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## Properties of particular solutions

A general view on [solutions](#) is presented aside, and assumed to be known. Now we present in more detail some particular solutions (as separate annexes bound together), to better grasp the variety of situations that may arise. The rationale for the selection has been:

- Solids dissolved in water: the salt-water and the sugar-water systems are chosen, as the most proximate to everybody's experience. They both show limits of solubility, as all solid-liquid mixtures, but one is electrolytic and the other not.
- Liquids dissolved in water: the alcohol-water and the hydrogen peroxide-water systems are chosen, as examples of totally miscible liquids of very different applications: one is a fuel and the other an oxidiser.
- Gases dissolved in water: the ammonia-water and the carbon dioxide-water systems are chosen, as examples of highly soluble gases (the oxygen-water or air-water systems are more important but their phase diagrams are less appealing).

Additional data useful to many other solutions can be found in tabulated data on [Solutions](#).

## Annex 1. Salt water solutions

We study here basically aqueous solutions of common salt ( $\text{NaCl}$ ,  $M=0.023+0.0355=0.0585$  kg/mol), i.e. water / sodium-chloride liquid mixtures, called brines. Although the main motivation is the study of sea water (that to a first approximation seawater with 3.5%wt salts is a 0.6 molal  $\text{NaCl}$  solution in water), common salt solutions have other interests: freezing mixtures, food conditioning, body fluids, de-icing (salt has been used as the most cost-effective road de-icer, since the mid 20th century). Pure water and pure sodium-chloride properties are compiled in Table 1.

Table 1. Properties of pure substances at 15 °C and 100 kPa, or at the phase change at 100 kPa.

Substance	Molar mass. $M$ kg/mol	Melting temp. $T_f$ K	Boiling temp. $T_b$ K	Melting enthalpy $h_{sl}$ kJ/kg	Boiling enthalpy $h_{lv}$ kJ/kg	Density (mass) $\rho$ kg/m <sup>3</sup>	Thermal expansion $\alpha \cdot 10^6$ K <sup>-1</sup>	Sound speed $c$ m/s	Thermal capacity $c$ J/(kg K)	Thermal conductivity $k$ W/(m K)
Water	0.018	273	373	333	2260	999	150	1500	4180	0.6
Ice	0.018	273	373	333	2260	921	150	3500	2040	2.3
Salt	0.058	1074	1690	496	2970	2170*	130		850	6.5
Molten salt	0.058	1074	1690			1490	110		1440	0.30

\*Density refers to a single-crystal sample of halite; granular material show lower densities according to the void fraction (typical values for table salt may be 1230..1290 kg/m<sup>3</sup>; and around 890 kg/m<sup>3</sup> for table sugar).

### Solubility and phase diagram

Water can only dissolve up to 26.4%wt of  $\text{NaCl}$  at 15 °C, slightly increasing with temperature; see the phase diagram is presented in Fig. 1. The interest is just on liquid solutions, since the components do not mix in the solid state, and the amount of salt vapours can be neglected below say 1000 °C. It is important to stir the mixture to have a quick mixing, otherwise, water left alone over a salt layer would take many days to dissolve.

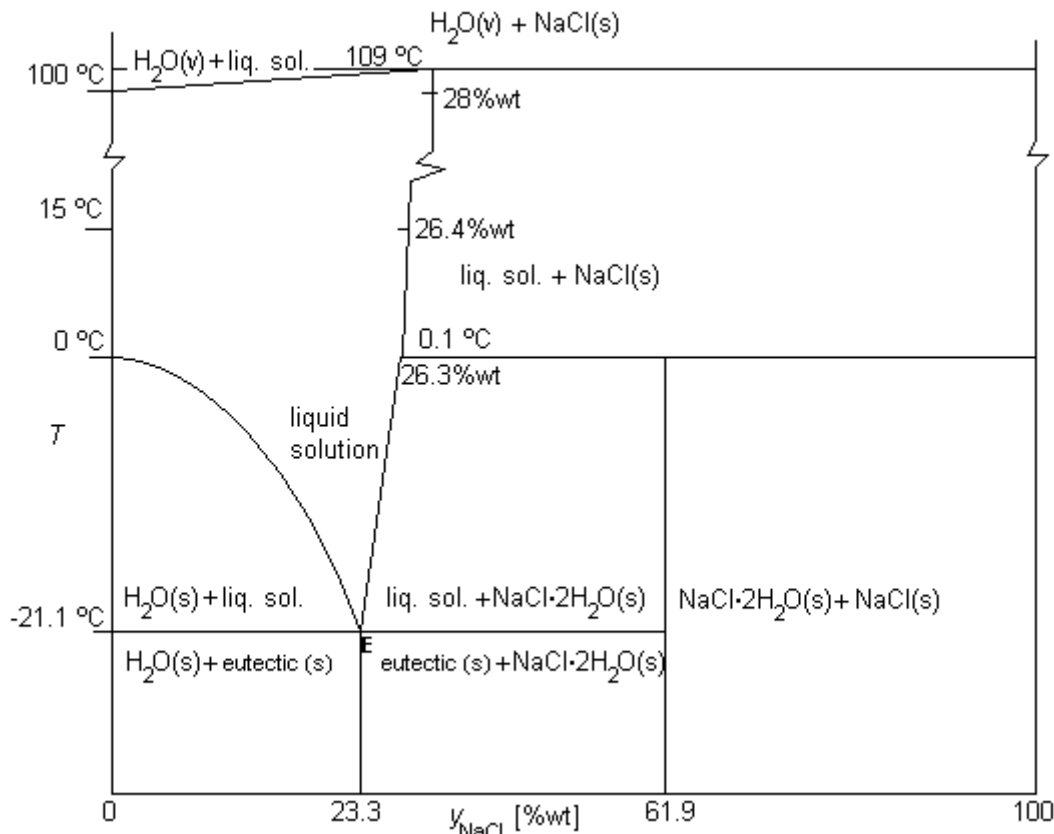


Fig. 1. Salt water solutions phase diagram at 100 kPa ( $\text{NaCl}$  -  $\text{H}_2\text{O}$ ). E, eutectic point.

Four solid phases appear in this phase diagram (and only one liquid phase). Besides  $\text{H}_2\text{O}(\text{s})$  and  $\text{NaCl}(\text{s})$ , the di-hydrate  $\text{NaCl}\cdot 2\text{H}_2\text{O}(\text{s})$  ( $\rho=1630 \text{ kg/m}^3$ ) and the eutectic phase may appear. The eutectic phase is not a solid solution but a solid mixture of fixed composition of the two components  $\text{H}_2\text{O}(\text{s})$  and  $\text{NaCl}\cdot 2\text{H}_2\text{O}(\text{s})$ ; at the eutectic point, E (23.3%wt,  $-21.1^\circ\text{C}$ ), three phases exist in equilibrium:  $\text{H}_2\text{O}(\text{s})$ ,  $\text{NaCl}\cdot 2\text{H}_2\text{O}(\text{s})$  and the liquid solution. The solidification enthalpy drops from 333 kJ/kg for pure water at  $0^\circ\text{C}$  to 235 kJ/kg at the eutectic point.

$\text{NaCl}$  has a solubility of 0.359 kg per litre of pure water at  $15^\circ\text{C}$  (if more salt is added, it settles), producing a brine with  $y_{\text{NaCl}}=0.264$ ,  $\rho=1204 \text{ kg/m}^3$  (Fig. 1). This brine boils at  $108^\circ\text{C}$  (unsaturated), starts freezing at  $+0.1^\circ\text{C}$  forming di-hydrate crystals, and ends freezing at  $-21.1^\circ\text{C}$  (the last crystals having  $y_{\text{NaCl}}=0.233$ ; see Fig. 1). Solubility slightly increases with temperature, almost linearly from 0.357 kg/L of water at  $0^\circ\text{C}$  to 0.40 kg/L of water at  $100^\circ\text{C}$ . Table 2 presents a summary of solubility values in different units for  $\text{NaCl}$  in water at  $15^\circ\text{C}$ .

Table 2. Summary of solubility values for  $\text{NaCl}$  in water at  $15^\circ\text{C}$ .

Value	Comment	Seawater concentration
356 $\text{kg/m}^3$ of water =0.356 kg/L of water ( $\approx 0.356 \text{ kg/kg}$ of water) $y=0.264$ =26.4%wt	Mass of solute per unit volume of solvent  ( $\approx$ Mass of solute per unit mass of water) Mass of solute per unit mass of solution	0.035 kg/L solvent  ( $\approx 35 \text{ g/kg}$ solvent) 35 g/kg solution
4.7 mol/kg of water =4.7 m (4.7 molal)	Moles of solute per unit mass of solvent	0.6 mol/kg solvent (0.6 m)
5600 $\text{mol/m}^3$ of solution =5.6 M (5.6 molar)	Moles of solute per unit volume of solution	0.6 mol/L solution (0.6 M)

Many important fluids, particularly in bioscience, are salt-water solutions. Blood plasma is basically a 0.15 M aqueous  $\text{NaCl}$  solution. Urine is also a water/salt solution. Normal urine composition is 950 g/L  $\text{H}_2\text{O}$  + 20 g/L urea + 10 g/L  $\text{NaCl}$  +...The yellow colour is due to the presence of urochrome, a pigment derived from the breakdown of haemoglobin. Its density is in the range  $\rho=1005..1035 \text{ kg/m}^3$ , according to salt concentration. The average pH of urine is 6 but ranges from 4.6 to 8.0. Pure urea is a solid  $\text{CO}(\text{NH})_2(\text{s})$ ,  $M=0.60 \text{ kg/mol}$ ,  $c_p=93 \text{ J/(mol}\cdot\text{K)}$ , that has a heating value PCS=632 kJ/mol.

Question 1. Why seawater is bad for drinking?

Answer: A small gulp is not so bad (there are some people accustomed to drink a cup of seawater each day), but by the litre it causes dehydration by osmosis (body fluids with  $y_{\text{sal}}=4 \text{ ‰}$  try to dilute seawater,  $y_{\text{sal}}=35 \text{ ‰}$ , in the digestive truck). Sea ice may have an average of  $y_{\text{sal}}=10 \text{ ‰}$  as trapped brine droplets, decreasing with time because of seepage (one-year-old sea-ice is good for drinking). Sea animals do not dehydrate by osmosis because they segregate an oily mucus (that makes them slippery) to increase insulation.

Desalination of seawater and other salty solutions may be done by different methods, e.g. by reverse osmosis (i.e. forcing the brine across a semi-permeable membrane), by distillation (i.e. boiling and condensation) usually under vacuum, by freezing, by spraying the brine on hot air (the water evaporates quickly, leaving a salt dust, and the vapours can be condensed), etc.

As for other solutions, the freezing point refers to the first appearance of solid crystals when cooling the liquid solution, but this is not the end of the process; e.g. a salty solution like seawater starts to freeze at  $-1.9\text{ }^{\circ}\text{C}$ , 75% of the water is frozen at equilibrium at  $-10\text{ }^{\circ}\text{C}$ , and there remains some liquid down to  $-21\text{ }^{\circ}\text{C}$  (the eutectic point for  $\text{NaCl} / \text{H}_2\text{O}$  (some seawater is liquid even down to  $-70\text{ }^{\circ}\text{C}$  because of the effect of other dissolved salts). By the way, are ice-cubes made from seawater salty? When a salt-water solution starts to freeze, only pure water-ice is formed, but if the cooling rate is fast some salty droplets may be trapped and give a salty taste; in any case, most of the salt would remain in the last regions to freeze (also for dissolved gases; that is why ice-cubes may show a whitish central core).

Solubilities for other salts are presented in Table 3 (and Fig. 2). The solubility curve ( $y$ - $T$ ) for  $\text{CaCl}_2$  has slope-jumps because of hydration ( $0..30\text{ }^{\circ}\text{C}$   $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $30..40\text{ }^{\circ}\text{C}$   $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $40..85\text{ }^{\circ}\text{C}$   $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , ...)

Table 3. Solubility of common inorganic compounds in grams of solute per 100 mL of  $\text{H}_2\text{O}$ .

Substance	0 $^{\circ}\text{C}$	10 $^{\circ}\text{C}$	20 $^{\circ}\text{C}$	30 $^{\circ}\text{C}$	40 $^{\circ}\text{C}$	50 $^{\circ}\text{C}$	60 $^{\circ}\text{C}$
LiBr, lithium chloride	59	60	61	62	63	65	66
LiCl, lithium chloride			45.5				
NaCl, sodium chloride	35.5	35.5	35.7	36.0	36.3	36.7	
KCl, potassium chloride	27.6	31.0	34.0	37.0	40.0	42.6	
KI, potassium iodide	127.5	136	144	152	160	168	
$\text{NaHCO}_3$ , sodium bicarbonate	6.9	8.15	9.6	11.1	12.7	14.4	16.4
NaOH, sodium hydroxide			109	119	145	174	
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , (epsom salt) magnesium sulfate heptahydrate		23.6	26.2	29	31.3		

Lithium bromide,  $\text{LiBr(s)}$ , is a white bitter hygroscopic powder, soluble in water, alcohol and glycol, with  $M=0.097\text{ kg/mol}$ ,  $\rho=3465\text{ kg/m}^3$ ,  $T_m=547\text{ }^{\circ}\text{C}$ ,  $T_b=1265\text{ }^{\circ}\text{C}$ , the main working fluid in absorption refrigeration and air-conditioning systems.

Lithium chloride,  $\text{LiCl(s)}$ , is a white cubical crystal (powder or particles up to 6 mm size) with  $M=0.0424\text{ kg/mol}$ ,  $\rho=2070\text{ kg/m}^3$ ,  $T_m=613\text{ }^{\circ}\text{C}$ ,  $T_b=1360\text{ }^{\circ}\text{C}$ .  $\text{LiCl}$  is made from lithium hydroxide with  $\text{HCl(aq)}$ , is used in the production of lithium metal, the manufacture of welding additives, and air conditioning systems.

Sodium bicarbonate or baking soda (sodium hydrogen carbonate,  $\text{NaHCO}_3$ ) has  $M=0.084\text{ kg/mol}$ ,  $\rho=2160\text{ kg/m}^3$ ,  $c=87.5\text{ J/(mol}\cdot\text{K)}=1040\text{ J/(kg}\cdot\text{K)}$ ,  $h_{f25}=-950\text{ kJ/mol}$ . Decomposes, without melting, into  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$  at  $270\text{ }^{\circ}\text{C}$ .

## Density and other properties

Brines are easily characterised by their density; a good enough approximation around  $15\text{ }^{\circ}\text{C}$  is  $\rho_{\text{brine}}=\rho_{\text{H}_2\text{O}}+A y_{\text{NaCl}}$ , with  $\rho_{\text{H}_2\text{O}}=1000\text{ kg/m}^3$  and  $A=770\text{ kg/m}^3$ , valid in the whole range  $0 < y_{\text{NaCl}} < 26.4\%\text{wt}$  (e.g. for the eutectic composition  $\rho_{\text{brine}}=1180\text{ kg/m}^3$ ). Every 100 g of table salt added to 1 kg of water adds  $34 \pm 1\text{ cm}^3$  to the volume.

Table 4. Other properties of  $\text{NaCl-H}_2\text{O}$  mixtures at  $15\text{ }^{\circ}\text{C}$ .

Composition, $y_{\text{NaCl}}$	0%	5%	10%	15%	20%	25%
Density, $\rho\text{ [kg/m}^3\text{]}$	999	1036	1074	1112	1152	1193

Thermal capacity, $c$ [J/(kg·K)]	4185	3930	3720	3560	3410	3310
Thermal conductivity, $k$ [W/(m·K)]	0.59	0.56	0.53	0.51	0.48	0.45
Viscosity, $\mu \cdot 10^3$ [Pa·s]	1.14	1.2	1.3	1.5	1.8	2.1
Heat of solution, $\Delta h_{\text{solution}}$ [J/mol]	3900					
Freezing point*, $T_f$ [°C]	0	-3.0	-6.5	-11.1	-16.6	-9.8
Electrical conductivity*, $\sigma$ [S/m]	$<10^{-3}$	10	16	20	21	22

\* A good approximation for the freezing point of brines is  $T_{f,\text{brine}} = T_{f,\text{H}_2\text{O}} + Ay_{\text{NaCl}} + By_{\text{NaCl}}^2$ , with  $T_{f,\text{H}_2\text{O}} = 0$  °C,  $A = -45$  °C and  $B = -194$  °C valid in the range  $0 < y_{\text{NaCl}} < 23.3\%$ wt (i.e. up to the eutectic point). For dilute solutions, there is a linear approximation between electrical conductivity and solute mass-fraction:  $\sigma = Ay_{\text{NaCl}}$ , with  $A = 200 \text{ S/m} = 2000 (\mu\text{S/cm})/(\text{g/kg})$ . Notice that the linear approximation based on the freezing-point depression constant only gives  $T_{f,\text{brine}} = T_{f,\text{H}_2\text{O}} + Ay_{\text{NaCl}}$  with  $A = -1.86/0.058 = -32$  °C.

**Exercise 5.** Find the final temperature after adiabatically adding 25 g of NaCl-salt to 100 cm<sup>3</sup> of water at 15 °C.

Sol.: From the energy balance,  $0 = \Delta H = n_s \Delta h_{\text{solution}} + mc\Delta T$ , one gets  $n_s = 25/56 = 0.46$  mol,  $\Delta h_{\text{solution}} = 3900$  J/mol from Table 4,  $m = 25 + 100 = 0.125$  kg,  $c = 3410$  J/(mol·K) from Table 4 for a 20%wt brine (25 over 125), and finally  $\Delta T = 3900 \cdot 0.46 / (0.125 \cdot 3410) = -4.2$  °C (in practice, a quick-look trial gave a value of  $-3.0 \pm 0.5$  °C, the difference being ascribed to the imperfect insulation during the several minutes it lasted, and the decrease of the heat of solution with concentration).

Notice that if the same experiment is made with sugar, only a small decreases in the temperature of the mixture occurs (some third that of the salt case).

A freezing mixture is a mixture of two substances, usually salt and ice, which are very endothermic, giving temperatures below 0 °C. Freezing mixtures were first described in Muslim Spain in the 13th century, and first explained by Raoult in 1878. Common-salt and water-ice form the most used freezing mixture; although other salts have larger freezing point depressions; e.g. with ice/ $\text{CaCl}_2$  the eutectic is at  $-55$  °C (but it is difficult to go below  $-40$  °C). Even further cooling can be achieved using dry ice,  $\text{CO}_2(\text{s})$ , instead of water-ice: e.g.  $-78$  °C with dry-ice/acetone, and  $-100$  °C (it is difficult to go below  $-80$  °C) with dry-ice/diethyl-ether.

The pH of  $\text{NaCl}/\text{H}_2\text{O}$  solutions should be neutral (pH=7), although it may be sometimes mildly acid (pH=6..7). It is mildly basic in seawater (pH=8).

Seawater has  $y_{\text{NaCl}} = 0.035$ , starts freezing at  $-1.9$  °C producing pure ice crystals, ends freezing at  $-21.1$  °C with  $y_{\text{NaCl}} = 0.233$  (see Fig. 1), and boils at 100.5 °C. A rudimentary separation setup, rather inefficient, but very simple, consists on a pot, where the saline waters is heated, and a large lid held above and inclined so as the condensate drips on a recipient. Being more precise, seawater salinity varies a lot at the surface from point to point, with a global average of  $y_{\text{NaCl}} = 34.7\%$ , increasing with depth up to  $y_{\text{NaCl}} = 35.0\%$  at 1000 m, and decreasing downwards to a very uniform  $y_{\text{NaCl}} = 34.6\%$ . Ocean surface salinity can be measured from satellites as changes in radiative properties due to the effect of salinity on the dielectric constant of water. Average seawater properties at 15 °C are:  $r = 1026 \text{ kg/m}^3$ ,  $c = 3990 \text{ J/(kg·K)}$ ,  $\alpha = 0.13 \cdot 10^{-6} \text{ m}^2/\text{s}$ ,  $n = 1.8 \cdot 10^{-6} \text{ m}^2/\text{s}$ ,  $D_s = 0.74 \cdot 10^{-9} \text{ m}^2/\text{s}$ ,  $T_b = 100.5$  °C,  $c = 1508 \text{ m/s}$ .

## ***The melting of ice on fresh water, on sea water, and on a salt layer***

An ice-cube melts faster on fresh water than on sea water because of the high-density sea-water prevents natural convection. Warning: it must not to confuse the slower melting of ice over salt-water (thermal convection), with the faster melting of ice on a dry place when sprinkling salt over (adiabatic dissolution).

For instance, having 100 g of tap water in a thermally-isolated container, initially at 18 °C, its temperature quickly drops to 16 °C when 15 g NaCl are added (after dissolving by stirring), because of the endothermic mixing. When a 31 g ice-cube from a fridge is added, water temperature exponentially drops to 2 °C, before the unavoidable heat gain through the insulation starts to heat it up (the drop is from 16 °C to 9 °C in 300 s and to 4 °C in 1700 s).

A similar trial with a 13 g ice-cube drops the sea-water temperature exponentially from 16 °C to 6 °C in <1000 s (the drop is from 16 °C to 11 °C in 75 s). A simple energy balance rightly predicts the limit: i.e., from  $mc\Delta T = m_{ice}h_{sl}$ ,  $\Delta T = 0.013 \cdot 330 / (0,1 \cdot 4,2) = 10,2$  °C, i.e. from 16 °C to 6 °C.

A similar trial with three 13 g ice-cubes drops the sea-water temperature exponentially from 16 °C to –5 °C, whereas in tap water temperature drops from 16 °C to 0 °C

But the most curious trial is the 31 g ice-cube on 100 g fresh water; temperature starts to drop quickly but, at 3 °C it rises and stabilises at 4 °C for a while, decreasing again down to 2 °C. The expected final temperature can be predicted from  $mc\Delta T = m_{ice}h_{sl}$ ,  $\Delta T = 0.031 \cdot 330 / (0,1 \cdot 4,2) = 24$  °C, what would imply that the ice-cube does not melt completely; in fact, the small heat loss over such long times (up to 10 000 s) help to explain the deviation.

If the initial temperature in the fresh-water case were below 4 °C, then there would be no difference in the melting time of the ice-cube (convection inhibited on both cases because melting water is lighter than the surrounding water in both cases).

To make a guess for the cooling time, the heat transfer rate  $\dot{Q} = UA\Delta T$  is combined with the energy balance  $Q = m_{ice}h_{sl}$ , to yield a melting time of  $t_m = Q / \dot{Q} = m_{ice}h_{sl} / (UA\Delta T)$ . For instance, for the 13 g ice-cube in fresh water, assuming  $U = 10^2$  W/(m<sup>2</sup>·K),  $A = 10^{-3}$  m<sup>2</sup> and  $\Delta T = 10$  K,  $t_m = 0.013 \cdot (330 \cdot 10^3) / (10^2 \cdot 10^{-3} \cdot 10) = 4300$  s. Notice that  $t_m$  increases linearly with the linear dimension of the ice cube, and decreases inversely proportional to both the temperature difference and the  $U$ -value. Notice that, ceteris paribus,  $U_{salt-w} / U_{fresh-w} = t_{fresh-w} / t_{salt-w} \approx 0.4$  from the trials described above.

Question 2. What is the influence of the number of ice-cubes on melting?

Answer. For the same ice mass, the more wetted surface the quickest the melting, with the same final temperature.

For two equal ice-cubes, the melting time would be in between the one for a single ice-cube and the one for an equivalent ice-cube with the same double mass. In the limit case of a negligible interaction (small ice-cubes far apart), the melting time would approach that of a single one.

Question 3. What happens when an ice-cube is put over a salt layer?

Answer. A trial was done with room temperature  $T=19\text{ }^{\circ}\text{C}$ . The ice-cube was at  $-9\text{ }^{\circ}\text{C}$  when taken out of the fridge. Thermocouples placed over the salt bed show a sudden drop in temperature (with large fluctuations due to uneven contact) to below  $0\text{ }^{\circ}\text{C}$  in some 10 s, with a minimum at  $-8\text{ }^{\circ}\text{C}$  after 50 s, whereas ice-cube temperature rises from  $-9\text{ }^{\circ}\text{C}$  to  $-5\text{ }^{\circ}\text{C}$  after some 20 s and then falls to  $-14\text{ }^{\circ}\text{C}$  after 100 s. Afterwards, for some 1300 s the ice-cube remains at  $-10\text{ }^{\circ}\text{C}$  and the interface just below  $0\text{ }^{\circ}\text{C}$ . Beyond that, ice-cube temperature rises to  $0\text{ }^{\circ}\text{C}$ , stays there for some 100 s and then increases (up to  $13\text{ }^{\circ}\text{C}$  after 3100 s). When repeating the experiment with a sugar bed, thermocouple reading slowly drops (without fluctuations due to uneven contact) to  $3\text{ }^{\circ}\text{C}$  in some 300 s, whereas ice-cube temperature rises from  $-9\text{ }^{\circ}\text{C}$  to  $0\text{ }^{\circ}\text{C}$  after some 150 s and stays there for more than the 3000 s of trial, the interface temperature approaching  $0\text{ }^{\circ}\text{C}$  also.

## Annex 2. Sugar water solutions

We study here basically water / sucrose mixtures ( $\text{H}_2\text{O}$  /  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). Sucrose, or saccharose, is a disaccharide found in many plants and extracted from sugar-cane (since XV c.) and sugar-beet (since XVII c.), and used as a sweetening agent in food and drinks (before Columbus, only honey was used as sweetener).

Sugar extraction is roughly as follows: the crushed raw material, containing some 80%wt water and 15%wt sucrose, is heated and treated with chemicals (lime, sulphuric acid, phosphoric acid,...) to remove impurities, and then evaporated under vacuum until a thick syrup remains (some 70%wt sucrose at 110 °C); then, the syrup is centrifuged to separate the sugar crystals. The heat is obtained from bagasse, a by-product of the process.

Other sugars of interest besides common sugar (sucrose, a disaccharide) are monosaccharides as glucose and its isomers (all with molecular formula  $\text{C}_6\text{H}_{12}\text{O}_6$ : dextrose (the most abundant), fructose (fruit-sugar), and galactose), and other disaccharides (lactose), since polysaccharides are insoluble in water (starch, glycogen, cellulose, chitine, pectine). grape-sugar, barley-sugar (maltose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ), milk-sugar (lactose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). The molecular structure changes from the pure solid phase, where it is an open zigzag chain with the end carbons not too far of each other, to a cycle molecule when in solution, by bonding of an aldehyde group with an hydroxyl group (hemiacetal bond). According to the side of the -OH group in the hemiacetal bond, two isomers appear  $\alpha$  and  $\beta$ . In reality, up to 5% of glucose molecules in solution can be found as open chains.

The interest here is just on liquid solutions of sucrose in water, called syrups, since the components do not mix in solid state, and sugar decomposes at high temperatures. Table 1 compiles some properties of pure water and pure sugars.

Table 1. Properties of pure substances at 15 °C and 100 kPa, or at the phase change at 100 kPa.

Substance	Molar mass.	Melting temp.	Boiling temp.	Melting enthalpy	Boiling enthalpy	Density (mass)	Thermal expansion (vol.)	Sound speed	Thermal capacity	Thermal conductivity
	$M$ kg/mol	$T_f$ K	$T_b$ K	$h_{sl}$ kJ/kg	$h_{lv}$ kJ/kg	$\rho$ kg/m <sup>3</sup>	$\alpha \cdot 10^6$ K <sup>-1</sup>	$c$ m/s	$c$ J/(kg·K)	$k$ W/(m·K)
Water	0.018	273	373	333	2260	999	150	1500	4180	0.6
Glucose	0.180	415 <sup>a</sup>				1540 <sup>b</sup>			1210	
Fructose	0.180	376 <sup>a</sup>				1690 <sup>b</sup>				
Sucrose	0.342	457 <sup>a</sup>				1590 <sup>b</sup>			1340	0.6

<sup>a</sup>Decomposition temperature (sugar turns to caramel).

<sup>b</sup>Density refers to a single-crystal sample of sugar; granular materials show lower densities according to the void fraction (typical values for table sugar may be 870..890 kg/m<sup>3</sup>; around 1200 kg/m<sup>3</sup> for table salt). Similarly, apparent thermal conductivity of table sugar can be 0.2..0.3 W/(m·K).

Many foodstuff and biological fluids consist of aqueous solutions of sugar with other solutes: salt, fat, proteins. The freezing-point depression of sugar is small; it is mainly the fat micelles what cause the freezing-point depression in ice-cream. Even at the typical ice cream serving temperature of -16 °C, only about 3/4 of the water is frozen, the rest remains as a very concentrated sugar solution. This helps to give ice



cream its ability to be scooped and chewed at freezer temperatures. A typical composition of ice-cream is: 60% water, 15% milk-fat, 10% non-fat-milk-solids (casein and whey proteins plus lactose), 15% of a combination of sucrose and glucose-based corn syrup sweeteners, plus some 0.5% added stabilizers and emulsifiers.

Sugars are very important carbohydrates in nutrition, with high heating values of  $\text{HHV}_{\text{sucrose}}=5650 \text{ kJ/mol}$  and  $\text{HHV}_{\text{glucose}}=2810 \text{ kJ/mol}$ . With the help of ferments (natural or artificial), sugar-water solutions transform to alcoholic drinks (e.g. wine, cider). When the feedstock is starch (e.g. corn, barley), it is first soaked in hot water to transform starch to maltose by hydrolysis with amylase (only present on barley), then the maltose solution is boiled with seasoning hops, then cooled, and then yeast added for fermentation to yield the alcoholic drink (e.g. beer) and a carbon dioxide (sometimes added to the drink). Strong drinks are prepared by distillation and aromatisation to yield the different liqueurs: cognac from wine, whisky from corn and malt, sake from rice, vodka from potato and grain, etc. Non-distilled alcoholic drinks may undergo another natural process: acidulation by the vinegar bacteria in the presence of oxygen, transforming ethanol into acetic acid (that is why wine and beer must be kept free of air).

### ***Solubility and phase diagram***

Pure water can only hold up to 60%wt of sugar in solution at 0 °C, growing to 80%wt at 100 °C (e.g. at 15 °C, up to 1.6 kg of sugar can be dissolved in 1 kg of pure water, forming a saturated solution containing 790 kg/m<sup>3</sup> of sucrose and 500 kg/m<sup>3</sup> of water). Metastable and supersaturated solutions might allow up to 2.3 kg of sugar to be dissolved with 1 kg of pure water at 15 °C. Most used syrups have some 40%wt of sugar; see the phase diagram is presented in Fig. 1. It is important to apply an effective stirring for dissolving (better done on heating); otherwise, water over a layer of sugar would take days to reach the equilibrium concentration. Sucrose concentration in water is also measured in Brix degrees (°Bx), a synonym for weight percent of a sucrose in solution.

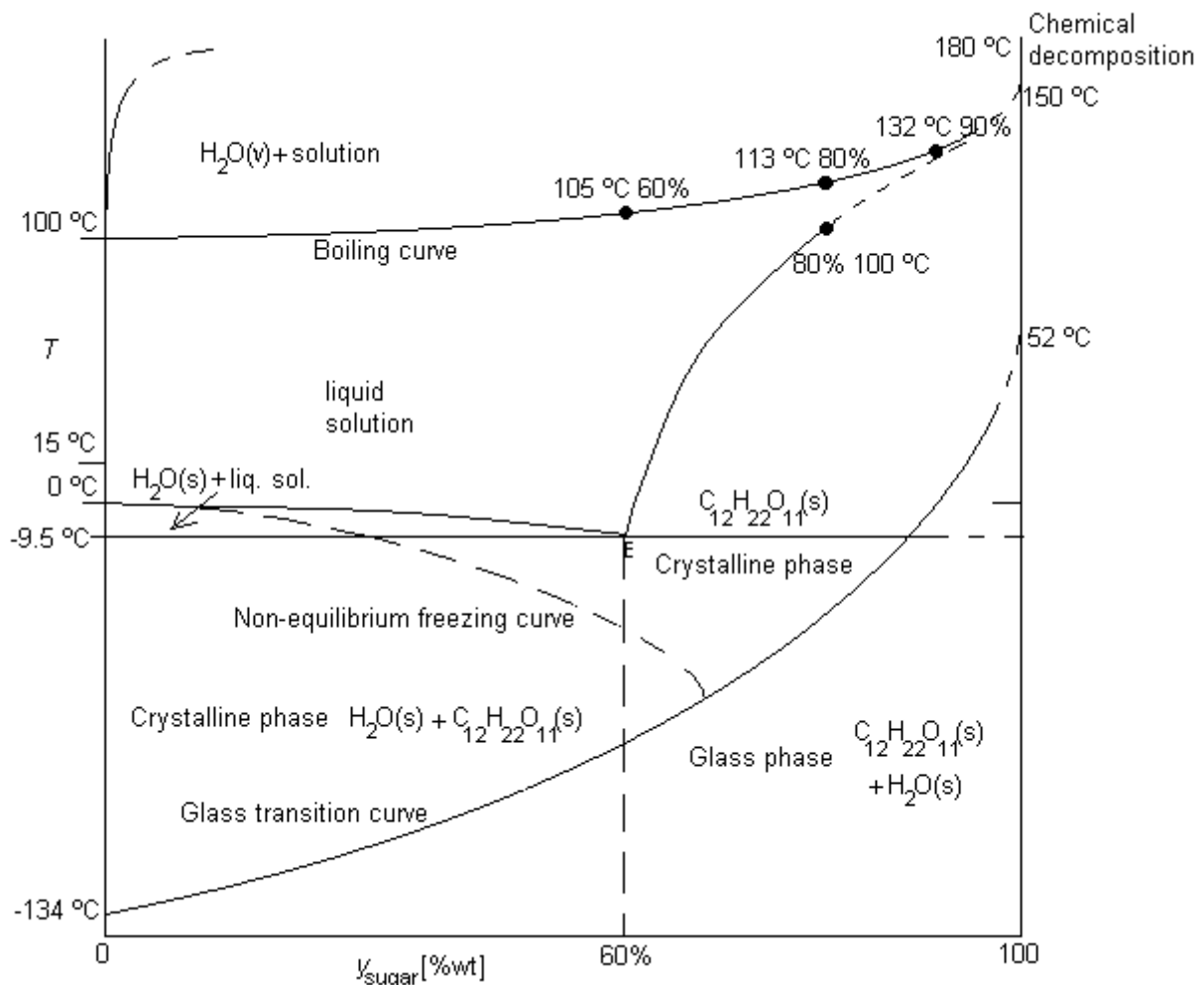


Fig. 1. Phase diagram for water-sucrose solutions at 100 kPa.

Glucose has a solubility of 47%wt in water at 15 °C (i.e. up to 890 g of glucose can be dissolved in 1 kg of pure water, or 570 kg/m<sup>3</sup> in solution). Lactose can be dissolved up to 150 g/kg of pure water. Fructose the most soluble sugar; at 25 °C up to 4 kg of fructose can be dissolved with 1 kg of pure water (in the same conditions, only 2.0 kg of sucrose, or 1.0 kg of dextrose, or 0.85 kg of maltose, or 0.23 kg of maltose, can be dissolved), and has nearly double sweetening power than sucrose.

### **Density and other properties**

Density of aqueous sugar solutions at 15 °C can be approximated as a function of solute mass fraction  $y_s$  (linear correlation) by  $\rho_m = \rho_{dis} + Ay_s$ , with  $\rho_{dis} = 1000 \text{ kg/m}^3$  and  $A = 400 \text{ kg/m}^3$ . More accurate values are presented in Table 2. Every 100 g of table sugar added to 1 kg of water adds  $61 \pm 1 \text{ cm}^3$  to the volume.

Table 2. Other properties of sucrose-water mixtures at 15 °C.

Composition, $y_{\text{sugar}}$	0%	10%	20%	30%	40%	50%	60%
Density, $\rho \text{ [kg/m}^3\text{]}$	999	1038	1079	1120	1190	1230	1290
Viscosity, $\mu \cdot 10^3 \text{ [Pa}\cdot\text{s]}$	1.14	1.33	1.9	3.2	7.2	12.4	94
Freezing, $T \text{ [}^\circ\text{C]}$	0	-1.5	-2.8	-4.2	-5.8	-7.8	-9.5

## Annex 3. Alcohol water solutions

Alcohols are organic compounds with hydroxyl groups (OH) bonded to a carbon atom in linear carbon chains (phenols are OH-groups bonded to benzene rings). They may have just one OH-group (methanol, ethanol, propanol...), two OH-groups (ethylene glycol, propylene glycol...), three OH-groups (glycerol or glycerine), or more (e.g. cholesterol). Alcohols do not ionise when dissolved in water.

### Solubility and phase diagram

Alcohols with small molecules are colourless, volatile, flammable liquids, soluble in water. As the molar mass increases, the boiling point, melting point, and viscosity increase, while solubility in water decreases (methanol, ethanol and propanol are miscible, butanol is already partially miscible, to 1.1 mol/kg at 20 °C, pentanol only to 0.3 mol/kg, and so on). Adding hydroxyl groups increases the boiling point and solubility in water and often produces sweetness. Branching in the carbon chain increases solubility in water and decreases the boiling point. Physical properties may be altered by the presence of other functional groups. Phase diagrams are sketched in Fig 1, whereas Fig. 2 shows deviation to ideal mixture behaviour (i.e. to Raoult's law). Table 15 summarises the properties for the pure components

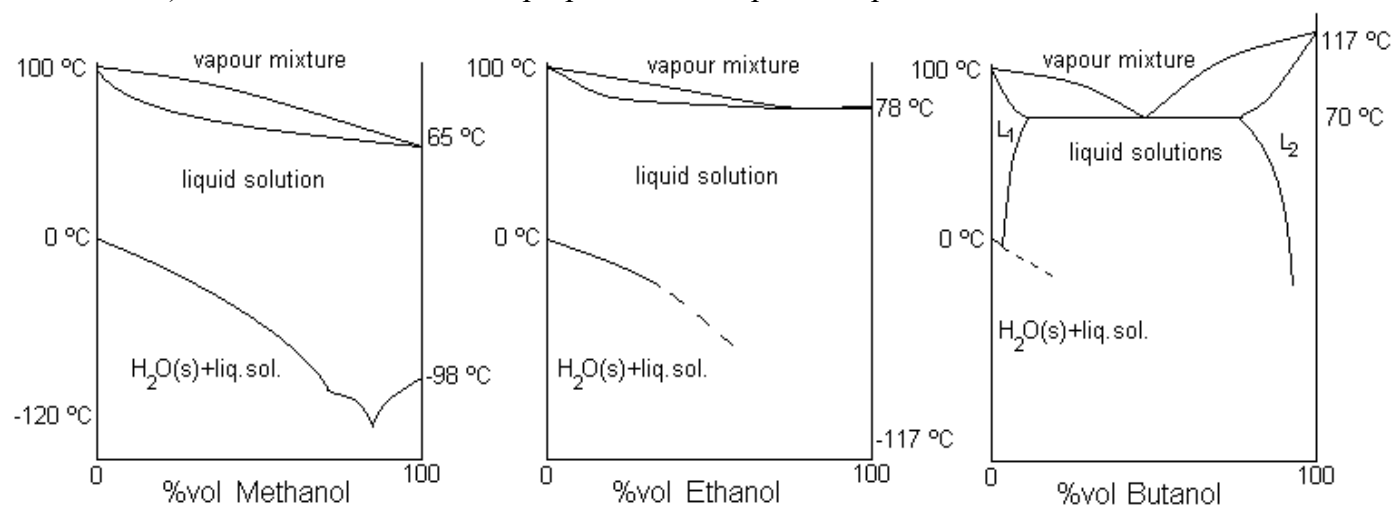


Fig. 1. Phase diagram for several alcohol water solutions at 100 kPa: a) methanol, b) ethanol, c) butanol.

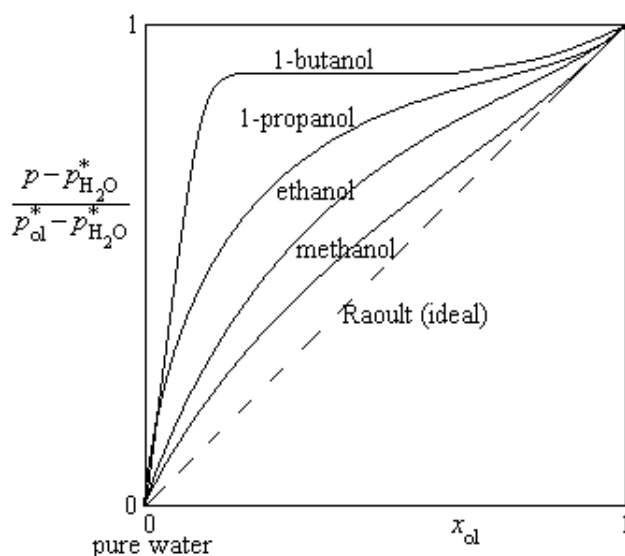


Fig. 2. Deviation from ideal mixture behaviour for several alcohol solutions.

Table 1. Properties of pure substances at 15 °C and 100 kPa, or at the phase change at 100 kPa.

Substance	Formula	Molar mass. $M$ kg/mol	Melting temp. <sup>a</sup> $T_f$ K	Boiling temp. $T_b$ K	Melting enthalpy $h_{sl}$ kJ/kg	Boiling enthalpy $h_{lv}$ kJ/kg	Density (mass) $\rho$ kg/m <sup>3</sup>	Thermal expansion $\alpha \cdot 10^6$ K <sup>-1</sup>	Compressibility <sup>b</sup> $\kappa \cdot 10^9$ Pa <sup>-1</sup>	Vapour pressure $p_v$ Pa	Surface tension <sup>b</sup> $\sigma$ N/m	Thermal capacity $c_p$ J/(kg K)	Thermal conduct. $k$ W/(m K)	Kinematic viscosity $\nu \cdot 10^6$ m <sup>2</sup> /s
Water	H <sub>2</sub> O	0.018	273	373	334	2257	999	150	0.45	1700	0.073	4180	0.60	1
Methanol	CH <sub>4</sub> O	0.032	175	338	99	1100	791	1490		9700	0.023	2510	0.21	0.75
Ethanol	C <sub>2</sub> H <sub>6</sub> O	0.046	156	352	108	855	790	1000	0.87	4300	0.023	2840	0.18	1.5
1-Propanol	C <sub>3</sub> H <sub>8</sub> O	0.060	147	371			805					2400		2.3
2-Propanol <sup>c</sup>	C <sub>3</sub> H <sub>8</sub> O	0.060	184	356	88	733	785					2680		3.6
Ethylene glycol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	0.062	262	471	181	800	1110	650		7	0.048	2400	0.26	18
Propylene glycol	C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	0.076	213	462			1040			10				
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	0.092	293 <sup>a</sup>	453		663	1260	500	0.21		0.063	2430	0.30	1200

<sup>a</sup> Melting and freezing may differ in 1 K.

<sup>b</sup> The compressibility coefficient,  $\kappa$ , is related to the speed of sound,  $c$ , and the density by  $c=(\rho\kappa)^{-1/2}$ .

<sup>c</sup> Isopropanol or isopropyl alcohol.

Mono-hydric alcohols are used as solvents, fuels and for chemical synthesis. Ethanol (ethyl alcohol in IUPAC notation) solutions have been known from ancient times since they are a natural product in fermentation of fruit sugars (e.g. wine) and cereal starch (e.g. beer); an important point in that mixture is the existence of an azeotrope (a mixture that boils without change of composition), at 96%vol ethanol (pure or absolute ethanol can be obtained by desiccation with CaO(s) or by triple distillation with benzene). Thermodynamics show that azeotropic mixtures can only occur at extrema in the LVE  $T$ - $x$  diagram (Gibbs-Konovalow theorem). Methanol (or methyl alcohol) is also known as wood alcohol since it was obtained by distilling wood. It is extremely toxic for >200 ppm, causing blindness, and death by ingestion of as little as 30 cm<sup>3</sup>. Iso-propanol (or 2-propanol, or isopropyl alcohol, CH<sub>3</sub>-CHOH-CH<sub>3</sub>,  $M=0.060$  kg/mol,  $\rho=785$  kg/m<sup>3</sup>) is also known as rubbing alcohol.

Di-hydric alcohols are named glycols (from Gr. *glukus*, sweet), the main one being ethylene glycol (or 1,2.ethanediol, or simply EG, OHCH<sub>2</sub>-CH<sub>2</sub>OH), a sweet odourless clear viscous non-volatile liquid, used mainly as antifreeze solution with water (see Antifreeze, below). Propylene glycol (or 1,2-propanediol, or simply PG, OHCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH) is also used as antifreeze and in cosmetics (it retains skin moisture because it is hygroscopic). Glycol ethers are widely used for paints, adhesives and cosmetics due to their dissolving power for both polar and non-polar substances. All quoted glycols are miscible with water.

Glycerol (or glycerine, C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) has solubility characteristics similar to those of the simple aliphatic alcohols. It is completely miscible with water (Fig. 5), methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec.-butyl alcohol, tertiary amyl alcohol, ethylene glycol, propylene glycol, trimethylene glycol and phenol. Glycerine has limited solubility in dioxane and ethyl ether. It is practically insoluble, however, in higher alcohols, fatty oils, hydrocarbons, and chlorinated solvents such as chlorhexane, chlorobenzene and chloroform. It is completely miscible with ethylene glycol monoethyl ether but is miscible with only a limited amount of ethylene glycol monobutyl ether. Glycerine refractive index is 1.474.

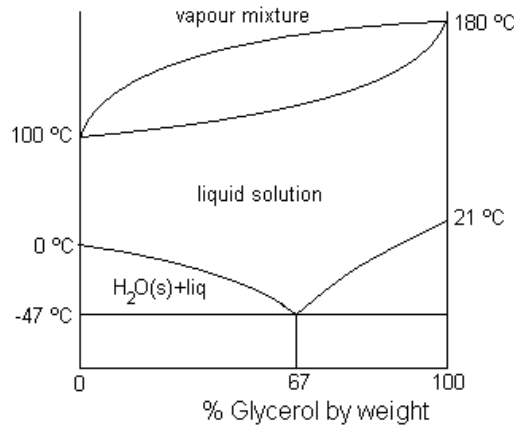


Fig. 3. Phase diagram for glycerol water solutions at 100 kPa.

## Density and other properties

Density of solutions can be approximated in the following way:

- Methanol water solutions at 15 °C:  $\rho = 998 - 133y_{\text{methanol}} - 56y_{\text{methanol}}^2$  kg/m<sup>3</sup>, with  $y_{\text{methanol}}$  being the mass fraction, or  $\rho = 998 - 80y_{\text{methanol}} - 130y_{\text{methanol}}^2$  kg/m<sup>3</sup>,  $y_{\text{methanol}}$  being now the volume fraction.
- Ethanol water solutions at 15 °C: for <30%vol,  $\rho = 998 - 145y_{\text{ethanol}}$  kg/m<sup>3</sup>, and for >30%vol,  $\rho = 790 + 235y_{\text{ethanol}}$  kg/m<sup>3</sup>,  $y_{\text{ethanol}}$  being here the volume fraction, which is the gradation used in spirits (e.g. a 40° whisky has 40% alcohol in volume,  $y_{\text{ethanol}} = 0.40$ , corresponding approximately to  $y_{\text{ethanol}} = 0.35$  by weight). Mixing ethanol and water at constant temperature and pressure, reduces the overall volume, with a maximum reduction of 3.5% for 60% ethanol with 40% of water.
- Ethylene-glycol water solutions at 15 °C:  $\rho = 998 + 110y_{\text{EG}}$  kg/m<sup>3</sup>,  $y_{\text{EG}}$  being the mass fraction. Other properties are presented below in Antifreeze.

Table 4. Other properties of methanol-water mixtures at 15 °C.

methanol in solution, $y_M$ [%wt]	0%	10%	20%	30%	40%	50%	60%	70%	80%	90%
Density, $\rho$ [kg/m <sup>3</sup> ]	999	985	969	954	938	919	899	878	852	828
Freezing point*, $T_f$ [°C]	0	-8	-16	-26	-37	-50	-70	-102	-115	-107
Boiling point, $T_b$ [°C]	100	92	86	82	79	76	73	70	68	66
Flash point, $T_{\text{flash}}$ [°C]	NA	55	42	35	29	24	20	16	14	12

\*A good approximation for the freezing point of methanol-water mixtures is  $T_{f,\text{solution}} = T_{f,\text{H}_2\text{O}} + Ay_M + By_M^2$ , with  $T_{f,\text{H}_2\text{O}} = 0$  °C,  $A = -56$  °C and  $B = -96$  °C valid in the range  $0 < y_M < 60\%$ wt. Notice that the linear approximation based on the freezing-point depression constant only gives  $T_{f,\text{solution}} = T_{f,\text{H}_2\text{O}} + Ay_M$  with  $A = -1.86/0.032 = -58$  °C.

## Antifreeze

An antifreeze is a substance added to water to avoid it freezing when temperatures are below 0 °C (freezing would cause pipe clogging and bursting because of the expansion on freezing). Sometimes the solutions also named antifreeze. Glycols are the main commercial antifreeze solutions. Commercial antifreeze (the undiluted liquid) is usually 95%wt ethylene glycol with some anti-foaming, anti-oxidant, and colorants. Antifreeze mixture (i.e. antifreeze solution) is prepared nearly 50/50 water-antifreeze. Fig. 8 presents the phase diagram for glycols. There are other natural antifreeze substances; besides alcohols, sugars and salts, there are some antifreeze proteins that may keep cells alive down to -15 °C.

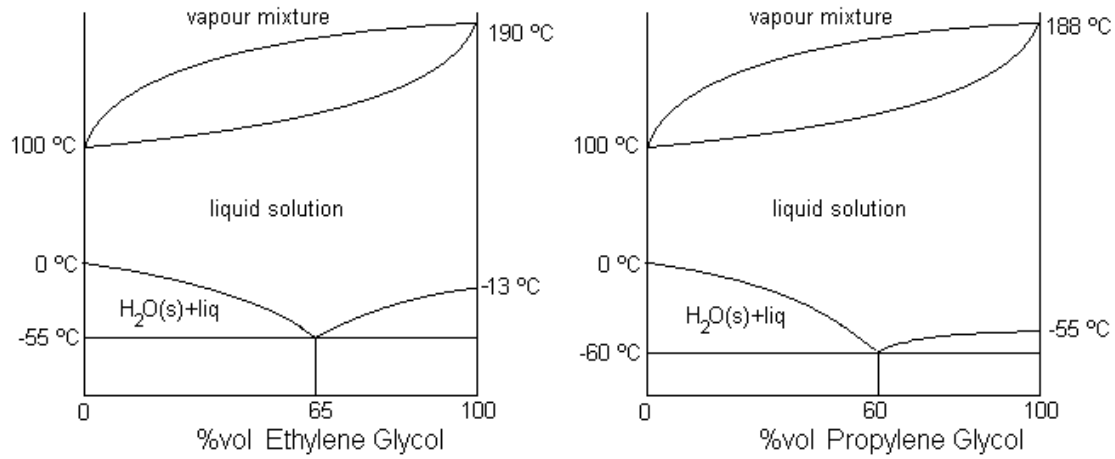


Fig. 4. Phase diagram for ethylene glycol water solutions and propylene-glycol water solutions, at 100 kPa.

Antifreeze solutions are used for refrigeration of internal combustion engines, as solar heating fluids, airplanes de-icing, and in refrigeration installations, because they are less corrosive and much less volatile than mono-hydric alcohols. The concentration of antifreeze is usually measured by densitometry or by refractometry.

EG is a colourless oily liquid, toxic, possessing a sweet taste and mild odour near odourless. It is produced commercially from ethylene oxide, which is obtained from ethylene. Its vapour pressure at 20 °C is  $p_v=8$  Pa, its autoignition temperature  $T_{\text{autoignition}}=400$  °C, flash point  $T_{\text{flash}}=111$  °C, and has flammability limits LFL=3.2% and UFL=15.3%.

PG resembles ethylene glycol in its physical properties (transparent, tasteless and odourless) and it is not toxic; it is used extensively in foods, cosmetics, and oral hygiene products as a solvent, preservative, and moisture-retaining agent; it is manufactured in large amounts from propylene oxide, which is obtained from propylene. Its vapour pressure at 20 °C is  $p_v=11$  Pa, its autoignition temperature  $T_{\text{autoignition}}=400$  °C, flash point  $T_{\text{flash}}=103$  °C, and flammability limits LFL=2.6% and UFL=17.4%.

Table 5. Other properties of EG-H<sub>2</sub>O mixtures and PG-H<sub>2</sub>O mixtures, at 15 °C.

Composition [%vol EG in solution]	0%	20%	30%	40%	50%	60%	70%	100%
Density, $\rho$ [kg/m <sup>3</sup> ]	999	1026	1039	1052	1066	1079	1090	1120
Thermal capacity, $c_p$ [J/(kg·K)]	4185	4020	3930	3750	3570	3400		
Thermal conductivity, $k$ [W/(m·K)]	0.59	0.52	0.49	0.46	0.42	0.39		
Viscosity, $\mu \cdot 10^3$ [Pa·s]	1.14	1.8	2.3	3.1	4.1	5.6		
Freezing point*, $T_f$ [°C]	0	-9	-15	-24	-36	-50	-50	-13
Boiling point, $T_b$ [°C]	100				106		113	198
Composition [%vol PG in solution]	0%	20%	30%	40%	50%	60%	70%	100%
Density, $\rho$ [kg/m <sup>3</sup> ]	999	1016	1025	1032	1040			
Freezing point*, $T_f$ [°C]	0	-9	-15	-23	-35	-60		-60
Boiling point, $T_b$ [°C]	100				104			189

\*A good approximation for the freezing point of EG-H<sub>2</sub>O mixtures is  $T_{f,\text{solution}}=T_{f,\text{H}_2\text{O}}+Ay_{\text{glycol}}+By_{\text{glycol}}^2$ , with  $y_{\text{glycol}}$  being volume percents and not mass fractions,  $T_{f,\text{H}_2\text{O}}=0$  °C,  $A=-22$  °C and  $B=-98$  °C valid in the range  $0 < y_{\text{glycol}} < 65\%$  (i.e. up to the eutectic point). Notice that the linear approximation based on the freezing-point depression constant only gives  $T_{f,\text{solution}}=T_{f,\text{H}_2\text{O}}+Ay_{\text{glycol}}$  with  $A=-1.86/0.062=-30$  °C.

Other glycols include di-ethylene glycol (DEG, decomposes at 165 °C), tri-ethylene glycol (1,3-butanediol, TEG, C<sub>6</sub>H<sub>14</sub>O<sub>4</sub>), tetra-ethylene glycol, 1,4-butanediol (used in polyurethanes and in polyester resins for coatings and plasticizers), and polyethylene glycol (PEG), a water-soluble waxy-solid polymer that is used extensively in the cosmetic and toiletry industry. Although PEG is water soluble, solubility is greatly reduced at temperatures approaching 0°C, allowing experiments to run for 15..20 minutes before dissolution of PEG becomes pronounced; as polymer molar-mass increases, viscosity and freezing point increase. PEG 600 has a freezing point just below room temperature (about 19.5°C).

TEG (tri-ethylene glycol) is miscible with water, being highly hygroscopic (the most used liquid desiccant, also used as a starting material for the manufacture of brake fluids and of plasticizers for resins). TEG has been traditionally used to dry natural gas, and recently used in dry air conditioning. TEG is a clear odourless liquid with  $M=0.150$  kg/mol,  $\rho=1130$  kg/m<sup>3</sup>,  $T_m=-7$  °C,  $T_b=285$  °C,  $c=2220$  J/(kg·K), thermal expansion  $\alpha=680\cdot10^{-6}$  K<sup>-1</sup>, surface tension  $\sigma=0.042$  N/m, autoignition temperature  $T_{\text{autignition}}=370$  °C, flash point  $T_{\text{flash}}=180$  °C, and flammability limits LFL=0.9% and UFL=9.2%. TEG must be used at  $T>10$  °C to have good fluidity but at  $T<55$  °C to avoid evaporation (pressure has no effect on absorption); pure TEG decomposes at  $T>205$  °C; a 90%wt aqueous TEG solution boils at 128 °C. DEG (di-ethylene glycol) is similar to TEG, a water miscible liquid also used as desiccant, and has  $M=0.106$  kg/mol,  $\rho=1120$  kg/m<sup>3</sup>,  $T_m=-8$  °C,  $T_b=246$  °C, its critical point at  $T_{\text{cr}}=407$  °C and  $p_{\text{cr}}=4.6$  MPa,  $c=2120$  J/(kg·K), thermal expansion  $\alpha=640\cdot10^{-6}$  K<sup>-1</sup>, thermal conductivity  $k=0.21$  W/(m·K), surface tension  $\sigma=0.045$  N/m, viscosity  $\nu=26\cdot10^{-6}$  m<sup>2</sup>/s, vaporisation enthalpy  $h_{\text{lv}}=541$  kJ/kg, autoignition temperature  $T_{\text{autignition}}=229$  °C, and flash point  $T_{\text{flash}}=143$  °C. Other non-glycol desiccants are the hygroscopic solutions LiBr(aq) and LiCl(aq), besides some solid desiccants like LiCl(s) or the traditional silica-gel.

Glycols are also used to create artificial fog: a mixture of water, propylene glycol and tri-ethylene glycol is heated and a mist forms, consisting of a plume of water vapour that entrains very small droplets of the glycols because they readily clog to water-vapour molecules by H bonds (usual alcohols like ethanol in water do not produce mist because they vaporise more readily than water). Glycol-solution fogs are the most common artificial fogs; they are rising plumes of hot vapour, whereas artificial fogs may with dry ice produce falling plumes (these are made by dropping dry-ice flakes on water, yielding a fog of small water-ice crystals entrained by the expanding CO<sub>2</sub> gas; even without liquid water, a weak fog develops around dry-ice flakes because of the condensation of air humidity).

Example 1. How much ethylene glycol is needed to lower the freezing point of water to -10 °C?

A linear approximation based on the colligative freezing-point-depression constant for water,  $K_f=1.86$  K/(mol/kg) from Table 8, with  $T_{f,\text{solution}}=T_{f,\text{H}_2\text{O}}+K_fm_i$ , would yield  $m_i=-10/(-1.86)=5.4$  molal solution, i.e. 5.4 mol EG per kg of pure water, corresponding to a mass fraction of  $y_{\text{glycol}}=5.4\cdot0.062/(1+5.4\cdot0.062)=0.33$ . From Table 17 data, interpolating freezing-point data one deduces  $y_{\text{glycol}}=0.22$ , from the linear approximation  $T_{f,\text{solution}}=T_{f,\text{H}_2\text{O}}+Ay_{\text{glycol}}$  with  $A=-30$  K one deduces  $y_{\text{glycol}}=-10/(-30)=0.33$ , and from the quadratic fitting  $T_{f,\text{solution}}=T_{f,\text{H}_2\text{O}}+Ay_{\text{glycol}}+By_{\text{glycol}}^2$  with  $T_{f,\text{H}_2\text{O}}=0$  °C,  $A=-22$  °C and  $B=-98$  °C one gets  $y_{\text{glycol}}=0.23$ .

## Annex 4. Hydrogen-peroxide water solutions

Hydrogen peroxide or hydrogen dioxide,  $\text{H}_2\text{O}_2$ ,  $M=0.034$  kg/mol, is one of the most powerful oxidizers, and it is safe to handle diluted in water. High-concentration hydrogen-peroxide, however, is corrosive to mucous tissue, eyes and skin, and may be fatal if swallowed. It doesn't burn, but it may start fires (or serve as an additional source of oxygen for flames). Contact with organic matter (wood, paper, grass) can cause fire; e.g. a 70%  $\text{H}_2\text{O}_2$  solution coming in contact with leather gloves will ignite after a while. Pure  $\text{H}_2\text{O}_2$  may explosively decompose to water and oxygen because  $\text{H}_2\text{O}_2(\text{l})=\text{H}_2\text{O}(\text{l})+(1/2)\text{O}_2(\text{g})+98.4$  kJ/mol is very exothermic, and may occur by traces of metal salts (of a few ppm!), by light or by heat. Decomposition cannot always be prevented, thus, storage tanks should be vented and kept cool

Hydrogen peroxide was discovered by Thénard in 1815 in the residue of water electrolysis (it is also formed by the action of sunlight on water, and it is a natural metabolite of many organisms, too). It can be obtained in the lab by ion displacement in a metal peroxide with a strong acid (e.g.  $\text{BaO}_2+2\text{ClH}=\text{Cl}_2\text{Ba}+\text{H}_2\text{O}_2(\text{aq})$  yields some 3%wt  $\text{H}_2\text{O}_2$ , that can be concentrated by electrolysis and distillation). Table 18 summarises the properties for the pure components.

Table 1. Properties of pure substances at 15 °C and 100 kPa, or at the phase change at 100 kPa.

Substance	Formula	Molar mass. $M$ kg/mol	Melting temp. $T_f$ K	Boiling temp. $T_b$ K	Melting enthalpy $h_{sl}$ kJ/kg	Boiling enthalpy $h_{lv}$ kJ/kg	Density (mass) $\rho$ kg/m <sup>3</sup>	Thermal expansion $\alpha \cdot 10^6$ K <sup>-1</sup>	Compressibility <sup>a</sup> $\kappa \cdot 10^9$ Pa <sup>-1</sup>	Vapour pressure $p_v$ Pa	Surface tension <sup>b</sup> $\sigma$ N/m	Thermal capacity $c_p$ J/(kg K)	Thermal conduct. $k$ W/(m K)	Kinematic viscosity $\nu \cdot 10^6$ m <sup>2</sup> /s
Water	H <sub>2</sub> O	0.018	273	373	334	2257	999	200	0.45	1700	0.073	4180	0.60	1.0
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	0.034	270	399			1580							0.79

$\text{H}_2\text{O}_2$  is miscible in water; really, it is solely used in the form of aqueous solutions (if >8%vol, it must be labelled as 'oxidiser'). Trading is usually at 30%wt (or 70%wt at large). It is odourless at low concentrations, but has a slightly pungent smell at high concentrations. It is used as a disinfectant and bleaching agent, and for propulsion in rockets and underwater-vehicles, since liquid storage is more efficient than compressed-oxygen gas storage. It is a strong oxidiser, but it may also yield a stronger one through catalytic conversion to hydroxyl radicals (OH) with reactivity second only to fluorine (see oxidation potentials in [Thermochemical data of solutes](#)). Ozone is most used as oxidising agent in food industry; ozone is 12.5 times more soluble than oxygen, in water; it is highly unstable and is generated on site from dry air or from oxygen by passing these gases through an electric arc.

The molecular structure of  $\text{H}_2\text{O}_2$  differs a lot from that of water: each OH bond forms an angle of 100° with the O-O bond, but the two are not coplanar: one H-O-O plane forms an angle of 106° with the other. The phase diagram of  $\text{H}_2\text{O}_2$  water solutions is presented in Fig. 1, and some other properties in Table 2 (see [www.h2o2.com](http://www.h2o2.com) for further details).



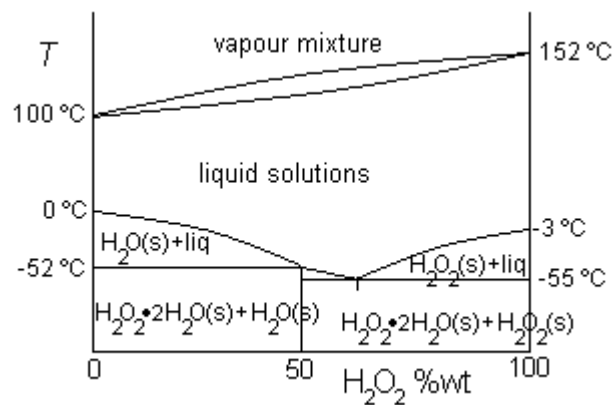


Fig. 1. Phase diagram for  $\text{H}_2\text{O}_2$  water solutions at 100 kPa.

Table 2. Some properties for  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  solutions at 20 °C.

Concentration [%wt]	Density [kg/m <sup>3</sup> ] at 20°C	Boiling [°C]	Freezing [°C]	Viscosity [Pa·s] at 20° C	$p_v(20\text{ °C})$ [kPa]	pH
0	998	100	0	0.00100	2.34	7
30	1110	106	-28	0.00111	2.4	3..4
50	1200	114	-52	0.00117		1..2
70	1288	130	-37	0.00124		1
100	1580	152	-3	0.00124	0.5	

## Annex 5. Ammonia water solutions

Ammonia water solutions are used in many thermodynamic processes (e.g. absorption refrigeration and Kalina power cycles), as well as in cleaning and chemical synthesis. Anhydrous ammonia is a pungent gas at room temperature and pressure, usually handled in liquid form when compressed to  $>0.7$  MPa or cooled to  $<240$  K (or dissolved in water). It is easily detected and at only 50 ppm in air is enough to prompt a person to escape (a concentration of  $>5000$  ppm is fatal). Pure ammonia was first prepared by Joseph Priestley in 1774, and its exact composition was determined by Claude-Louis Berthollet in 1785. Because ammonia can be decomposed easily to yield hydrogen, it is a convenient portable source of atomic hydrogen (e.g. for welding). Although difficult to ignite, ammonia is a fuel (some explosions have been reported after accidental leakage), with a heating value of  $\text{HHV}=383$  kJ/kg, a stoichiometric air/fuel ratio  $A_0=6.05$ , flammability limits  $\text{LFL}=15.5\%$  and  $\text{UFL}=27\%$ , and autoignition temperature of 925 K. Table 1 summarises the properties for the pure components.

Table 1. Properties of pure substances at 15 °C and 100 kPa, or at the phase change at 100 kPa.

Substance	Formula	Molar mass. $M$ kg/mol	Melting temp. $T_f$ K	Boiling temp. $T_b$ K	Melting enthalpy $h_{sl}$ kJ/kg	Boiling enthalpy $h_{lv}$ kJ/kg	Density (mass) $\rho$ kg/m <sup>3</sup>	Thermal expansion $\alpha \cdot 10^6$ K <sup>-1</sup>	Compressibility <sup>a</sup> $\kappa \cdot 10^9$ Pa <sup>-1</sup>	Vapour pressure $p_v$ Pa	Surface tension <sup>b</sup> $\sigma$ N/m	Thermal capacity $c_p$ J/(kg K)	Thermal conduct. $k$ W/(m K)	Kinematic viscosity $\nu \cdot 10^6$ m <sup>2</sup> /s
Water	H <sub>2</sub> O	0.018	273	373	334	2257	999	200	0.45	1700	0.073	4180	0.60	1
Ammonia	NH <sub>3</sub>	0.017	195	240	332	1357	697	2400		720000	0.022	4601	0.50	266

Ammonia is highly soluble in water, with a limit of solubility at 20 °C of 0.518 kg per kg of pure water ( $y_s=0.34$ ), forming a highly reactive alkaline solution with  $\text{NH}_4^+$  and  $\text{OH}^-$  ions (the most used weak electrolyte), usually named ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), although this molecule is unstable in all phases, i.e. inexistent; besides these ions, most of dissolved ammonia rest in molecular form in solution; the density of a concentrated  $\text{NH}_3(\text{aq})$  reagent of  $y_s=0.29$  is 900 kg/m<sup>3</sup>.

Ammonia is handled as a compressed liquefied gas, as a refrigerated liquid, or as a concentrated aqueous solution (labelled either  $\text{NH}_3(\text{aq})$ , or incorrectly  $\text{NH}_4\text{OH}(\text{l})$  as said in the paragraph above). Ammonia and ammonium salts can be readily detected, in very minute traces, by the addition of Nessler's solution (a solution of mercuric iodide in potassium iodide and potassium hydroxide), which gives a distinct yellow coloration in the presence of the least trace of ammonia or ammonium salts. Here we only present the phase diagram for ammonia water solutions (Fig. 1) and the solubility change with temperature, in Table 21; a full set of properties can be found at [www.mrc-eng.com/aquaammonia.htm](http://www.mrc-eng.com/aquaammonia.htm).

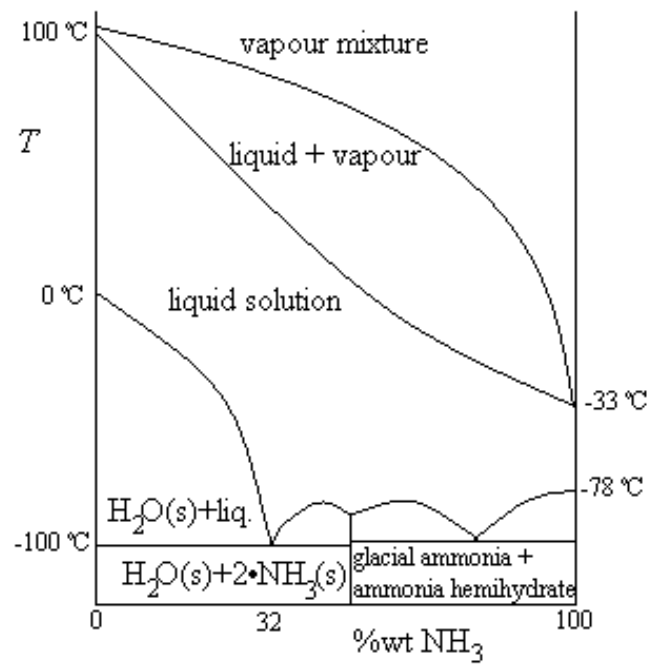


Fig. 1. Phase diagram for ammonia water solutions at 100 kPa.

Table 2. Solubility data for ammonia water solutions.

$T$ [ $^{\circ}\text{C}$ ]	0	10	20	30	40	50	60	70	80	90	100
g/kg H <sub>2</sub> O	895	684	529	410	316	235	168	111	65	30	0

## Annex 6. Carbon-dioxide water solutions

The intention here is to analyse carbon-dioxide water solutions at moderate pressures (i.e. solutions in equilibrium with a gaseous phase, not with a liquid-CO<sub>2</sub> phase), with emphasis on water carbonation.

Like water, carbon dioxide is vital for life on Earth (it is the basic nutrient of photosynthetic organisms), and CO<sub>2</sub>-H<sub>2</sub>O mixtures play a key role in the respiration of living beings, and on the carbon cycle in nature in general, and in particular its effect on global warming (greenhouse effect), the weathering of rocks (sedimentation), and in many natural and manufactures drinks, both soft and alcoholic (beer, champagne). Carbon dioxide gets trapped in water ice and helps to guess ancient climatic changes.

### ***Carbon dioxide: sources, detection, and properties***

Pure carbon dioxide (CO<sub>2</sub>) is a gas at normal conditions, with the peculiarity that its critical temperature is close to room temperature ( $T_{cr}=31\text{ }^{\circ}\text{C}$ ), so, that no wonder it was the working fluid used at the discovery of critical-point phenomena in the 19th century.

In nature, CO<sub>2</sub> is naturally present in air, with a nearly uniform and small molar fraction, 389 ppm average in 2010, but that happens to be crucial to overall weather on Earth (global warming); in contrast, CO<sub>2</sub> makes up >95% of Venus and Mars atmospheres. CO<sub>2</sub> is also found dissolved in natural waters. Practically all living beings produce CO<sub>2</sub> in their metabolism to get energy from the environment, either by aerobic or anaerobic respiration, or by fermentation. The primary natural source of CO<sub>2</sub> is out-gassing from the Earth's interior at mid-ocean ridges and hotspot volcanoes.

Commercial CO<sub>2</sub> is produced as a sub-product of other industries, as from clean-combustion applications, from natural-gas reforming from hydrogen production, from fermentation (cellars, breweries and distilleries), or extracted from flue gases or on-purpose combustion after scrubbing. Carbon dioxide is used for the synthesis of urea and methanol, as refrigerant fluid, as a fire-fighting agent, to produce dry ice, for cleaning (as dry ice or as supercritical fluid), and in the food industry (carbonated drinks and ‘rising’ powders), and it is the source of carbon for living matter through photosynthesis. CO<sub>2</sub> is traded as compressed liquefied gas, as refrigerated dry ice, or in gas form (pure at low pressure, or mixed with nitrogen at high pressure). An easy way to generate CO<sub>2</sub> in the lab is by dripping an acid over a carbonate; if a small stream of CO<sub>2</sub> is wanted (as to enhance plant growth in aquariums), a little spoon of yeast on a sugar-sweetened water-bottle may work.

In respiration, we inhale air with a typical composition of 77% N<sub>2</sub> + 21% O<sub>2</sub> + 1% H<sub>2</sub>O + 1% Ar + 0.04% CO<sub>2</sub>, and we exhale with a typical composition of 74% N<sub>2</sub> + 17% O<sub>2</sub> + 4% H<sub>2</sub>O + 1% Ar + 4% CO<sub>2</sub>. Although CO<sub>2</sub> is not toxic by reaction, breathing air should not have more than 1% CO<sub>2</sub> in the long run (a 10% CO<sub>2</sub> in air is mortal after a few minutes) to allow blood decarboxylation at the alveoli (where  $x_{\text{CO}_2}=6\%$ ). Carbon dioxide is transported in the blood stream from the body cells back to the lungs by different means:

- 60% as bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) formed when CO<sub>2</sub> (released by cells when making ATP) combines with H<sub>2</sub>O.

- 30% as carbamino-haemoglobin, formed when CO<sub>2</sub> combines with haemoglobin (haemoglobin molecules that have given up their oxygen).
- 10% dissolved in the plasma (around 1 g/L).

The presence of CO<sub>2</sub> in gas mixtures can be precisely detected by gas- chromatography or infrared-radiometry. For liquid solutions, a chemical indicator may be used; e.g. when a CO<sub>2</sub>-containing gas is bubbled through a bromothymol-blue solution, carbonic acid forms and the indicator turns from dark blue to green, yellow, or very pale yellow depending on the CO<sub>2</sub> concentration (lighter colours mean higher concentrations). The presence of CO<sub>2</sub>(aq) can be tested by addition of a Ca(OH)<sub>2</sub> solution, because the carbonate anions formed by dissociation ( $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- = 2\text{H}^+ + \text{CO}_3^{2-}$ ) combine with calcium cations to form the insoluble CaCO<sub>3</sub> salt, that precipitates. Titration coulometry is also used to measure total inorganic carbon in solution, and deduce from it CO<sub>2</sub> concentrations.

There are several substances that readily absorb CO<sub>2</sub>, what is used get rid of, or to concentrate it; metal hydroxides, as used in the Orsat analyser of exhaust flues, work in the way  $2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{heat}$ , where K and Li may replace Na; on the other hand, mono-ethane-amine (MEA) absorbs CO<sub>2</sub> at room temperature and desorbs it when heated to some 135 °C. Water is also a good CO<sub>2</sub> absorber at global scale (oceans). Pure water and pure carbon-dioxide properties are compiled in Table 1. Detailed properties of CO<sub>2</sub> are presented in Table 2 and 3, and Fig. 1.

Table 1. Properties of pure substances.

Substance	Formula	Molar mass. $M$ kg/mol	Critical pressure $p_{cr}$ MPa	Critical temp. $T_{cr}$ K	Critical density. $\rho_{cr}$ kg/m <sup>3</sup>	Melting temp. $T_f$ K	Boiling temp. $T_b$ K	Melting enthalpy $h_{sl}$ kJ/kg	Boiling enthalpy $h_{lv}$ kJ/kg
Water	H <sub>2</sub> O	0.018	22.1	647	317	273	373	334	2257
Carbon dioxide	CO <sub>2</sub>	0.044	7.38	304	364	217 <sup>a</sup>	195 <sup>b</sup>	185	350

a) Triple point (−56 °C, 416 kPa), b) Sublimation point (−78 °C, 100 kPa).

Table 2. Properties of pure carbon dioxide as a function of temperature.

Temperature [K]	195 <sup>a</sup>	217 <sup>b</sup>	273	288	298	304.2 <sup>c</sup>
Density of gas at 100 kPa, $\rho$ [kg/m <sup>3</sup> ]	2.8	2.5	2.0	1.87	1.78	1.74
Density of saturated vapour, $\rho$ [kg/m <sup>3</sup> ]	2.8	14	97	160	241	466
Density of saturated liquid, $\rho$ [kg/m <sup>3</sup> ]	NA	1179	929	823	714	466
Density of solid, $\rho$ [kg/m <sup>3</sup> ]	1560	-	-	-	-	-
Vapour pressure, $p_v$ [kPa]	100	518	3470	5067	6409	7383
Vaporisation enthalpy, $h_{lv}$ [kJ/kg]	571	345	235	178	122	0
Thermal capacity of gas at 100 kPa, $c_p$ [J/(kg·K)]	728	755	817	830	840	850
Thermal capacity of saturated vapour, $c_p$ [J/(kg·K)]	720	957	1860	3200	8010	∞
Thermal capacity of saturated liquid, $c_p$ [J/(kg·K)]	1112	1707	2540	3420	6350	∞
Thermal capacity ratio of gas at 100 kPa, $\gamma$ [-]	1.37	1.35	1.31	1.30	1.29	1.29
Thermal capacity ratio of saturated vapour, $\gamma$ [-]	1.4	2.0	2.1	3.2	6.8	∞
Thermal conductivity of gas at 100 kPa, $k$ [W/(m·K)]	0.009	0.011	0.014	0.016	0.017	0.017
Thermal conductivity of saturated vapour, $k$ [W/(m·K)]	0.009	0.011	0.018	0.025	0.034	∞
Thermal conductivity of saturated liquid, $k$ [W/(m·K)]	0.21	0.18	0.11	0.09	0.07	∞
Thermal expansion of saturated vapour, $\alpha \times 10^3$ [K <sup>-1</sup> ]	5.1	6.1	13.1	24.6	65.6	∞
Thermal expansion of saturated liquid, $\alpha \times 10^3$ [K <sup>-1</sup> ]	-	3.1	7.4	13.8	37.1	∞

Sound speed in vapour (saturated vapour), $c$ [m/s]	231	223	212	201	189	0
Sound speed in liquid (saturated liquid), $c$ [m/s]	-	967	538	393	276	0

a) Sublimation point ( $-78\text{ }^{\circ}\text{C}$ , 100 kPa), b) Triple point ( $-56\text{ }^{\circ}\text{C}$ , 416 kPa), c) Critical point ( $31.1\text{ }^{\circ}\text{C}$ , 7.38 MPa).

Table 3. Properties of pure carbon dioxide gas as a function of pressure at  $15\text{ }^{\circ}\text{C}$  (288.15 K).

Pressure [MPa]	0	0.1	0.5	1	2	5.087 <sup>a</sup>
Density $\rho$ [ $\text{kg}/\text{m}^3$ ]	0	1.85	9.5	19.5	41.8	161
Thermal capacity, $c_p$ [ $\text{J}/(\text{kg}\cdot\text{K})$ ]	833	841	874	922	1048	$\infty$
Thermal capacity ratio, $\gamma$ [-]	1.29	1.30	1.33	1.37	1.47	$\infty$
Sound speed, $c$ [m/s]	265	264	261	257	247	$\infty$

<sup>a</sup>Saturated vapour at  $15\text{ }^{\circ}\text{C}$ .

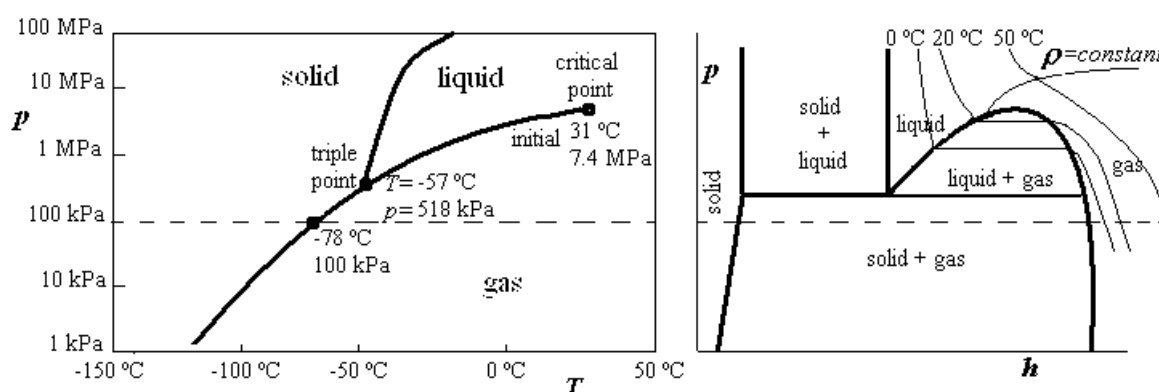


Fig. 1. Phase changes ( $p$ - $T$  diagram), and  $p$ - $h$  diagram for pure  $\text{CO}_2$ .

## Solubility and phase diagram

Carbon dioxide is one of the most soluble non-polar gases in water, its solubility being larger than that of  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ , but smaller than that of  $\text{NH}_3$  because the latter is dipolar (see [Solubility data for aqueous solutions](#)).  $\text{CO}_2$  solubility in water decreases in the presence of other solutes (e.g. seawater can hold 15% less  $\text{CO}_2$  than fresh water). The dissolution of  $\text{CO}_2$  and  $\text{O}_2$  gases in water is essential to respiration and other life science processes. Solubility data for carbon dioxide in water is presented in Table 4, and several phase diagrams are sketched in Fig. 2.

Table 4. Solubility data for carbon-dioxide in water at several temperatures and pressures, and in different magnitudes:  $K^{cc}$  is in  $\text{mol}/\text{m}^3$  of dissolved  $\text{CO}_2$  per  $\text{mol}/\text{m}^3$  of  $\text{CO}_2$  in the gas phase,  $K^{cp}$  is in  $\text{mol}/\text{m}^3$  of dissolved  $\text{CO}_2$  per bar of  $\text{CO}_2$  partial pressure in the gas phase,  $K^{pp}$  is in  $\text{kg}/\text{m}^3$  of dissolved  $\text{CO}_2$  per bar of  $\text{CO}_2$  partial pressure in the gas phase,  $K^{vv}$  is in volume that would occupy the dissolved  $\text{CO}_2$  if it were in the gas phase at  $0\text{ }^{\circ}\text{C}$  and 100 kPa, and  $K^{xx}$  is the molar fraction in solution in ppm. Notice that Henry law does not apply at large pressures.

Solubility	0 $^{\circ}\text{C}$	15 $^{\circ}\text{C}$	25 $^{\circ}\text{C}$	50 $^{\circ}\text{C}$
0.1 MPa	$K^{cc}=1.8\text{ mol/mol}$ $K^{cp}=80\text{ mol}/\text{m}^3$ $K^{pp}=3.5\text{ kg}/\text{m}^3$ $K^{vv}=1.8\text{ vol/vol}$ $K^{xx}=1430\text{ ppm}$	$K^{cc}=1.1\text{ mol/mol}$ $K^{cp}=46\text{ mol}/\text{m}^3$ $K^{pp}=2.0\text{ kg}/\text{m}^3$ $K^{vv}=1.0\text{ vol/vol}$ $K^{xx}=830\text{ ppm}$	$K^{cc}=0.80\text{ mol/mol}$ $K^{cp}=32\text{ mol}/\text{m}^3$ $K^{pp}=1.4\text{ kg}/\text{m}^3$ $K^{vv}=0.7\text{ vol/vol}$ $K^{xx}=580\text{ ppm}$	$K^{cc}=0.5\text{ mol/mol}$ $K^{cp}=19\text{ mol}/\text{m}^3$ $K^{pp}=0.8\text{ kg}/\text{m}^3$ $K^{vv}=0.4\text{ vol/vol}$ $K^{xx}=340\text{ ppm}$
1 MPa	$K^{cc}=1.8\text{ mol/mol}$ $K^{cp}=800\text{ mol}/\text{m}^3$ $K^{pp}=35\text{ kg}/\text{m}^3$ $K^{vv}=18\text{ vol/vol}$ $K^{xx}=14300\text{ ppm}$	$K^{cc}=1.1\text{ mol/mol}$ $K^{cp}=460\text{ mol}/\text{m}^3$ $K^{pp}=20\text{ kg}/\text{m}^3$ $K^{vv}=10\text{ vol/vol}$ $K^{xx}=8300\text{ ppm}$	$K^{cc}=0.80\text{ mol/mol}$ $K^{cp}=320\text{ mol}/\text{m}^3$ $K^{pp}=14\text{ kg}/\text{m}^3$ $K^{vv}=7\text{ vol/vol}$ $K^{xx}=5800\text{ ppm}$	$K^{cc}=0.5\text{ mol/mol}$ $K^{cp}=190\text{ mol}/\text{m}^3$ $K^{pp}=8\text{ kg}/\text{m}^3$ $K^{vv}=4\text{ vol/vol}$ $K^{xx}=3400\text{ ppm}$

10 MPa	$K^{cc}=0.8 \text{ mol/mol}$ $K^{cp}=3500 \text{ mol/m}^3$ $K^{pp}=155 \text{ kg/m}^3$ $K^{vv}=80 \text{ vol/vol}$ $K^{xx}=63000 \text{ ppm}$	$K^{cc}=0.5 \text{ mol/mol}$ $K^{cp}=2040 \text{ mol/m}^3$ $K^{pp}=89 \text{ kg/m}^3$ $K^{vv}=44 \text{ vol/vol}$ $K^{xx}=37000 \text{ ppm}$	$K^{cc}=0.35 \text{ mol/mol}$ $K^{cp}=1420 \text{ mol/m}^3$ $K^{pp}=62 \text{ kg/m}^3$ $K^{vv}=31 \text{ vol/vol}$ $K^{xx}=26000 \text{ ppm}$	$K^{cc}=0.22 \text{ mol/mol}$ $K^{cp}=840 \text{ mol/m}^3$ $K^{pp}=35 \text{ kg/m}^3$ $K^{vv}=18 \text{ vol/vol}$ $K^{xx}=15000 \text{ ppm}$
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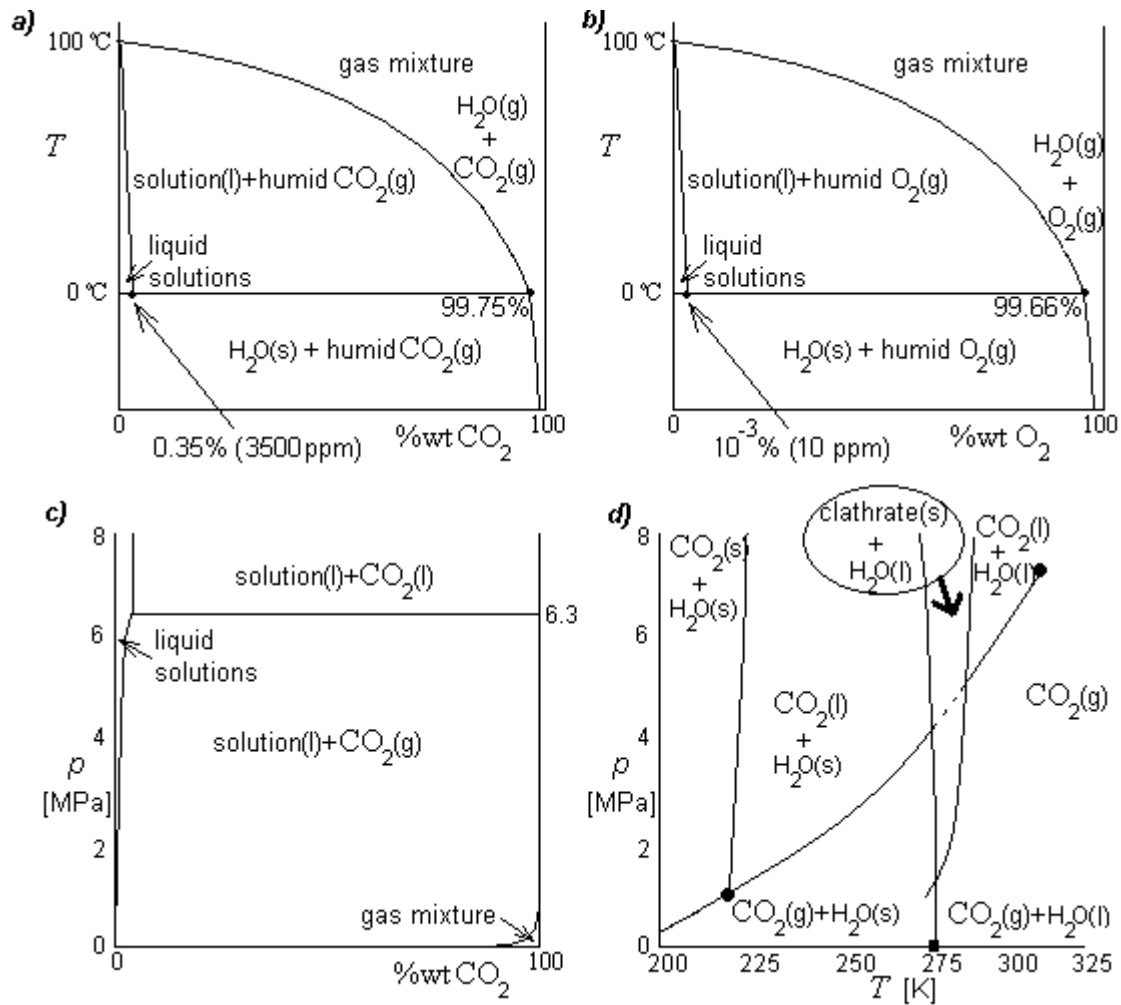


Fig. 2. Sketch of phase diagrams for carbon-dioxide water mixtures: a)  $T$ - $y$  diagram at 100 kPa, b)  $T$ - $y$  diagram at 100 kPa for oxygen water mixture (for comparison); c)  $p$ - $y$  diagram at 298 K ( $\text{CO}_2$  gas-liquid transition at 6.3 MPa; the solubility of water in liquid  $\text{CO}_2$  is negligible), d)  $p$ - $T$  phase diagram, showing the clathrate region.

The effect of pressure on the phase-change diagram of gas solutions is very important. For the  $\text{CO}_2$ - $\text{H}_2\text{O}$  system at 15 °C, for instance, at 0.1 MPa (Fig. 2a) there may be a liquid solution for  $0 < y_{\text{CO}_2} < 0.35\%$  ( $0 < x_{\text{CO}_2} < 0.14\%$ ), a two-phase mixture for  $0.35\% < x_{\text{CO}_2} < 99.66\%$ , or a gas mixture for  $99.66\% < x_{\text{CO}_2} < 100\%$  ( $99.4\% < x_{\text{CO}_2} < 100\%$ ). Increasing pressure isothermally increases both bounds at first, but above the pure vapour pressure of  $\text{CO}_2$ , the bounds start to decrease again. At supercritical temperatures and pressures (i.e.  $T > 31$  °C,  $p > 7.4$  MPa) solubilities increase with temperature and pressure (both,  $\text{CO}_2$  in  $\text{H}_2\text{O}$  solubility and  $\text{H}_2\text{O}$  in  $\text{CO}_2$  solubility). Moreover, at low temperatures and high pressures (i.e.  $T < 8$  °C and  $p > 2$  MPa), the  $\text{CO}_2$ - $\text{H}_2\text{O}$  system may form crystalline clathrates ([see Clathrates, in Solutions](#)), with 8 molecules of  $\text{CO}_2$  getting trapped in a cage of 46 water molecules in an endothermic reaction:  $\text{CO}_2 + (46/8)\text{H}_2\text{O} = \text{CO}_2 \cdot 5.75\text{H}_2\text{O} - 60.2 \text{ kJ/mol}$  at 4 °C.

Most non-metal oxides (like  $\text{CO}_2$ ,  $\text{SO}_2$ , or  $\text{NO}_2$ ) dissolve in water forming acid solutions (except for  $\text{CO}$ ,  $\text{NO}$  and  $\text{N}_2\text{O}$  which are neutral). When  $\text{CO}_2$  dissolves in water, a small amount of it gets hydrated to carbonic

acid:  $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$ , that further dissociates to bicarbonate and carbonate ions. Carbon dioxide, bicarbonate ion, and carbonate ion comprise the most important acid-base system in natural waters, and the equilibria between them regulate the pH of all waters: seawater, rainwater, river water, and groundwater. By the way, because of this dissociation, aqueous  $\text{CO}_2$  solutions dissolve much more calcium carbonate than plain water (but solubility decreases with temperature). Other gases that react with water and get ionised (e.g.  $\text{HCl}$ ), have much greater solubilities than those that not. Carbon dioxide and oxygen are very soluble in certain silicone oils and fluorocarbon liquids (also called perfluorocarbons, PFC, when all hydrogen atoms are substituted by fluorine atoms).

The dissolution of carbon-dioxide in water increases the density ( $\text{CO}_2$  molecule being heavier than  $\text{H}_2\text{O}$ ), the rise being  $\partial\rho/\partial y_{\text{CO}_2} = 274 \text{ kg/m}^3$  for both, fresh water and seawater; e.g. if  $\text{CO}_2$  were dissolved in seawater 1 km deep in the ocean (proposed for  $\text{CO}_2$  sequestration), where water conditions may be  $p = 10 \text{ MPa}$ ,  $T = 5 \text{ }^\circ\text{C}$ , and  $y_{\text{salt}} = 35\%$ , density would rise from  $\rho = 1035 \text{ kg/m}^3$  for  $y_{\text{CO}_2} = 0$  to  $\rho = 1050 \text{ kg/m}^3$  for  $y_{\text{CO}_2, \text{sat}} = 0.05$ . There is normally much more carbon dioxide in water than expected by Henry's law (most lakes are supersaturated with  $\text{CO}_2$ ).

In Oceanography, carbon dioxide is measured on line, i.e. while the research ship is under-way, sampling a continuous flow of seawater and spraying it into a chamber where the dissolved  $\text{CO}_2$  gets in equilibrium with out-gassed  $\text{CO}_2$  to the air in the chamber, and then measured by infrared-radiometry (temperature must be measured carefully throughout the process since the solubility of  $\text{CO}_2$  in water is very sensitive to temperature). The measured concentration (the ppm of  $\text{CO}_2$  in the equilibrium chamber air) changes widely with the presence of sources and sinks of  $\text{CO}_2$  (e.g. plankton consumption or up-welling), and the difference with the atmospheric concentration gives an indication of the flux exchanged, that depends on sea surface temperatures, circulating currents, and the biological processes of photosynthesis and respiration.

Exercise 1: Where is more  $\text{CO}_2$ , in air or in water at equilibrium with air?

Sol.: Ostwald solubility of  $\text{CO}_2$  in water at  $15 \text{ }^\circ\text{C}$  is, from [Solubility data for aqueous solutions](#),  $K^{\text{cc}} = c_{\text{liq}}/c_{\text{gas}} = 1.1$ , with  $c$  being concentrations (e.g.  $\text{mol/m}^3$  of solution), meaning there is slightly more amount of  $\text{CO}_2$  per unit volume in the liquid phase than in the gas phase; but it depends on temperature, e.g.  $K^{\text{cc}} = c_{\text{liq}}/c_{\text{gas}} = 0.8$  at  $25 \text{ }^\circ\text{C}$ . On the other hand, solubility also depends on the presence of other solutes (the solubility of  $\text{CO}_2$  in seawater is smaller than in fresh water). In 2002 the average atmospheric concentration is 375 ppm, varying from some 365 ppm in summer due to plant absorption to some 385 ppm in winter due to plant decay release, besides other geographical, altitudinal and seasonal variations. This concentration is equivalent to  $0.015 \text{ mol/m}^3$  or  $0.665 \text{ g/m}^3$ , what corresponds to an equilibrium concentration in the liquid of  $1.1 \cdot 0.015 = 0.016 \text{ mol/m}^3$  or  $0.73 \text{ g/m}^3$  or a molar fraction of  $0.016/55555 = 0.3 \text{ ppm}$ . The concentration of dissolved gases from the air at  $15 \text{ }^\circ\text{C}$  are summarised in Table 5.

Table 5. Equilibrium concentration of dissolved gases from air at  $15 \text{ }^\circ\text{C}$ . The mL/L values refer to the volume as pure gas at  $0 \text{ }^\circ\text{C}$  and  $100 \text{ kPa}$  that would occupy the dissolved gas (by volume of solution).

Air				Solution			
$\text{N}_2$	$\text{O}_2$	Ar	$\text{CO}_2$	$\text{N}_2$	$\text{O}_2$	Ar	$\text{CO}_2$



78%mol	21%mol	1%mol	375	10	5.7	0.3	0.3
			ppm_mol	ppm_mol	ppm_mol	ppm_mol	ppm_mol
32.6	8.8	0.4	0.015	0.59	0.32	0.016	0.016
mol/m <sup>3</sup>	mol/m <sup>3</sup>	mol/m <sup>3</sup>	mol/m <sup>3</sup>	mol/m <sup>3</sup>	mol/m <sup>3</sup>	mol/m <sup>3</sup>	mol/m <sup>3</sup>
754	233	13	0.013	21	10	0.62	0.71
mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
739	199	9.5	0.355	14	7.3	0.38	0.38
mL/L	mL/L	mL/L	mL/L	mL/L	mL/L	mL/L	mL/L

Exercise 2: In air-saturated water, which one is more concentrated: O<sub>2</sub> or CO<sub>2</sub>?

Sol.: From [Solubility data for aqueous solutions](#), at 15 °C, Ostwald solubility is  $K^{cc}=c_{liq}/c_{gas}=1.1$  for CO<sub>2</sub>, i.e. at 15 °C there is always more moles per unit volume in the liquid phase (but at 25 °C it is already the contrary,  $c_{liq}/c_{gas}=0.80$  from [Solubility data for aqueous solutions](#)). For O<sub>2</sub> we get from the same source  $K^{cc}=c_{liq}/c_{gas}=0.037$ , i.e. CO<sub>2</sub> is 30 times more soluble than O<sub>2</sub>, but there is 21% O<sub>2</sub> in air, and only 0.0375% of CO<sub>2</sub>, i.e. there is 560 times more O<sub>2</sub> than CO<sub>2</sub> in the air, thus, there is 20 times more moles per cubic meter of oxygen than of carbon dioxide in air-water equilibrium at 15 °C (0.32 mol/m<sup>3</sup> of O<sub>2</sub> against 0.016 mol/m<sup>3</sup> of CO<sub>2</sub>, from Table 5).

Exercise 3: A bottle of carbonated water has 1 L of liquid and 50 cm<sup>3</sup> of gas when corked at 0 °C and 150 kPa. What pressure it will attain when tempered at 25 °C?

Sol.: First the amount of CO<sub>2</sub> at the time of filling is computed, and then the constancy of the total amount will yield the result, all the time assuming thermodynamic equilibrium. In the gas phase the only important component is CO<sub>2</sub> (air is flushed when filling, and water vapour has approximately a molar fraction of  $x=p^*(T)/p=611/150000=0.2\%$ ); thence,  $n_G=pV/(RT)=0.15 \cdot 10^6 \cdot 50 \cdot 10^{-6}/(8.3 \cdot 273)=3.3 \cdot 10^{-3}$  mol. In the liquid phase, the amount of CO<sub>2</sub> is  $n_L=K^{cp}pV=80 \cdot 0.15 \cdot 10^6 \cdot 0.001=0.120$  mol, where at 0 °C  $K^{cp}=80$  (mol/m<sup>3</sup>)/bar from Table 5. The total amount of CO<sub>2</sub> is then  $n_L+n_G=0.123$  mol, and at 25 °C it is now  $n_L+n_G=K^{cp}pV+pV/(RT)=32 \cdot p \cdot 0.001+p \cdot 50 \cdot 10^{-6}/(8.3 \cdot 298)=0.123$  yielding  $p=353$  kPa.

## Carbonated water

Carbonated water is also known as soda water (from the soda salt, Na<sub>2</sub>CO<sub>3</sub>, initially used to produce it), effervescent water, bubbly water, sparkling water, fizzy water, Seltzer water (from a German town so named), or club soda. It is a solution of carbon dioxide in water, usually containing sodium hydrogen carbonate and other dissolved minerals, and sometimes sterilised by ozone addition or UV radiation. Carbonated water eases the symptoms of dyspepsia (abdominal pain due to indigestion), due to its stirring effect and the anti-acid action of NaHCO<sub>3</sub>, and constipation (infrequent or difficult evacuation of the bowels). The average consumption of carbonated drinks in the West is some 0.1 m<sup>3</sup>/yr (by the way, although in negligible amounts, this contributes to global warming). The taste of carbonated water is dominated by the level of carbonation; the more carbon dioxide gas present, the more acidic the taste

Because carbonated water is so widely used for drinks, some special comments on drinking water are here included. Pure water is an idealised model: the purest water in a laboratory already contains some 0.02 ppm of impurities. Fresh water is the one found in rivers, lakes, some ground sources, and ice caps. Fresh water may be drinkable (known as potable water, with 50..1000 mg/L of total dissolved solids, TDS) or non-

drinkable, according to its natural contaminants, and people adaptation. Salt water, from the seas or from some grounds, is non-drinkable (water with  $<2000$  TDS can be used in agriculture).

There are naturally carbonated waters (issuing through limestone rock), artificially carbonated waters, and naturally carbonated waters with gas added from the same source (i.e. re-injected back after natural separation during extraction), in the same or higher concentration than it was at the origin. Sometimes the adjective 'mineral' is added if  $\text{TDS} > 1000 \text{ mg/L}$  (demineralised usually means  $\text{TDS} < 10 \text{ mg/L}$ ) Non-carbonated waters, named flat waters or plain waters, may come from natural springs, ponds, rivers, desalinisation, icebergs,... or by carbonated waters losing the  $\text{CO}_2$ . Carbonated waters are marketed in glass bottles and in PET (polyethylene terephthalate) bottles.

Soda water invention is credited to Joseph Priestley, that in 1771 wrote on 'how to impregnate water with fixed air... for long voyages'. It seems that Priestley was intrigued about the gas released in a neighbour beer-brewery, which stopped a candle and was heavier than air. He tasted the water trap (hydraulic seal) where he held the  $\text{CO}_2$  produced (he later used mercury to avoid gases dissolving in water) and found it tasting as the rare natural-carbonated water springs. It was believed that the effervescence of the water contained healthful properties, and soon the production of artificial-carbonated water started (first patent was in the 1790s, in London, for Joseph Campbell).

By the way, it was for this invention that Priestley was elected to the French Academy of Sciences in 1772, and received a medal from the Royal Society in 1773. Priestley also isolated most of the common gases; before him, all gases were 'kinds of air'. He isolated 'flammable air' ( $\text{H}_2$ ) in 1766 by dripping a strong acid over a metal. He isolated 'fixed air' ( $\text{CO}_2$ , also called heavy air) in 1771 by dripping a strong acid over limestone. He isolated 'laughing air' ( $\text{N}_2\text{O}$ ) in 1793 by heating ammonium nitrate in the presence of iron filings, and then passing the gas that came off ( $\text{NO}$ ) through water to remove toxic by-products, i.e.  $\text{NH}_4\text{NO}_3 = 2\text{NO} + 2\text{H}_2\text{O}$  and  $2\text{NO} + \text{H}_2\text{O} + \text{Fe} = \text{N}_2\text{O} + \text{Fe}(\text{OH})_2$ . He isolated what he called dephlogisticated air ( $\text{O}_2$ ) in 1774 by anaerobic heating of  $\text{HgO}_2$  (obtained by heating Hg in air). He also isolated  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{SH}_2$  and  $\text{SO}_2$ , amongst other discoveries, as the electrical conductivity of graphite, the graphite eraser (he gave it the name rubber), etc. Priestley was the main defender of phlogiston theory. Phlogisticated air ( $\text{N}_2$ ), was isolated by Rutherford in 1772 by dripping a nitric acid over a metal in presence of air. Mephitic air was synonymous to foul air (non breathable), and the name was applied indistinguishably to  $\text{N}_2$  and  $\text{CO}_2$ .

Carbonated drinks are prepared either naturally by fermentation (or from natural carbonated water sources)), or artificially by forcing carbonation with a  $\text{CO}_2$  supply, and adding flavouring and sweetening substances. Beer, sparkling wines, and cider can get their  $\text{CO}_2$  from their own fermentation process (usually a second fermentation, inside the bottle or in a large tank), or from external sources (air-tight fermentation may yield a  $\text{CO}_2$  pressure of 200..300 kPa). Regular (non-diet) soft drinks are carbonated water sweetened with sucrose, or high fructose corn syrup (HFCS), or some low-calorie sweeteners: saccharine, aspartame (200 times as sweet as sugar), sucralose, etc. The amount of sweetener in a regular soft drink may be in the range 7..14% in weight (e.g. some 100 g of sugar in a litre), and the density may be some  $1080 \text{ kg/m}^3$ , whereas diet soft drinks are only slightly above the density of pure water. A puzzle is sometimes posed as why a diet soft-

drink-can floats on water, in spite of the aluminium container, and a non-diet soft-drink-can sinks on water; the explanation is due to the small gas space left inside to prevent spilling while opening.

The most famous soft drink has been Coca-Cola, a dilute and carbonated caramel-coloured syrup, patented in 1893 after the death in 1888 of its inventor, John Pemberton, an Atlanta pharmacist. The name comes from the syrup that originally contained cocaine from the coca leaf and caffeine from the kola nut. The cocaine was removed in 1905 for health reasons. Robinson also pioneered the idea, in 1899, of selling the Coca Cola syrup under license to bottlers and soda water manufacturers. A typical can of Coca-Cola classic has 3.7 volumes of carbon dioxide dissolved in the product, and is canned at 4 °C, at an equilibrium pressure of 180 kPa (at 20 °C, the pressure inside is 380 kPa). Other soda-waters are canned at 4 °C with just 3 volumes of carbon dioxide, at 120 kPa, that rise to 250 kPa at 20 °C.

Large savings take place if carbonated drinks are prepared at the consumer place, saving the container, transport and storage expenses, because only the trade-named syrup is transported; tap water is used, usually cooled in a vapour-compression-refrigerator, then the appropriate syrup is added (some 30 g per drink), and finally CO<sub>2</sub> is added under pressure (just over 1 g per drink), before flowing out of the tap in the counter. For a non-pressurised liquid supply, like for draft beer, CO<sub>2</sub> is also used to pump the liquid (for non-carbonated drinks, like wine, nitrogen is used; for mildly carbonated beers, a mixture of CO<sub>2</sub> and N<sub>2</sub> can be used).

### ***Kinetic effects***

So much emphasis is put on equilibrium thermodynamics that one may overlook the fact that we live in a non-equilibrium world. Can we have ice at room conditions? Of course, from the time we take it from its equilibrium state inside the refrigerator, until it becomes at equilibrium with room air (i.e. in the form of vapour, not liquid, that is just another transient state, although lasting more).

That is why we can drink carbonated water, since we drink it at room conditions but quickly enough to avoid the dissolved gas to find its equilibrium state with room air (i.e. mostly dissolved in the air and not in the water); the equilibrium content of CO<sub>2</sub> in water at room conditions is unappreciable to taste. To slow down this relaxation process, once the ambient pressure is fixed (we do not consider drinking in pressurised containers), one may:

- Serve and keep the carbonated drink cool.
- Procure the smallest free surface.
- Pour slowly, and avoid shaking and stirring.
- Procure a stable head foam to slow-down out-gassing, because the nearly pure CO<sub>2</sub> buffer layer trapped within the liquid lamella in the foam, reduces mass transfer. The foaming effect when CO<sub>2</sub> is released in plain water is negligible, but increases with sugar content and other solutes (e.g. in coke and beer).

Do not retard the drinking, but do not drink too quickly either, or the bubbling at the throat, oesophagus and mainly at the stomach will cause pain instead of a gentle belch.

Gas solubility in water decreases with the concentration of other solutes, but the fact that when adding sugar or salt to carbonated water it quickly fizzes, is not due to a decrease in solubility but to the sudden increase of nucleation points, which greatly accelerates phase transition in the supersaturated solution.

Question 4. When bottled carbonated water is shaken, it clearly bubbles and the pressure increases (it might even explode), but, does not higher pressure mean more gas solubility?

Answer: The explanation is based on kinetic effects. Shaking has two main effects: greatly increasing interface area by dispersing the unfilled gas space, and producing great pressure jumps due to inertia forces, the latter giving rise to pressure build-up because the sudden expansion with a large interface-area yields some gas release, and because the sudden compression adiabatically heats the bubbles and the dissolving process is retarded. After the shaking stops, the interface area diminishes again, but it takes a lot of time to re-equilibrate to the former value. The main effect of shaking, however, is the spraying on opening the bottle, caused by the dispersed gas bubbles pushing the liquid mass when suddenly expanding. Notice that, if a gentle sloshing were performed instead of an active shaking, some gas from the headspace may be trapped as bubbles within the liquid (usually attached to the walls), without a significant increase in internal pressure (because, at constant temperature, liquid volume and gas volume are invariant in a rigid container), but liquid would be expelled anyway by expansion of the trapped bubbles when opening.

The rate of diffusion of CO<sub>2</sub> out of an open beverage into the atmosphere depends on the instantaneous degree of carbonation; highly carbonated liquids effervesce in the atmosphere, while lightly carbonated liquids outgas slowly and invisibly.

Question 5. Would a recapped bottle of a carbonated drink retain the gas?

Answer: It depends. If the bottle is full, it is gently opened, and soon recapped, it would retain practically all the gas, since only the small amount of gas in the headspace and some slow outgassing while open would be lost. But if the bottle is nearly empty, or if it is shaken, or if it is left open for long, most of the gas will escape and the drink becomes flat.

The principle behind soda siphon dispensers (first patent from 1829, in France) is to avoid air within the bottle, by pushing the carbonated water from the bottom through a pipe (the siphon itself), instead of pouring it, so as to keep the headspace permanently filled with pure CO<sub>2</sub> instead of air, and the only CO<sub>2</sub> that exits the system is that which is dissolved in the beverage, not from the headspace. Bottles are filled with filtered plain water (at 5..10 °C), and pressurised with CO<sub>2</sub> (carbonation, up to 600 kPa, typical 300..400 kPa), at the manufacturer's premises, or by the end user by means of small disposable gas cylinders and special tap fittings. Additionally, before pressurization, a sodium or potassium alkaline compound such as sodium bicarbonate may be added to later reduce acidity due to CO<sub>2</sub>.

Question 6. What is the pressure inside a small CO<sub>2</sub> cartridge of 18 mm in diameter and 66 mm long, made of steel, with a capacity of 10 cm<sup>3</sup>, and a charge of 8 g of CO<sub>2</sub>?

Answer: It depends on temperature. According to NIST data, for a constant density of  $\rho=800 \text{ kg/m}^3$ :

-20 °C	1.99 MPa
-10 °C	2.65 MPa
0 °C	3.49 MPa
10 °C	4.50 MPa
20 °C	6.63 MPa
30 °C	11.45 MPa
40 °C	16.38 MPa

Pinching out the headspace in a flexible bottle after a pour preserves more carbonation in the liquid versus exchanging air into the headspace, but you have to maintain the pinch. If you relax the pinch on the bottle, the dissolved CO<sub>2</sub> will outgas and expand the bottle, creating a pure CO<sub>2</sub> headspace, and losing some carbonation in the liquid.

A typical carbonated soft-drink bottle may freeze at some -9 °C, but not because of the freezing-point depression due to the CO<sub>2</sub> dissolved, but because of the much larger solute-concentration of sweeteners and other additives. The effect of the CO<sub>2</sub> is just  $\Delta T = -K_F m = -K_F K^{cp} p = -1.86 \cdot 0.080 \cdot 3 = -0.45$  °C, with a freezing-point-depression coefficient  $K_F = 1.86$  K/(mol/L) for water (from [cryoscopic tabulations](#)), a CO<sub>2</sub> solubility  $K^{cp} = 80$  (mol/m<sup>3</sup>)/bar from Table 4 above, and an inside pressure  $p = 3$  bar. If the content of a soft-drink bottle freezes, the volume increase may break the glass, or permanently deform a metal can or a plastic bottle, but usually without explosions, since the CO<sub>2</sub> in the ullage gets dissolved as pressure increases. Notice however that even low-sweetened beverages can remain liquid at those low temperatures, but in metastable state; as soon as it is shaken or opened it suddenly freezes.

### ***Application of CO<sub>2</sub> to supercritical extraction of solutes***

The first industrial application of supercritical fluid (SCF) extraction was to get rid of caffeine from coffee and tea, and the extraction of hops and other aromatic herbs. Nowadays, carbon dioxide is becoming a major industrial solvent: it is the second cheapest (after water), non-toxic, non-flammable, and has the most accessible critical point.

A typical SCF-extraction is as follows. Hops, the dried ripe female flowers of the hop plant, is the main flavour used in the brewing of beer, to give it a bitter taste. Compacted hop flowers are put in the extraction vessel, and pressurised with carbon dioxide, adjusting temperature and pressure to supercritical conditions of about 60 °C and 30 MPa. Hop flavours and lipids are extracted as the carbon dioxide flows through the charge of hops, and the solution is depressurised to about 6 MPa in a valve. Because the dissolving power of the carbon dioxide decreases a lot, the solutes precipitate from the gas phase and collect in the separator; the carbon dioxide is recompressed and recycled to the extractor, and the process continues until all the flavours are extracted.

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