

1 Introduction

2 This site explains the affect that Henry's Law in association with [Le Chatelier's](#)
3 [principle](#), [Fick's Law](#), and [Grahams Law](#) have on the dynamic equilibrium of the
4 net gaseous carbon dioxide in the Earth's atmosphere and dissolved carbon
5 dioxide in the Earth's extensive biosphere, to wit: the ocean covers over 70% of
6 the Earth's surface. This is a temperature dependent function.

7 Temperature increases always precede releases of CO₂ from water into the air.
8 into the air. Decreases in temperature always result in greater concentration of
9 dissolved CO₂ at the air/water surface boundary.

10 [ClimateCite](#), a US 501(c)(3)compliant nonprofit educational and research
11 institute has written and published this scientifically authoritative website which
12 explains the physical chemistry of Henry's Law and its operation controlling and
13 regulating the Earth's net CO₂ atmospheric content. It is structured for both
14 advanced Ph.D. level scientists and scientifically lay people.

15 Mankind and its introduction of carbon dioxide (CO₂) into the atmosphere
16 through his use of hydro- carbon based fuels (sometimes referred to as fossil
17 fuels) does not and cannot increase the total net atmospheric CO₂ concentration.
18 The term net atmospheric concentration means all remaining CO₂ in the
19 atmosphere after introduction of all CO₂ from all sources, natural and
20 anthropogenic, and absorption in the Earth's biosphere "sinks". Concepts such
21 as the half-life of man's CO₂ are without scientific merit. Total net
22 CO₂ atmospheric concentration is controlled and regulated solely by Henry's Law
23 and subject to its variables including temperature which is the primary driver of
24 CO₂ increases and decreases per period time. Just as Newton's Universal Law
25 of Gravitation defines the mechanics of gravity, Henry's Law defines the
26 dynamic equilibrium of gases in continuous contact with liquids, including for
27 example CO₂ gas in the atmosphere in contact with Earth's ocean and other
28 water bodies.

29 Henry's law states that at a constant temperature, the amount or concentration
30 of a given gas that dissolves in a given type and volume of liquid is directly
31 proportional to the partial pressure of that gas. Consumers experience Henry's
32 law at work every day when a carbonated beverage is taken out of the
33 refrigerators and slowly loses its carbonization fizz as it reaches room
34 temperature. Henry's law 100% controls or regulates the Earth's atmospheric
35 concentration of carbon dioxide (CO₂). As the surface temperature of a body of
36 water increases it liberates CO₂. Conversely when that body of water decreases
37 in temperature it absorbs CO₂. The Earth's surface is over 70% water. Like

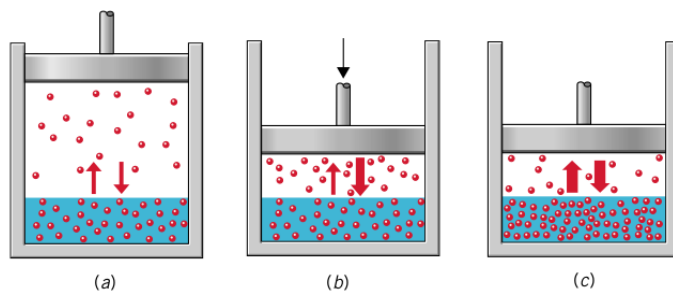
1 Newton's laws of motion, acceleration, and gravity, Henry's law is just that; a
2 constant law of physics.

3 Why is it that so many well qualified scientists including those with Ph.D.
4 degrees in physics, chemistry, and geology do not discuss Henry's law and the
5 fact that it is nature's CO₂ control mechanism and regulator? Unlike Newton's
6 Universal Law of Gravity which is taught in grade school, Henry's Law is not
7 taught in high school physics or chemistry and the vast majority of university
8 undergraduate and graduate physics books do not discuss Henry's Law. Thus
9 there is a critical hole in the scientific knowledge that leads to the confusion and
10 misunderstanding of man's contribution of net atmospheric CO₂ and the related
11 fictitious concept of AGW commonly called climate change. CO₂ is a
12 fundamental building block of life.

10 Explanation of Henry's Law

11 The solubility of a gas in a liquid increases with increasing pressure. To
12 understand this at the molecular level, imagine the following equilibrium
13 established in a closed container fitted with a movable piston.

14 If the piston is pushed down (Figure 13.11b), the gas is compressed and its
15 pressure increases. This causes the concentration of the gas molecules over the
16 solution to increase, so the rate at which the gas dissolves is now greater than
17 the rate at which it leaves the solution. Eventually, equilibrium is reestablished
18 when the concentration of the gas in the solution has increased enough to make
19 the rate of escape equal to the rate at which the gas dissolves (Figure 13.11c).
20 At this point, the concentration of the gas in the solution is higher than before.



21 Figure 13.11 | How pressure increases the
22 solubility of a gas in a liquid. (a) At some
23 specific pressure, equilibrium exists between the
24 vapor phase and the solution. (b) An increase in
25 pressure upsets the equilibrium. More gas
26 molecules are dissolving than are leaving the
27 solution. (c) More gas has dissolved and
28 equilibrium is restored.

26 Adapted from ***Chemistry the Molecular Nature of Matter*** 6th Ed. by
27 Jespersion, Brady and Hyslop. © 2000-2012, pages 595-597

28 The graphic above illustrates mixed gases in the volume of a closed container.
Work is done to compress the volume which increases the total pressure and

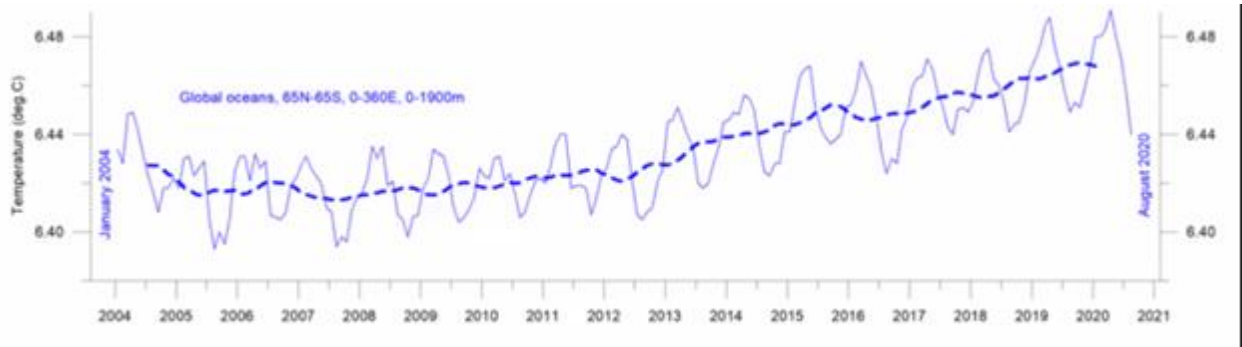
1 temperature of all the gas molecules in that volume, which in turn increases the
2 absorption of each of those molecules in the liquid. In the open atmosphere,
3 when a gas such as CO_2 is added, then the volume of the atmosphere increases
4 but the total pressure and temperature of the atmosphere do not increase.
5 Usually, when CO_2 is added, O_2 has been removed, so the volume change is
6 negligible; but the ratio of the number of CO_2 molecules with respect to the O_2 ,
7 N_2 , H_2O and other atmospheric gas molecules changes. That is, the partial
8 pressure of CO_2 increases relative to the other atmospheric gas molecules.
9 Similar to Figure 13.11, when the partial pressure of CO_2 increases, then the rate
10 of collision of CO_2 molecules with all surfaces increases relative to the other gas
11 molecules since there are numerically more of them. The absorbance of
12 CO_2 molecules into all liquid surfaces increases relative to the other gas
13 molecules. And also absorbance of CO_2 molecules into liquid surfaces increases
14 relative to the emission of CO_2 molecules from liquid surfaces. In the natural
15 environment, absorption of gases into liquids surfaces and emission of gases
16 from liquid surfaces are happening simultaneously and continuously. Note that
17 the surface is dominantly the surface of sea water in the ocean, about 71% of
18 earth's surface, but also the surface of lakes, rivers, and water in soil, water in
19 leaf tissue, water in lung tissue, raindrops, and bubbles.

20 Existentially important for all life on earth, CO_2 is plant food, absolutely
21 necessary for all green plants for their use in photosynthesis in their cells by
22 sunlight to grow the carbohydrate structure and cells of the plant. The only way
23 CO_2 enters plants is by absorption of CO_2 from air into water in the plant's
24 tissues. Oxygen emitted to the air is a by-product of the plant's photosynthesis of
25 CO_2 . Not only are plants on land and in ocean feeding all animal life, but they are
26 also providing oxygen for animals to breath. In other words, efforts by so-called
27 environmentalists and proponents of Net Zero and Climate Crisis to reduce
28 CO_2 are a planetary suicide pact. The ONLY way CO_2 gets into plants to feed
them is by absorption of CO_2 from the air.

21 Henry's Law defines the ratio of (1) a gas absorbed into liquid surfaces versus
22 (2) the same gas emitted from that surface. As previously discussed here, the
23 ratio (or coefficient) of absorption to emission is an inverse function of the
24 temperature of the surface interface between the liquid and the gas. In other
25 words, cold surfaces absorb more gas than warm surfaces. This inverse function
26 is true for all natural gases and liquids. Warm liquid surfaces emit more gas than
27 cold liquid surfaces. The coefficient or ratio of absorption versus emission is
28 known as the Henry's Law constant k_H which is dependent on temperature. A
 k_H is not a function of nor dependent on the source of the gas nor on the amount
of the gas. A k_H is an intensive property of matter, like a boiling point or specific
heat.

1 There is a unique k_H for each combination of a liquid solvent and a gas solute.
 2 Thus k_H for seawater and oxygen is different than k_H for seawater and CO_2 . But
 3 absorption of both oxygen and carbon dioxide increase as the temperature of
 4 the surface decreases, and vice-versa. Warmer ocean surface causes larger
 5 numbers of CO_2 gas molecules (and all other gas molecules) to be emitted to air
 6 compared to the number of CO_2 gas molecules (and all other gas molecules)
 7 colliding with ocean surface and being absorbed into the ocean water. Since the
 8 temperature of the ocean surface is changing continuously by various causes
 9 including day/night, clouds, seasons, air and ocean currents, convection, wind,
 10 waves, etc, no static equilibrium condition exists; Henry's Law defines dynamic
 11 equilibriums in the real world.

12 The probable reason for the slowly increasing trend in net global
 13 CO_2 concentration (e.g., the Keeling Curve) is not CO_2 emissions by humans
 14 burning fossil fuels but is instead the slowly increasing trend in sea surface
 15 temperature, as shown in the following graphic presented by Ole Humlum in his
 16 Dec 7, 2020 lecture to CLINTEL ICSF.



17 This short video illustrates the different relative solubilities of gases in water.

18 Using Henry's Law we can calculate the concentration of any known gas in any
 19 known liquid at any known temperature if we measure the concentration or the
 20 partial pressure of the gas above the liquid. The gas measurement in the gas
 21 matrix is much more accurate and reproducible than the gas measurement in
 22 the liquid matrix. For example, we can calculate the concentration of nitrogen
 23 gas (N_2) in water at 25 degrees C. We measure or look up in a textbook that N_2 is
 24 78.08% of air by volume. Thus the partial pressure of nitrogen in air by volume is
 25 $0.7808 = p_{\text{N}_2}$. We also find in a textbook or online software that the Henry's Law
 26 constant for N_2 in water is 6.48×10^{-4} . The Henry's Law equation arranged for
 27 partial pressure is at 25 C,

28
$$k_H = c_{\text{N}_2\text{aqueous}} / p_{\text{N}_2}$$

where k_H is the Henry's Law constant for N_2 gas solute in water solvent = $6.48 \times$

1 10^{-4}

2 $c_{N_2\text{aqueous}}$ is the concentration of the N_2 gas which is dissolved in the water, which
is our unknown in this example.

3 p_{N_2} is the partial pressure on N_2 gas in the air above the water = 0.7808
this simple algebra:

4
$$c_{N_2\text{aqueous}} = k_H \times p_{N_2} = 6.48 \times 10^{-4} \times 0.7808$$

5 Thus $c_{N_2\text{aqueous}}$ (i.e., the concentration of N_2 gas in water at 25 C) = 5.06×10^{-4}
6 moles of N_2 gas per liter of water.

7 Conveniently, there are several different derivations of the Henry's Law equation
8 for different purposes. The U.S. National Oceanographic and Atmospheric
9 Administration (NOAA) lab and Scripps Oceanographic Institute (Scripps) co-
10 manage a set of laboratories around the globe called the Global Monitoring
11 Laboratories (GML) which measure net CO_2 in air as well as other gases in air.
12 The NOAA-Scripps GML lab at Mauna Loa, Hawaii is generally accepted as the
13 defacto gold standard for comparison to other labs. The NOAA-Scripps GML lab
14 at Mauna Loa has for many decades measured CO_2 in air by molar mass in
15 dried air rather than by volume; the GML labs report CO_2 as micromoles of
16 CO_2 per moles of air, which is equivalent to parts per million (ppm), not ppmv.
17 Thus the dimensionless version of k_H is most convenient for atmospheric gases.
18 The version of the Henry's Law equation for molar mass for a given temperature
19 of the liquid surface is:

15
$$k_H = c_{aq} / c_g$$

16 where:

17 c_{aq} = concentration by molar mass of the gas dissolved in the liquid

18 c_g = concentration by molar mass of the gas in air above the liquid

19 $c_{aq} / c_g = c_{aq}$ divided by c_g

20 the resulting k_H is dimensionless or unitless since the units are cancelled out in
the division arithmetic

21 Now we can look up the dimensionless version of k_H for CO_2 in water at a given
22 temperature of ocean surface and use this along with the Mauna Loa-measured
23 net CO_2 in ppm to calculate the CO_2 in water. Thus units in our calculation
24 formula match units for gold standard CO_2 measurements, avoiding the difficult
25 conversion of ppmv volume units of air which contain continuously varying
amounts of water vapor to the gold standard measured units of ppm molar mass
in dry air reported by the GML.

26 It is important to point out that these labs do not measure human CO_2 emissions,
27 nor could they do so with acceptable accuracy and reproducibility. These labs
28 measure net CO_2 , which is total CO_2 emissions by all sources (natural and
human) minus total CO_2 absorptions by all sinks (natural and human). This is

1 rarely pointed out to the public, which, due to this omission, the general public is
2 allowed to erroneously believe that the famous Keeling Curve (example below)
3 shows the growth in human CO₂ emissions.

4
5 Dimensionless k_H values can be found here Sander
(2023): <https://acp.copernicus.org/articles/23/10901/2023/> or in the
6 attached pdf Sander (1999). Sander presents theoretical background, tabular
7 constants, conversion factors between the various version of k_H and the
8 derivation of Henry's Law for its temperature dependence, as well as copious
9 references.

9 It is worthwhile to mention that these results are consistent with peer reviewed
10 published results of well executed experiments. Here is an abstract of one
11 example, work reviewed by Charles Keeling founder of the GML lab at Mauna
12 Loa ([pdf](#)).

12 *“Associations between the sea-surface temperature (SST) in the eastern
13 equatorial Pacific (0°-10°s, 1800-80°W) and changes in atmospheric
14 CO₂ concentration have been examined. The CO₂ records at Mauna Loa and the
15 South Pole of the Scripps Institution of Oceanography, and the shorter records
16 of the Geophysical Monitoring for Climatic Change program at Barrow, Samoa,
17 the South Pole and Mauna Loa, were used after the annual cycles and the
18 growth due to fossil fuel emissions had been removed. We find that warmer than
19 average SST precedes above-average increases in CO₂ by about one season at
20 Mauna Loa and two seasons at the South Pole. The shorter records at Samoa
21 and Barrow support longer lags - 2 to 3 seasons at Samoa and 3 to 5 seasons at
22 Barrow. The correlations and their lags change with time, however, there being
23 periods of relatively high correlation associated with El Niño events and periods
24 of lower correlation when El Niño is not present. Furthermore, there is a
25 seasonal preference for these high correlations. At Mauna Loa, the change of
26 CO₂ from (NH) fall to spring is better correlated with antecedent SST than the
27 changes from spring to fall. At the South Pole, a similar pattern is found with a
28 one-season shift.”*

23 William P. Elliott & James K. Angell (1987) On the relation between atmospheric
24 CO₂ and equatorial sea-surface temperature, Tellus B: Chemical and Physical
25 Meteorology, 39:1-2, 171-183, DOI: 10.3402/tellusb.v39i1-2.15335 To link to this
26 article: <https://doi.org/10.3402/tellusb.v39i1-2.15335>

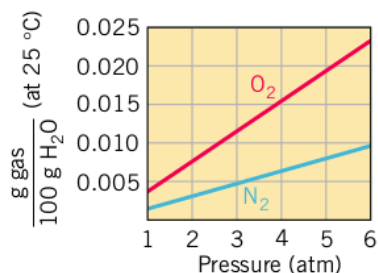
27 The effect of pressure on the solubility of a gas can also be explained by Le
28 Châtelier's principle. In this case, the disturbance is an increase in the pressure
of the gas above the solution. How could the system counteract the pressure

1 increase? The answer is: by having more gas dissolve in the solution. In this
2 way, the pressure of the gas is reduced and the concentration of the gas in the
3 solution is increased. In other words, increasing the pressure of the gas will
4 cause the gas to become more soluble.

4 Figure 13.12 shows how the solubility in water of oxygen and nitrogen vary with
5 pressure. The straight lines on the graph indicate that the concentration of the
6 gas is directly proportional to its pressure above the solution. This is expressed
7 quantitatively by **Henry's law**, which states that *the concentration of a gas in a
8 liquid at any given temperature is directly proportional to the partial pressure of
9 the gas over the solution.*

$$9 \quad C_{\text{gas}} = k_{\text{H}} P_{\text{gas}} \quad (\text{T is constant}) \quad (13.4)$$

10 where C_{gas} is the concentration of the gas and P_{gas} is the partial pressure of the
11 gas above the solution. The proportionality constant, k_{H} , called the Henry's law
12 constant, is unique to each gas. The equation is an approximation that works
13 best at low concentrations and pressures and for gases that do not react with
14 the solvent.



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Figure 13.12 | Solubility in water versus pressure for two gases. The amount of gas that dissolves increases as the pressure is raised.

21 An alternate (and commonly used) form of Henry's law is

$$22 \quad \frac{C_1}{P_1} = \frac{C_2}{P_2}$$

(13.15)

24 where the subscripts 1 and 2 refer to initial and final conditions, respectively. By
25 taking the ratio, the Henry's law constant cancels.

26 Adapted from ***Chemistry the Molecular Nature of Matter*** 6th Ed. by
27 Jespersion, Brady and Hyslop. © 2000-2012, pages 595-597

1
2 Seventy one percent of the Earth's surface is water-covered. The oceans hold
3 about 96.5 percent of all Earth's water. Water also exists in the air as water
4 vapor, in rivers, lakes, icecaps, and glaciers, in the ground as soil moisture,
5 aquifers, and in all living organisms.

6 There are winds and ocean currents and the mass transfer coefficients between
7 the atmosphere and oceans are extremely varied, numerous and chaotic. Ocean
8 cycles go to great depths and have cycle periods of hundreds of years. The
9 surface of the sea may be calm, wavy, or frothy with bubbles forming foam and
10 sprays of droplets, and even ice. All of these impact the mass transfer
11 coefficients. But all these are independent from the partial pressure differential of
12 CO₂ between the atmosphere and the biosphere's many sectors which is
13 controlled solely by Henry's Law and its variables; principally the water surface
14 temperature at any air water surface boundary.

12 **Henry's Law Controls Atmospheric CO₂ Level**

- 14 1. Henry's Law does not apply to the chemical reactions and chemical
15 reaction products which begin with and are subsequent to the ionization of
16 CO₂ gas with water ions. Henry's Law does not apply to H₂CO₃, CO₃⁻²,
17 HCO₃ and the hundreds of other carbonate reactions that occur in
18 seawater and biosphere which occur subsequent to the ionization of
19 CO₂ gas in water. The Henry's Law constant is a physical partition ratio of
20 a specific gas (i.e., the solute gas) dissolved in a specific liquid (i.e., the
21 liquid solvent) in continuous contact with the same solute gas immediately
22 above the same liquid surface; Henry's Law defines a physical phase-
23 state partition, like a melting point or boiling point. Henry's Law does not
24 define chemical reactions, but defines the ratio of a change of phase of a
25 gas in a gas matrix versus the same gas in a liquid matrix.
- 26 2. Henry Law applies to all natural gases and liquids. For our interest here,
27 Henry's Law applies to the approximately 1% or less of CO₂ gas which
28 diffused into and is absorbed into water, and that ~1% is not ionized, is
electrically neutral, uncharged. It is "approximately" 1% because the exact
percentage depends on the temperature of the water. Temporarily local
conditions in the water including alkalinity, pH, salinity, temporarily change
CO₂ gas concentration in the local conditions by changing the equilibrium
of the several carbonate chemical reactions, similar to adding salt to
boiling water to raise the temperature of the water.

- 1 3. Henry's Law only applies to solute gases which are in minor
2 concentrations relative to the gas matrix and relative to the liquid matrix.
3 For avoidance of doubt, 400 ppm or 5000 ppm CO₂ gas in air or water are
4 minor concentrations. A solute is defined as a minor component dissolved
5 in a liquid.
- 6 4. The Henry's Law equilibrium is always a dynamic equilibrium. It is never a
7 static equilibrium as an equilibrium is commonly considered because the
8 temperature of natural waters such as the ocean, or a bubble, or a
9 raindrop, are never static, thus the Henry's law ratio is never static. There
10 is no average temperature of earth's surface, nor ocean surface, nor
11 atmosphere, nor column of ocean water, these are calculations not
12 measurable within the uncertainty required by science, thus there is no
13 average Henry's Law constant for a specific combination of liquid and gas.
14 There is no global Henry's Law constant for CO₂ and ocean. The Henry's
15 Law constant in polar latitudes is different from tropical latitudes due to
16 different sea surface temperatures.
- 17 5. Le Chatelier's Principle is the basis for all processes of absorption and
18 emission of gases into and out of all liquids. A liquid-gas system which is
19 not in equilibrium tends to approach equilibrium. Thus, if the liquid is not
20 saturated with a gas under the existing conditions, then the liquid tends to
21 absorb a gas at a higher rate than it emits a gas. Thus the Henry's Law
22 coefficient or constant describes the limiting condition, a condition which is
23 always being approached but never achieved because CO₂ gas reacts
24 (hydrates) with water ions and those ions subsequently react with other
25 ions and molecules in the water matrix. The result is CO₂ is being
26 continuously but converted to various forms of carbonate, dominantly one
27 of the forms of calcium carbonate since calcium ions are about 4 times as
28 abundant as the bicarbonate, carbonate and carbonic acid combined in
the well mix layers of ocean, and then slowly precipitated as solid
incorporated in stone or structure of coral, sea shells, or sea creatures.
With about 4 times more calcium ions as carbonate ions, ocean is only
saturated with CO₂ gas in temporary and local conditions and when those
conditions subside to absorption of CO₂ gas will begin again to approach
equilibrium. Unless some catastrophic geological or astronomic event
occurs that overcomes the multiple chemical buffering systems in ocean to
dramatically alter pH, alkalinity, or salinity, then it ocean will be an infinite
and perpetual sink for absorbing all CO₂ up to the limit of the Henry's Law
ratio.
6. Henry's Law is an intensive property of matter, like a boiling point, a
melting point or a specific heat. The defining characteristic of an intensive
property of matter is: the amount of matter does not change the constant.
Henry's Law is an Arrhenius Constant, which means the constant varies

1 with temperature. The amount of CO₂ added to the atmosphere by any
2 source natural or human, and the amount of CO₂ absorbed into any sink
3 natural or human, does not change the Henry Law constant at a given
4 temperature. Henry's constants are determined by the specific gas solute,
5 the specific liquid solvent and the specific temperature at the gas/liquid
6 interface. Henry's Law is valid for all known solute gas and solvent liquid
7 combinations, not only CO₂ gas and seawater.

- 6 7. Henry's Law constants are ratios of the molar mass of the unreacted
7 solute gas which is diffused into the liquid divided by the molar mass of the
8 unreacted solute gas in the air immediately above the liquid/gas interface
9 surface. Henry's Law constants are intensive properties of matter because
10 the diffusion rate of any solute gas into any liquid solvent is inversely
11 proportional to the square root of the molecular weight of the solute gas,
12 and the molecular weight of a gas is a constant; this is Graham's Law.
13 Solubilizing a gas follows diffusion of the gas into the surface.
- 11 8. Henry's Law constants are a function of the temperature of the interface
12 surface between the gas and the liquid, wherever that surface exists. The
13 absorption rate (or solubility) of all gases in all liquids is inversely
14 proportional to the temperature of the liquid surface. Emission of the gas
15 from the liquid surface is directly proportional to the temperature of the
16 liquid surface. The surface interface may be as vast as the surface of the
17 ocean, i.e. 71% of earth's surface, or as small as the surface of a small
18 bubble of gas released deep in the ocean, or the surface of a raindrop
19 condensing in a cloud. All of this paragraph applies to all atmospheric
20 gases, not only CO₂.
- 18 9. Unfortunately, many textbooks and science papers merge aqueous
19 CO₂ gas with carbonic acid and this causes misunderstanding and error
20 regarding Henry's Law. Henry's Law does not apply to carbonic acid, but
21 does apply to aqueous CO₂ gas. In these unfortunate documents, the two
22 combined chemical entities are usually given a hypothetical nomenclature
23 like CO₂* or similar, an entity which does not exist. This is done for
24 hypothetical and theoretical considerations in a supposed static
25 equilibrium which also does not exist; these hypotheticals result in
26 confusion and error regarding Henry's Law. These hypothetical
27 expressions are used because the CO₂ hydration reaction is almost
28 instant, and the reverse reaction is also nearly instant. The forward and
reverse reactions occur continuously and simultaneously due to
continuously variable temperature changes in the surface water thin layer,
changes in alkalinity, pH, salinity, changes partial pressure of the CO₂ gas
in the water surface thin layer, as well as changes in the gas thin layer
immediately above the water surface.

1 CO₂ gas in air (and all other gases in air) are continuously and
2 simultaneously colliding with the surfaces such as ocean at continuously
3 varying collision rates due to variations in air temperature/pressure and
4 variations in CO₂ partial pressure. Similarly, CO₂ effusion from ocean
5 surface occurs continuously and simultaneously with diffusion into the
6 surface; but the rate of emission and the rate of absorption are not parallel
7 due to the wide difference in density between the liquid matrix and the air
8 matrix and the intermolecular and interionic forces in the liquid thin layer
9 which are negligible or do not exist in the air thin layer matrix above the
10 liquid surface. Thus, effusion into air is faster than diffusion into water.
11 (Description of the chemistry and physics of the water thin layer and air
12 thin layer are interesting and important, involving virial forces between the
13 molecules and ions, van der Wals force, surface tension, but these are
14 beyond the topic here.)

15 The rapid and reversible CO₂ hydration reaction means the products,
16 reactants and activation energies of the CO₂ hydration reaction are difficult
17 or impossible to measure with sufficient accuracy or precision. In practice,
18 the molar mass concentration of the CO₂ gas in the head space above the
19 liquid surface is quantified by gas chromatography or gas chromatography
20 mass spectrometry and then the molar mass of the CO₂ gas in the liquid
21 are calculated by Henry's Law. Accurate and precise sampling of the
22 reactant CO₂ gas and the product carbonic acid in the hydration reaction is
23 extremely difficult if not impossible. For example, Keeling et al and many
24 others have sampled ocean water and air for CO₂ gas. But, sampling from
25 moving vessels e.g., the many voyages of Charles Keeling and many
26 others, or sampling in wind or ocean currents, or wave-disturbed surfaces,
27 causes changes in CO₂ partial pressure (and other variables) resulting in
28 measurement errors. The rapidly reversible CO₂ chemical hydration
reaction occurs in all layers of the ocean and the CO₂ physical phase state
reaction occurs at all layers of the ocean and in the troposphere.

10. Agitation of air or water increases their temperature as well as
increases the surface area of the interface and this changes the net flux
rate of the gas. The net flux of a gas through a surface interface is a
function of the surface area of the gas/liquid interface, and a function of
the thickness of that interface layer, and a function of the gradient of the
gas in the interface layer, and a function of the Graham's Law diffusion
constant for the solute gas. Net flux is the vector directional residual
difference between the molar mass of all solute gas emissions minus the
molar mass of all solute gas absorptions passing through a known amount
of surface area and known surface thickness in a known time period; for
example gigatons of CO₂ gas emitted into air per square mile of ocean
surface per year. Net flux is directional (either absorption or emission.) Net

1 flux is defined by Fick's 1st Law. The CO₂ concentration measured at
2 NOAA Mauna Loa is a generally accepted defacto standard for the
3 average net global CO₂ concentration. The slope of that Mauna Loa
4 concentration record with respect to time (often called the Keeling Curve)
5 is the slope of the net flux of CO₂ with respect of time, which is dominantly
6 (~ 71%) the record of Fick's 1st law for net flux CO₂ gas and ocean. The
7 Mauna Loa lab (and most NOAA and similar labs) measures by molar
8 mass the net residual difference of CO₂ gas emitted from all sources of
9 CO₂ gas natural and human minus all CO₂ gas sinks natural and human;
10 these labs do not and could not measure global human CO₂ emissions,
11 nor net human CO₂ emissions nor net human CO₂ flux.

9 The much higher density of water compared to the density of air causes
10 much higher CO₂ gas concentration in ocean water matrix compared to
11 CO₂ gas concentration in air. This occurs at all depths of ocean, regardless
12 of mixing. Geology texts calculate the ratio of CO₂ gas in ocean versus
13 CO₂ gas in air at about 50:1, which is a very broad average. The ratio
14 varies with temperature and altitude (air pressure/density) and ocean
15 depth (water pressure/density). Density of water increases rapidly with
16 depth while density of air decreases with altitude but less rapidly. There
17 are systemic processes as well as chaotic processes of mixing in both
18 atmosphere and ocean. There is layering within both atmosphere and
19 ocean and different physical and chemical reactions occur in the different
20 layers. The less-well mixed deep ocean layers contain much higher molar
21 concentration of CO₂ gas than the well-mixed medium ocean layer. The
22 more well mixed surface ocean layer (which is usually but not always
23 warmer than the layers below) contains lower concentration than the
24 ocean layers beneath it. Theoretically at the ideal limit, at the air/ocean
25 surface interface, in the ocean thin film layer of a few molecules thickness,
26 in calm flat seas with no water current and no wind, the Henry Law
27 constant for a given ocean surface temperature determines the molar
28 concentration of CO₂ in the water surface divided by the molar
concentration of the CO₂ in the air thin layer above the surface; practically,
this ideal theoretical condition does not exist except in transition.

24 The hypothetical equilibrium condition for Henry's Law means that the ratio of
25 the number of gas molecules of a specific gas being absorbed by a liquid
26 surface versus the number of molecules of the same gas being emitted from that
27 liquid surface is a constant for the given temperature of the surface. Unlike total
28 pressure of mixed gases where at equilibrium the amount of total gas emitted
equals amount of total gas absorbed, instead, Henry's Law applies to partial
pressure of a single specific gas, wherein, the ratio absorption vs emission of the
single gas is the Henry's Law partition ratio, or coefficient. Absorption and

1 emission are occurring simultaneously, but not at the same rate. The absorption
2 rate of a specific gas like CO₂ into water surface can be increasing while
3 simultaneously the rate of emission of CO₂ from the nearby water surface can
4 also be increasing; the conditions causing these two opposing perturbations to
the Henry's Law partition ratio for CO₂ gas and water are different in the gas
matrix and the liquid matrix.

5 When CO₂ is added to air by burning fossil fuels, other sources of CO₂ are
6 naturally reduced and/or sinks are naturally increased so that the Henry's Law
7 ratio is maintained for the surface local temperature. It is a dynamic equilibrium
8 and the control knob for the gas concentration, if you will, is the Henry's Law
9 ratio at the local surface temperature. CO₂ is not accumulating in the
10 atmosphere as hundreds of scientists and millions of dollars spent on annual
11 carbon budgets attempt to persuade. CO₂ has been increasing slowly in recent
12 years because sea surface temperatures (SST) have been increasing in recent
13 years. If and when SSTs begin decreasing, the CO₂ concentration in air will also
begin declining, though this decline is slow due to the enormous (orders of
magnitude) higher heat capacity of ocean compared to atmosphere. For now,
slowly warming SST and rising CO₂ are both good for life.

14 Warming and cooling of ocean are very slow processes requiring centuries or
15 millennia due to the enormous heat capacity of the ocean. The causes of
16 warming and cooling are beyond the scope of this email except to point out
17 firmly that they are definitely not caused by human-produced CO₂; this statement
does not require refutation or denial of the so-called "greenhouse gas" theory,
radiative emission theory, carbon budgeting, feedbacks, etc.

18 The Henry's Law coefficient is usually defined as $k_H = c_a/p_g$

19 Where:

- 20 • k_H refers to standard conditions, $T = \text{temperature} = 298.15 \text{ K} = 25 \text{ degrees}$
21 C , and total pressure is 1 atm.
- 22 • c_a is the concentration of the unreacted solute gas in the liquid phase
- 23 • p_g is the partial pressure of the same solute gas in the gas phase
24 in continuous contact with the surface of the liquid phase.

25 This version of Henry's Law above requires calculations and measurements in
26 volume for p_g .

27 One of the common problems encountered with Henry's Law is its dependence
28 on temperature. k_H is a constant (or coefficient, or ratio) that varies with
temperature. This is not a simple matter. For example, one of the teachers for

1 chromatography classes for the American Chemical Society, who was one of the
2 founding fathers of gas chromatography, published errors of Henry's Law
3 constants derived for temperature ranges; he was not alone. No doubt this
4 author's own writings on his personal web blog have errors too. Derivation of
5 Henry's law constants as a function of temperature is based on solution of the
6 Clapeyron or Van Hoff equations formulated for water-gas equilibrium. Great
7 care is required with the units.

$$6 \quad d \ln k_H / dT = \Delta H_{\text{dis}} / R_g T^2$$

7 Where:

- 8 • ΔH_{dis} is the enthalpy (or heat) of dissolution of the gas solute in water
- 9 • R_g is the gas constant
- 10 • T is temperature in Kelvin.

11 **Henry's Law constant for CO₂ gas and water solution. (as given in**
12 **reference 5 below)**

$$13 \quad k_H(T) = k_H^\circ \exp(d(\ln(k_H))/d(1/T) ((1/T) - 1/(298.15 \text{ K})))$$

14 k_H° = Henry's law constant for solubility in water at 298.15 K (mol/(kg*bar))

15 $d(\ln(k_H))/d(1/T)$ = Temperature dependence constant (K)

16 For our purposes studying CO₂, atmospheric gases and Henry's Law, a different
17 derivation of Henry's Law is much more convenient. Sander provides this
18 derivation also: the Henry's Law coefficient is derived in its dimensionless (or
19 unitless) form as the quotient (or ratio) of the molar concentration of the
20 unreacted solute gas dissolved in the liquid phase matrix divided by the molar
21 concentration of the same solute gas in the gas phase matrix. It is
22 dimensionless since the units drop out when dividing molar mass by molar
23 mass. But, the temperature derivation is still difficult. Today fortunately we look
24 up Henry's coefficients in reference books or by online software and then
25 carefully verify the units. There is a different k_H for each gas and liquid
26 combination and each temperature.

27 Henry's Law expert Rolf Sander provides further expansion of various
28 derivations in section 4.2 of the IUPAC Recommendations 2021 paper with other
29 detail on the other forms of Henry's law for various purposes

30 here: <https://www.degruyter.com/document/doi/10.1515/pac-2020-0302/html>

31 and references (4) and (5) below.

1 These two equations for Henry's law, the partial pressure version above and the
2 dimensionless version below, are related through the ideal gas law, where $k_H =$
3 $k_H \times RT$.

4 **The dimensionless version:**

5 $k_H = c_a/c_g$

6 Where:

- 7 • k_H = the Henry's Law coefficient
- 8 • c_a = concentration of the gas in moles in the aqueous phase
- 9 • and c_g is concentration of the same gas in the gas phase above the
10 liquid/gas surface.

11 Generally, the dimensionless version is most convenient because the defacto
12 NOAA-Scripps Mauna Loa "gold standard" CO_2 data has been diligently
13 measured and reported for many decades as micromoles of CO_2 per mole of dry
14 air. Micromoles of CO_2 per mole of dry air is identical to ppm, parts per million by
15 mass. This is a mass measurement, not a volume measurement, which is far
16 more practical, precise and accurate for measuring trends in atmospheric gases
17 since air always contains the gas water vapor, the quantity of water vapor in air
18 is highly variable which causes the sample volume to be highly variable. Water
19 vapor concentration in air is normally 10 to 100 times higher than the trace
20 gases like CO_2 , methane (CH_4), etc. Also, water vapor and CO_2 have overlapping
wavelengths of infrared light used in measurement instrumentation. These are
21 reasons NOAA-Scripps dries their air samples (by freezing) and measures by
22 mass instead of volume, i.e., micromoles of CO_2 per moles of dry air which
equals ppm.

21 Important note: ppm is not the same as ppmv. This is a common and large
22 source of error in measuring net CO_2 trends compared to the minor annual
change in net global CO_2 concentration.

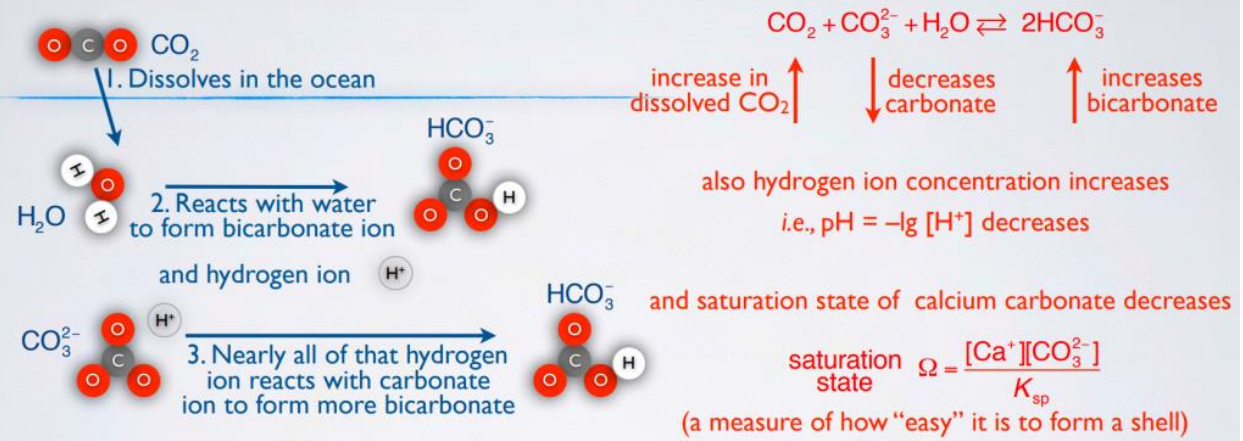
23 Henry law coefficients are available online, having been measured thousands of
24 times for thousands of combinations temperatures, liquid solvents and gas
25 solutes. The concentration of CO_2 in water is easily calculated from the gas
26 concentration and the Henry's coefficient, but the CO_2 and H_2CO_3 (carbonic acid)
27 concentrations are difficult or impossible to measure in water with acceptable
accuracy and precision because sampling procedures affect the hydration
28 reaction.

1 The gas-water surface interface can be the surface of a bubble at 3000 meters
2 depth in ocean, or the surface of a raindrop in a cloud at 3000 meters altitude,
3 lung tissue, leaf tissue, or dominantly the surface of the ocean.

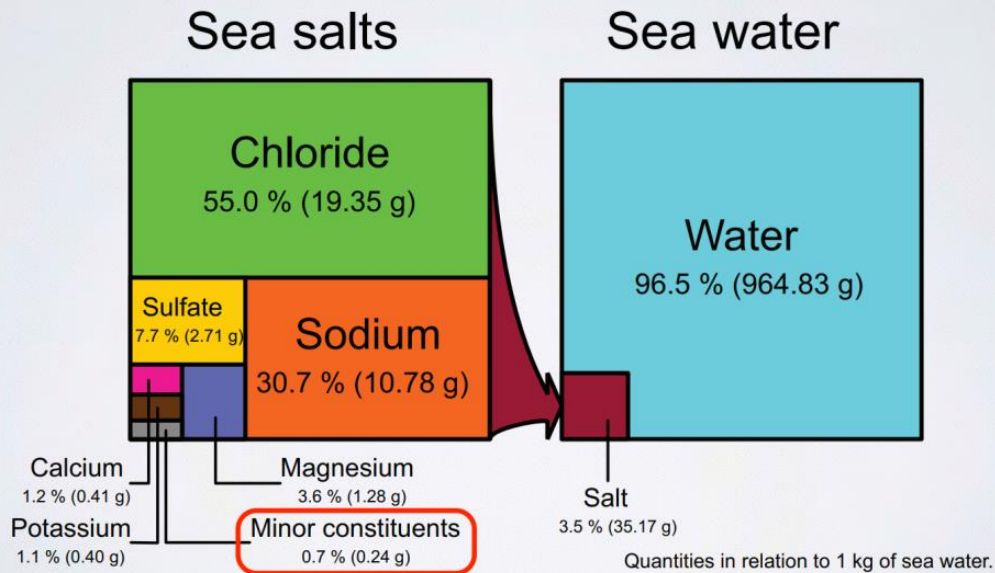
4 In a mixture of gases, the flux of one gas back and forth across the surface does
5 not affect the flux of a different gas until concentrations are very high. This was
6 demonstrated by Adolph Fick, a physiologist, who studied air gas fluxes in lung
7 tissues, a contemporary of William Henry, Thomas Graham, and John Dalton.

8 In nearly pure water like raindrops, the aqueous CO_2 gas concentration is high
9 and the H_2CO_3 (carbonic acid) concentration is high relative to the HCO_3^-
10 (bicarbonate) concentration. Thus raindrops are measured slightly acid.
11 Carbonic acid is a weak acid. But those raindrops also absorb other gases of
12 nitrogen and sulfur (for example near an urban area or a refinery) which create
13 strong acids in water. In contrast, in seawater HCO_3^- is the dominant species
14 because there are very many more ionic species (sodium, calcium, etc.)
15 dissolved in seawater which easily pull the first hydrogen ion away from the
16 H_2CO_3 . The concentration of calcium ion by itself is about 4 times as abundant in
17 seawater surface as the combined concentrations of unreacted CO_2 gas,
18 bicarbonate ion, carbonate ion, and carbonic acid. The first dissociation constant
19 for pulling away the first hydrogen atom from H_2CO_2 leaving HCO_3^- is very small
20 and the reaction is nearly instant. So, dependent on the seawater conditions,
21 HCO_3^- can be both a reaction product from the CO_2 gas hydration reaction and
22 also a reaction product from the dissociation reaction of H_2CO_3 .
23
24
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26
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28

EFFECT OF ADDING CO₂ TO SEA WATER



COMPOSITION OF SEA WATER (S = 35)



Graphics above from Andrew G. Dickson, Scripps Institution of Oceanography, UC San Diego, INTRODUCTION TO CO₂ CHEMISTRY IN SEA WATER.(6)

There are many simultaneous phenomena occurring at these air/liquid surfaces. I have not touched on most of them. The most important quantitatively is the physical phase state reaction, wherein the change in partial pressure of the solute gas within the gas matrix causes a proportional change in the solubility of that unreacted solute gas in the liquid phase. When humans or any other source add CO₂ to air, then the solubility of CO₂ gas in water increases proportionally to absorb that CO₂ gas. Double the partial pressure of CO₂, then solubility of CO₂ in water doubles. And vice versa.

1 The Henry's Law ratio is a variable of surface temperature, not a variable of the
2 amount of gas present, and not a variable of the source of the gas; it applies to
3 all gas solutes in low concentrations with respect to the liquid solvents with
4 which they are in continuous contact. The ratio does not apply to any portion of
5 the gas solute which has reacted with the liquid solvent itself or has reacted with
6 any component dissolved in the liquid solvent. Residence time, or half-life, or
7 residual fraction, of the CO₂ in air are not variables in the Henry Law phase-state
8 equilibrium and play no role in net global CO₂ concentration.

9 Next in importance is to understand that the CO₂ hydration reaction (CO₂ + H₂O
10 \leftrightarrow H₂CO₃) is nearly instantly reversible, for example by a very minor increase in
11 water temperature, or agitation of the water, or change in other variables. Then
12 the first dissociation constant K₁, which is dissociation on one hydrogen away
13 from H₂CO₃, this K₁ is small, yielding HCO₃²⁻. The subsequent K₂ dissociation
14 reaction to CO₃²⁻ is relatively larger. Both reactions are nearly instantly reversible.
15 But the hydration reaction CO₂ + H₂O \leftrightarrow H₂CO₃ is so fast it is unmeasurable.
16 Sampling changes the measurement. Unfortunately many textbooks merge
17 unreacted aqueous CO₂ gas and H₂CO₂ into a single hypothetical entity, which
18 has apparently led to misunderstanding.

19 There is a highly abundant (>90%) reservoir of these readily available carbonate
20 ions in seawater surface thin layer and well mixed layer which are not unreacted
21 aqueous CO₂ gas but which are very rapidly convertible to unreacted aqueous
22 CO₂ gas when the unreacted aqueous CO₂ gas in seawater is depleted. And
23 vice versa. We have shown this in Bromley & Tamarkin (2022). Depletion of
24 CO₂ in air as well as CO₂ in water occurs by many different processes, and
25 addition of CO₂ to air and water occurs by many different processes. For
26 example, outgassing of CO₂ from water to air occurs to rebalance to Henry's Law
27 coefficient when CO₂ concentration in air is being depleted by photosynthesis of
28 land plants or by surface winds; conversely when aquatic plants like plankton
bloom in ocean and absorb aqueous CO₂ gas for their photosynthesis, then
CO₂ gas will be absorbed into water from air at higher ratio than is being emitted
from water to air until the Henry's Law coefficient is achieved for the water
surface temperature. These opposing processes can and do occur
simultaneously, which is probably a reason climatologist rarely if ever attempt to
model Henry's Law.

To summarize so far, when the approximately 1% of aqueous CO₂ gas is either
increased or decreased by any amount, due to any source or sink, this
perturbation causes a recovery (following le Chatelier's Principle) to rapidly
return to that 1% by the using ocean's chemistry systems, and there is an
abundant reservoir of ionic carbonates in ocean water to achieve that recovery.
In other words, the amount of CO₂ emitted by humans replaces naturally emitted

1 CO₂ in the phase-state equilibrium, rather than accumulating in the atmosphere
2 in addition to naturally occurring CO₂. There is no CO₂ accumulation in
3 atmosphere. The ~1% can be perturbed in both directions by changes in
4 temperature, salinity, pH, alkalinity, and by changes in partial pressure of the
5 CO₂ in the water or in the air. Adsorption and emission of CO₂ are simultaneous
6 and continuous in both directions at normal earth temperatures since
7 CO₂ molecules are continuously colliding with the surface and being emitted
8 from the surface. The rate of absorption vs emission is the Henry's Law
9 coefficient for the local water temperature.

10 It is very important to mention that CO₂ gas molecules and the three forms of
11 carbonate ions (H₂CO₃, HCO₃²⁻, CO₃²⁻) do not need to migrate in water more than
12 molecular distances to react with each other. Scientific publications which are
13 adopted into the anthropogenic global warming (AGW) orthodoxy and climate
14 models, for example work by (1) Bert Bolin (1960) first administrator of UN
15 IPCC, and (2) Broecker and Peng (1974), and others, considered the thickness
16 of the water thin layer and limited their calculus of aqueous CO₂ migration to
17 thickness of the water matrix. They define the chemical pathways that convert
18 CO₂ to HCO₃⁻ and vice versa as "chemical enhancement." They calculate based
19 on the thickness of the thin layer and migration time of the carbon species in the
20 ocean matrix, however they ignore an equally critical variable which is the
21 surface area of the gas – liquid interface, omitting more than 100 million square
22 miles of air-water surface interface. This appears to be a major mistake in the
23 AGW orthodoxy and modeling. Keep in mind that in these years of early papers
24 seminal to IPCC orthodoxy, CO₂ emissions were said to cause global cooling; I
25 speculate they were focused on their modeling methods rather than empirical
26 observations.

27 For example, "The rate limiting step for removal of anthropogenic CO₂ from the
28 air is vertical mixing within the sea rather than transfer across the air-sea
29 interface."(2) This statement conflicts with Fick's 1st Law of net flux of gases.

30 Why did Bolin and Broecker & Pang (for example) consider only thickness of the
31 ocean thin layer and not the huge square surface area of ocean? It is a puzzle.
32 The 3 carbonate ionic species are distributed throughout the area of the thin
33 layer as well as the well mixed layer beneath it and they surround the uncharged
34 aqueous CO₂ gas molecules in the thin layer and well mixed layer in a ratio of
35 over 9:1. If the uncharged aqueous CO₂ gas molecule is removed from the liquid
36 matrix by either outgassing or by absorption into aquatic plants, then the
37 carbonate reactions reverse and produce more uncharged aqueous CO₂ gas
38 molecules. And vice versa. And when the carbonate ion CO₃²⁻ reacts with for
example a very abundant ion such as calcium Ca²⁺ and solidifies, then the
carbonate ion in water is thus reduced one for one. CO₃²⁻ + Ca²⁺ = CaCO₃. Then

1 as a consequence of this reaction (which occurs in warmer water near the
2 surface, and reverses in colder deeper, higher pressure water), the prior
3 carbonate and the hydration reactions are forced to re-equilibrate by absorbing
4 more CO₂ from air. Thus, there is a perpetual CO₂ gas sink rate absorbing
5 CO₂ from air even while warming SST is slowly increasing outgassing CO₂.
These simultaneously opposed dynamic processes are mediated by Henry's
Law and the carbonate reactions.

6 Attached is a pdf (reference 3) which documents one of several gas
7 chromatographic (GC) methods to quantify Henry's Law coefficients. To use this
8 method for CO₂, since CO₂ does not burn in the flame ionization detector (FID)
9 flame, instead the effluent from GC column is passed first over a rubidium
10 catalyst which stoichiometrically converts the CO₂ to CH₄, and then the effluent is
11 directed onward to the FID where the CH₄ is ionized and quantified. Alternatively,
12 the FID can be replaced by a mass spectrometer and no catalyst is needed. I
am pointing out that there is no mystery in Henry's Law, there are many of these
methods well documented by theory and experiment, but AGW proponents
either ignore it or fail to understand it or both.

13 [On the Exchange of Carbon Dioxide Between the Atmosphere and the Sea](#)
14 [\(PDF\)](#)

15 [Gas Exchange Between Air and Sea \(PDF\)](#)

16 [Introduction to CO₂ Chemistry in Sea Water \(PDF\)](#)

17 [A Laboratory Experiment To Measure Henry's Law Constants of Volatile Organic](#)
18 [Compounds with a Bubble Column and a Gas Chromatography Flame Ionization](#)
19 [Detector \(GC-FID\) \(PDF\)](#)

20 **Conclusion**

21 Henry's Law describes the ratio between two gas concentrations:

22 1. The concentration of a specific gas (e.g., CO₂) dissolved in a liquid phase,
(e.g., ocean water), versus... 2. The concentration of the same gas in the gas
23 phase which is in continuous contact with the liquid phase... (e.g., CO₂ in air
above ocean water.)

- 24 • where the ratio changes based on temperature of the surface interface
between the gas and liquid phases
- 25 • where the ratio does not change based on the amount of the gas present,
- where the ratio changes based on the identities of the gas and the liquid

26 A Henry's Law constant is a ratio which describes the net amount of a gas in
27 atmosphere versus that same gas in ocean water in contact with the
atmosphere. But more generally, it describes all gases in contact with all
28 liquids. Henry's Law is not a human invention, hypothesis or theory, but rather

1 carefully documented observations of nature. The primary gases in the
2 atmosphere are nitrogen (78.084%,) oxygen (20.947%,) and argon (0.934%,) in
3 the driest of conditions. However, water vapor (H_2O) can compose as much as

4 4% of the atmosphere in damp conditions and is highly variable.
5 The total of all other gases make up less than 1% of atmosphere and are called
6 trace gases. These trace gases include carbon dioxide, ozone, methane,
7 various oxides of nitrogen, neon, helium, hydrogen and other rare gases. They
8 are called trace gases because they exist in small amounts. For example, the
9 combined sum of natural and human-produced carbon dioxide is only 0.04% to
10 0.05% of the total atmospheric gases.

11 Carbon dioxide (CO_2) is both produced and used by many natural and human
12 processes. Plants, animals, and inorganic chemical reactions use CO_2 from air,
13 water, soil and rock and also return CO_2 in various chemical forms to the
14 environment as bones and cellular structures of living creatures, then later in
15 deposits such as shells, corals, and sedimentary rocks. The net result is
16 CO_2 gas is being continuously removed from the environment for thousands or
17 millions of years, and replaced by burning fossil fuels, cement production,
18 respiration, volcanoes and tectonics, and these enormous processes are
19 continuously mediated by Henry's Law and chemical balancing of the giant
20 dissolved carbon reservoir in the ocean and CO_2 emitted.

21 The amount of CO_2 man introduces into the atmosphere by the combustion of
22 carbon-based fuels is inconsequential, easily absorbed by the environment.
23 Man could reduce his use of hydrocarbon fuels by 100% or increase them by
24 500% and at the end of the day 0% change in net atmospheric
25 CO_2 concentration will be the result. This natural result occurs because any
26 increase in any atmospheric gas concentration is offset by a proportional
27 increase in absorption of that gas into nearby liquids. If CO_2 increases by 100%
28 in a local area, then 100% more CO_2 will be dissolved into water in the local
area. If CO_2 emission doubles, then water which is in contact with that
 CO_2 absorbs that increase and returns the CO_2 concentration to the
 CO_2 water/air ratio for the local temperature, and this is true for all gases not only
 CO_2 . For all gases, colder water absorbs more gas, warmer water emits more
gas. Oxygen which is dissolved in water and absorbed by fish gills for their
respiration, the CO_2 which is the necessary gas of life for all green plants and
thus all life, as well as the oxygen which is exchanged with CO_2 in the lungs of
animals and humans, each of these vital natural processes rely on Henry's Law.

**Henry's Law is a fundamental law of physical chemistry which naturally
regulates and controls the Earth's atmospheric content of CO_2 . This**

1 counteracts any net CO₂ increases in the atmosphere caused by the
2 worldwide combustion of hydrocarbon fuel sources.

3 References and Study Materials

- 4 1. Bolin, B., 1960. On the Exchange of Carbon Dioxide between the
5 Atmosphere and the
6 Sea. [https://onlinelibrary.wiley.com/doi/pdf/10.1111/j.2153-
3490.1960.tb01311.x](https://onlinelibrary.wiley.com/doi/pdf/10.1111/j.2153-3490.1960.tb01311.x) Attached pdf.
- 7 2. Broecker, W.S., and Peng, T.H., 1973. Gas Exchange rates between air
8 and sea. [https://onlinelibrary.wiley.com/doi/pdf/10.1111/j.2153-
3490.1974.tb01948.x](https://onlinelibrary.wiley.com/doi/pdf/10.1111/j.2153-3490.1974.tb01948.x) Attached pdf.
- 9 3. Lee, S-H. et al, A Laboratory Experiment To Measure Henry's Law
10 Constants of Volatile Organic Compounds with a Bubble Column and a
11 Gas Chromatography Flame Ionization Detector (GC-FID).(attached pdf,
12 copyrighted.)
- 13 4. Sander, R. Compilation of Henry's law constants (version 4.0) for water as
14 solvent. <https://acp.copernicus.org/articles/15/4399/2015/>
- 15 5. NIST Chemistry WebBook, SRD 69, for Carbon
16 Dioxide. [https://webbook.nist.gov/cgi/inchi?ID=C124389&Mask=10#Solub
17 ility](https://webbook.nist.gov/cgi/inchi?ID=C124389&Mask=10#Solubility)
- 18 6. Dickson, A.G, et al. Andrew G. Dickson, Scripps Institution of
19 Oceanography, UC San Diego, INTRODUCTION TO CO₂ CHEMISTRY
20 IN SEA WATER. [https://www.iaea.org/sites/default/files/18/07/oa-
21 chemistry-dickson-050916.pdf](https://www.iaea.org/sites/default/files/18/07/oa-chemistry-dickson-050916.pdf) (attached)

22 Henry's Law Constants.

23 Sander, R.: Compilation of Henry's law constants (version 5.0.0) for water as
24 solvent, Atmos. Chem. Phys., 23, 10901–12440, [https://doi.org/10.5194/acp-23-
10901-2023](https://doi.org/10.5194/acp-23-10901-2023), 2023. Note this is a compilation of thousands of measurements
25 made by many scientists over many decades; this is not new information yet it
26 seems barely known and rarely recognized in climate science. Henry's Law
27 constants can be measured in the lab or field; the math derives from the gas
28 laws of physics.

Sander, R. Compilation of Henry's law constants (version 4.0) for water as
solvent R. Sander. Atmos. Chem. Phys., 15, 4399–4981,
2015 <https://www.atmos-chem-phys.net/15/4399/2015/> doi:10.5194/acp-15-
4399-2015

1 Regarding Graham's law of effusion and diffusion:
2 <https://youtu.be/Kx22vLWDsqM?si=fpJMp-3YU2Authc->
3 [https://en.wikipedia.org/wiki/Thomas_Graham_\(chemist\)](https://en.wikipedia.org/wiki/Thomas_Graham_(chemist))
4 https://en.wikipedia.org/wiki/Graham%27s_law

4 **Pinatubo Study**
5 **climatecite.com**
6 **our plan to overturn the climate change alarmism and green energy**
7 **movements**

9 Henry's Law Constants

10 Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and
11 seasonal biological and temperature effects. Taro Takahashi a, Stewart C.
12 Sutherland a, Colm Sweeney a, Alain Poisson b, Nicolas Metzl b, Bronte
13 Tilbrook c, Nicolas Bates d, Rik Wannink_of e, Richard A. Feely f, Christopher
14 Sabine f, Jon Olafsson g, Yukihiro Nojiri December 2002. Deep Sea Research
15 Part II Topical Studies in Oceanography 49(9-10):1601-1622. DOI:
16 10.1016/S0967-0645(02)00003-6. Downloadable pdf
17 here: [https://www.researchgate.net/publication/232259896_Global_sea-](https://www.researchgate.net/publication/232259896_Global_sea-air_CO2_flux_based_on_climatological_surface_ocean_pCO2_and_seasonal_biological_and_temperature_effects)
18 [air_CO₂ flux based on climatological surface ocean pCO₂ and seasonal bio](https://www.researchgate.net/publication/232259896_Global_sea-air_CO2_flux_based_on_climatological_surface_ocean_pCO2_and_seasonal_biological_and_temperature_effects)
19 [logical and temperature effects](https://www.researchgate.net/publication/232259896_Global_sea-air_CO2_flux_based_on_climatological_surface_ocean_pCO2_and_seasonal_biological_and_temperature_effects)

20 (This reference above is one of many papers by this large group of climate
21 modelers who are focused on CO₂ and the air ocean interface. Primarily they are
22 working on their modeling and algorithm technologies. Also referenced and
23 summarized
24 here. [https://www.ideo.columbia.edu/res/pi/CO₂/carbondioxide/pages/air_sea flu](https://www.ideo.columbia.edu/res/pi/CO2/carbondioxide/pages/air_sea_flux_2000.html)
25 [x_2000.html](https://www.ideo.columbia.edu/res/pi/CO2/carbondioxide/pages/air_sea_flux_2000.html). They have a paper in 2015 which I have not yet read. Henry's Law
26 is implicit in these work but rarely if ever mentioned. Mike Brown referenced on
27 of their papers.)

28 1. The elements of experimental chemistry. By [Henry, William, 1774-1836. n](https://archive.org/details/b29329875_0001)
29 [84082167. Pub.1818. https://archive.org/details/b29329875_0001](https://archive.org/details/b29329875_0001)

30 2. Rocke, Alan J. (2005). "In Search of El Dorado: John Dalton and the Origins
31 of the Atomic Theory". Social Research. 72 (1): 125–158.
32 <https://doi.org/10.1353%2Fsr.2005.0003>. [JSTOR 40972005](https://www.jstor.org/stable/40972005). [S2CID](https://www.jstor.org/stable/40972005)
33 [141350239](https://www.jstor.org/stable/40972005)

34 3. Proceedings of the Royal Society, Volume 3, 1830-1837, page 439. (Ref. 506

1 42 R9 at Manchester, UK Central Library).

2 Henry's Law Research Paper from 1803

3 A Gas Chromatographic Method for the Determination of Bicarbonate and 4 Dissolved Gases

5 [https://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&Units=SI&Mask=10#Solubi](https://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&Units=SI&Mask=10#Solubility)
6 [lity](https://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&Units=SI&Mask=10#Solubility)

7 <https://henrys-law.org/henry/index.html> including [https://henrys-](https://henrys-law.org/henry/references.html)
8 [law.org/henry/references.html](https://henrys-law.org/henry/references.html)

9 https://en.wikipedia.org/wiki/Henry's_law

10 The Kinetic Molecular

11 Theory: [https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch4/kinetic4.](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch4/kinetic4.html)
12 [html](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch4/kinetic4.html)

13 Avoid Common Pitfalls when using Henry's Law. Allan H. Harvey, Francis L.
14 Smith (2007). NIST. [https://www.nist.gov/publications/avoid-common-pitfalls-](https://www.nist.gov/publications/avoid-common-pitfalls-when-using-henrys-law)
15 [when-using-henrys-law](https://www.nist.gov/publications/avoid-common-pitfalls-when-using-henrys-law)

16 Forms of Henry's Law: There are various forms Henry's law which are discussed
17 in the technical literature.

18 https://www.tau.ac.il/~tsirel/dump/Static/knowino.org/wiki/Henry's_law.html

19 The Solubility of Carbon Dioxide in Water at Low Pressure. John J. Carroll, John
20 D. Slupsky, Alan E. Mather; J. Phys. Chem. Ref. data 1 November 1991; 20 (6):
21 1201–1209. <https://doi.org/10.1063/1.555900> (avail in pdf only \$40.) Abstract:
22 “The system carbon dioxide-water is of great scientific and technological
23 importance. Thus, it has been studied often. The literature for the solubility of
24 carbon dioxide in water is vast and interdisciplinary. An exhaustive survey was
25 conducted and approximately 100 experimental investigations were found that
26 reported equilibrium data at pressures below 1 MPa. A model based on Henry's
27 law was used to correlate the low pressure data (those up to 1 MPa). The
28 following correlation of the Henry's constants (expressed on a mole fraction
basis) was developed $\ln(H_{21}/\text{MPa}) = -6.8346 + 1.2817 \times 10^4/T - 3.7668 \times 10^6/T^2$
 $+ 2.997 \times 10^8/T^3$ The correlation is valid for $273 < t < t$

26 **William Henry Biographical Sketch**

27 William Henry, M.D., (1774-1836) an English chemist, beginning in 1803 published results from an
28 extensive series of his experiments on various gases and their solubilities, partial pressures, and

1 other properties when these various gases are in contact with various liquids. His results were
2 published along with a series of his chemistry lectures in at least eight editions including Volume I
3 Henry's work was reviewed by Mr. John Dalton, (1766-1844) English chemist, physicist and
4 meteorologist, famously renown for his atomic theory including today's method for establishing
5 atomic weights for the chemical elements, and Dalton's Law of partial pressures.(2) The Dalton
6 (Da) in The International System of Units (SI) is named after John Dalton; one Dalton is defined as
7 an atomic mass equal to one twelfth of the mass of a neutral carbon atom, which is equal to one
8 hydrogen atom. Dalton and Henry were not without opposition. English Scientist Dr. William Hyde
9 Wollaston (1766-1828), also a Fellow of the Royal Society of London, and Irish mathematician Dr.
10 James Thomson, (1776-1849) father of famous scientist William Thomson Lord Kelvin, and
11 Swedish scientist Professor Baron Jöns Jacob Berzelius (1779-1848), on the other hand, asserted
12 oxygen as the decimal unit of atomic weight and reviewed the works of both Dalton and Henry.

9 "The principle, on which gases are absorbed and retained by liquids, is still a subject of controversy.
10 By Berthollet, Thomson, Saussure, and the generality of chemists, it is ascribed to the exertion of a
11 chemical affinity between the gas and the liquid; but it is contended by Mr. Dalton and myself that
12 the effect in most cases is chiefly, if not wholly, mechanical."

12 As discussed in the following paragraphs, Dalton and Henry held against their contemporary critics
13 that the principle was mechanical, that is the principle is physical, not chemical. They demonstrated
14 by ingenious experiments and reports by others to their scientific critics, for example:

14 "The general inference from his [i.e. De Grotthus'] experiments is, that the intensity of electric light
15 is always in a direct proportion to the density of the gas, and in the inverse proportion to the
16 conducting power of the gas for electricity."

16 "The comparative soniferous properties of the gases have been determined by Messrs, Kerby and
17 Merrick; but as these belong rather to mechanical than to chemical science, I shall content myself
18 with referring to the account of them in the 27th and 33d volumes of Nicholson's Journal, and in the
19 45th volume of the Philosophical Magazine." (1) page 134.

19 Today, misunderstanding of this critical difference between physics and chemistry leads to the
20 ongoing failure to understand and correctly compute the Henry's Law proportionality of carbon
21 dioxide gas between air and water, with the result that existential sums of money are being
22 squandered in the false belief that humans must reduce atmospheric carbon dioxide concentration.
23 The absorbance of any gas into any liquid and the emission of any gas from any liquid is a physical
24 phase-state reaction, that is, a change in the physical state of the gas, for example:

- 23 • its total pressure and partial pressures,
- 24 • its temperature and thermal dynamics,
- 25 • directional motions and migrations of its constituent molecules
- 26 • its volume and density
- 27 • the masses and sizes of the constituent molecules.
- 28 • the boiling point, freezing point, triple point, sublimation conditions
- specific heat

- opacity

In the bulleted list just above, the identity of the gas nor the amount of the gas changed, and the identity of the liquid nor the amount of the liquid changed. On the other hand, a chemical reaction of a gas and the liquid creates one or more new chemical product entities by changing or combining the reactant entities.

William Henry, confirmed by John Dalton and thousands of other scientists since them, discovered that a gas partitions between a liquid and a volume of gas in contact with that liquid, and that the partition ratio is a physical property like a boiling point or specific heat; these are properties which are not changed by the amount of matter present. Henry demonstrated that the partition ratio is a function of the absolute temperature of the liquid. That is, colder liquids absorb more gas than they emit and warmer liquids emit more gas than they absorb.

In other words, adding carbon dioxide to the atmosphere by burning fossil fuels does not increase the concentration of carbon dioxide in the atmosphere. A carbon dioxide concentration in air which exceeds the Henry's Law ratio for a given water temperature will be absorbed by water. Any carbon dioxide removed from air will be replaced from water and water containing surfaces everywhere until the Henry's ratio is restored for the local water temperature. Life evolved under this dynamic condition.

Obituary for William Henry, MD, FRS

"The last name that occurs in the melancholy list of our departed compatriot associates is that of Dr William Henry, to whom the science of chemistry generally and gaseous chemistry in particular, is under great obligation. He was the author of nine papers in our Transactions, many of them of great merit; and his System of Chemistry is one of the best written and best arranged compendiums of that important and extensive science which has been published of late years, whether in our own language or in any other. The Memoirs of the Manchester Society are chiefly indebted to him, in conjunction with Dr Dalton, for the high character which they have so long maintained. Dr. Henry, like Dr. Wollaston, made the results of science, obtained by the most original and difficult researches, the foundation of a splendid fortune, and few persons have contributed more effectually to the promotion of those arts and manufactures which form the foundation of the prosperity of a great commercial nation." (3)

The elements of experimental chemistry, by Henry, William, 1774-1836. Dedicated to John Dalton (about 47 megabytes in pdf, on file). Here is link for download or reading online: https://archive.org/details/b29329875_0001/mode/2up Experiments on the quantity of gases absorbed by water, at different temperatures, and under different pressures. William Henry. Published: 01 January 1832 <https://doi.org/10.1098/rspl.1800.0063> and <https://royalsocietypublishing.org/doi/abs/10.1098/rspl.1800.0063> 2 pages.

III. Experiments on the quantity of gases absorbed by water, at different temperatures, and under different pressures. William Henry. Published: 01 January 1803 <https://doi.org/10.1098/rstl.1803.0004>. <https://royalsocietypublishing.org/doi/10.1098/rstl.1803.0004>

Biography of Thomas Henry and his son William Henry. <https://www.thornber.net/cheshire/ideasmen/henry.html> A biographical account of the late Dr. [William] Henry (PDF), by his son Henry, William Charles, 1804-1892

In Praise of Famous Men – The John Dalton Bicentenary Celebrations, 1966. By Arnold Thackray.

1 <https://royalsocietypublishing.org/doi/pdf/10.1098/rsnr.1967.0006>

2 Dalton's Unfortunate Choice. by R.W. JONES.
3 (Pdf) <https://royalsocietypublishing.org/doi/pdf/10.1098/rsnr.2003.0194> page 18 (Note, John Dalton
4 appointed William Charles Henry, MD (1804-1892) as his biographer. William Charles Henry MD
5 was youngest son of our William Henry MD. Our William Henry MD committed suicide and pre-
6 deceased Dalton).

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9 This website was researched and composed by Claire (Bud) Bromley at <https://budbromley.blog/>,
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