, where L is the latent heat of the phase transition and dq is the amount of change of the substance (e.g., water vapour). This is the **moist static energy**.

The equation of state may be expressed as any of: $p=p(T,V)$; $T=T(p,V)$; $V=V(p,T)$. If

dV is a small change in volume, then

$$dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp$$

where the subscripts indicate that that variable is held constant. (Note: we are assuming isentropic processes here.)

Coefficient of isothermal compressibility:

By definition, the coefficient of isothermal compressibility is:

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

where the subscript T means the process is isothermal.

Coefficient of volume expansivity:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

Sometimes this is more commonly expressed in terms of density as the

Thermal expansion coefficient:

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p$$

For example, for a linear liquid the thermal expansion coefficient is defined in the state equation.