"Centrifuge," Encylopedia of Physics. R.A. Besancon (ed.), New York, Reinhold, 93-95 (1966).

a gr efficiency than a
g betw n those reservoirs.
s thus a standard against
gines can be compared.
ource of a number of ideas
study of thermodynamics.
not Cycle. In 1824 Sadi
analyzed a heat engine
perform mechanical work
er temperature to a lower
rk in falling from a higher
suming that since no water
ity, no heat should be lost
ceded by more than 20
ule and Helmholtz on the
e of heat.) In his study he
engine with the following
ated in a continuous cycle
He then showed that it is
operation to obtain work
t-temperature heat source
can be obtained from any
d to reverse it.
notice until 1834 when
d their merit, suggested
he device described above,
r on a P-V diagram. Again
ed until William Thomson
earned of Carnot's work
nemoir. In 1848, Thomson
ot engine could be used to
ale that was absolute in the
depend on what thermo-
sed. It was based on a series
ch c ich did the same
was t first important idea
f the Carnot cycle. In 1850
l of Carnot's ideas through
ron, showed how Carnot's
f heat) could be reconciled
of Joule and Helmholtz
basis of the first law of
was only required that the
at energy, by the amount
an it accepted. Thomson
l the same conclusion[5] in

n his study of the Carnot
physical property he later
s was the second important
fy of the Carnot cycle. In
the principle of Clausius
olve naturally toward states
hich is the second law of
basic point in his theory
d to consider the Carnot
principle was derived. It is
to discuss thermodynamics
nan historically so that the
r plays the important role
t complete discussions are
olumes,[8] but some recent
cycle in detail.[9] An histori-
lementary presentation of
lable.[10]

Robert A. Lufburrow

References

1. Carnot, S., "Reflexions sur la Puissance Motrice du Feu," Paris, Bachelier, 1824. Reprinted (together with references 2 and 4, below) by Dover Publications, New York.
2. Clapeyron, E., reprinted in *Pogg. Ann.*, 59, 446–451, 566–586 (1843). See reference 1.
3. Thomson, W., "Mathematical and Physical Papers," Vol. I, pp. 100–106, Cambridge, University Press, 1882.
4. Clausius, R., *Pogg. Ann.*, 79, 368–397, 500–524 (1850). See reference 1.
5. Thomson, W., *Pogg. Ann.*, 79, 174–316 (1850).
6. Clausius, R., *Pogg. Ann.*, 93, 481–506 (1854); 125, 390 (1865).
7. Boltzmann, L., "Lectures on Gas Theory," (translated by S. G. Brush) Berkeley, University of California Press, 1964.
8. Birtwistle, G., "The Principles of Thermodynamics," Cambridge, University Press, 1925.

Preston, T., "The Theory of Heat," Third edition, London, The Macmillan Co., 1919.

9. Shortley, G. H., and Williams, D. E., "Principles of College Physics," Englewood Cliffs, N. J., Prentice-Hall, Inc., 1959.

Zemansky, M. W., "Heat and Thermodynamics," Fourth edition, New York, McGraw-Hill Book Co., Inc., 1957.

10. Sandfort, J. F., "Heat Engines," Garden City, N.Y., Doubleday & Co., Inc., 1962.

Cross-references: HEAT, THERMODYNAMICS.

CATHODE RAYS. *See* ELECTRON.

CAVITATION

Cavities may form, grow, and collapse in a liquid when variational tensile stresses are superimposed on the prevailing ambient pressure. Pure liquids have theoretical tensile strengths which are estimated on various grounds to be of order 300 to 1500 atmospheres (bars), but the observed tensile strengths of real liquids are much lower. It is presumed, therefore, that the observed tensile strength is a measure of the stress required to enlarge the minute cavities, or cavitation nuclei, which already exist in the liquid rather than the stress required to form new interior interfaces.

The transient cavities formed by tensile stress are unstable and would grow indefinitely if the stress were maintained. After the cavitation nuclei have been expanded to many times their original size, however, they may collapse violently if the stress is reduced or removed. The kinetic energy of the liquid that follows each inwardly collapsing interface becomes highly concentrated as the cavity collapses. If such transient cavities contain very little permanent gas, the peak pressures at collapse may reach thousands of bars, the temperature may reach thousands of degrees, and strong SHOCK WAVES may be radiated to a distance of several cavity radii. Similar cavities formed in saturated liquids will usually contain more gas and their collapse will be less violent, but the peak pressures attained are still sufficient to produce unique mechanical effects such as the corrosion and pitting of metallic surfaces (as in marine propellers and sonar projectors) and the beneficial removal of embedded dirt (as in ultrasonic cleaners). In the latter case, the soil to be removed provides a prolific source of cavitation nuclei at exactly the sites where cavitation is desired.

In hydrodynamic cavitation, the tensile stress is of relatively long duration and plenty of cavitation nuclei are usually available. As a result, cavitation occurs when the total net pressure, or the stagnation pressure, becomes approximately equal to the vapor pressure of the liquid. In acoustic cavitation, the cyclic pressure required to produce cavitation is a function of the frequency, the partial pressure of any dissolved gas, and the population of cavitation nuclei. For frequencies above about 200 kc/sec, the threshold pressure for cavitation increases with the square of the frequency and is almost independent of the degree of gas saturation. For frequencies below 200 kc/sec, the threshold pressure is a function of the partial pressure of the dissolved gas. In saturated liquids, at sound pressures less than a few bars, stable bubbles can grow from cavitation nuclei by the process of rectified diffusion. At higher levels of acoustic excitation, transient cavities can be formed. The threshold sound pressure at which they appear and the violence of their collapse increase as the partial pressure of the dissolved gas is lowered.

The physical nature of the cavitation nucleus, the details of its dynamic growth from submicroscopic to visible size, and the peak pressures and temperatures achieved at the climax of collapse are current topics of active research interest.

F. V. Hunt

Reference

Flynn, H. G., "Cavitation," in Mason, W. P., Ed., "Physical Acoustics," Vol. 1B, Ch. 9, New York, Academic Press, (1964).

Cross-references: ACOUSTICS, ULTRASONICS, LIQUID STATE.

CENTRIFUGE

In most cases, the centrifuge is used for producing sedimentation in fluids, i.e., for the concentration and purification of materials.[1,2] However, it also has been used extensively as an analytical tool for determining particle or molecular weights and sizes [1,3,4]; as a means of determining the strength of materials, and numerous other research and practical problems.[1] Centrifugal fields of 10^9 times gravity have been employed in some experiments. The effective centrifugal force, F, on a particle of mass m and density ρ in a fluid of density ρ' is given by the relation $F = m(\rho - \rho')\omega^2 r/\rho$. This force is opposed by the frictional force of the fluid on the particle. If the speed of sedimentation v is not too large, i.e., the Reynolds number, $v\rho d/\eta$ does not exceed the order of unity, where d is the diameter of the particle and η the coefficient of viscosity, and if the wall effects are neglected, the force of friction f is given by Stokes law. In the case of sedimentation in a liquid for a particle of effective radius a

$$4/3\pi a^3(\rho - \rho')\omega^2 r = 6\pi\eta a v \qquad (1)$$

Since ω, r, ρ, ρ' and η are measurable, a and hence the mass of the particle m can be determined. If we are concerned with a substance of molecular weight M, partial specific volume $\bar{V}$, molar frictional constant f, density of solution ρ, and diffusion constant D, the corresponding equation is[3]

$$M(1 - \bar{V}\rho)\omega^2 r = f\frac{dr}{dt} \qquad (2)$$

For a dilute solution $f = RT/D$ where R is the gas constant and T is the absolute temperature. Hence,

$$v = \frac{dr}{dt} = \frac{MD(1 - \rho\bar{V})}{RT}\omega^2 r \qquad (3)$$

The velocity of sedimentation in a unit field $s = \dfrac{dr/dt}{\omega^2 r}$. If M is known s can be calculated since the other factors in the equation can be determined, or if s is measured, M can be found. The quantity s is called the sedimentation constant and is expressed in Svedberg units $(10^{-13}\ \mathrm{sec})^{-1}$ named in honor of the great pioneer in the field of molecular weight measurement by ultracentrifugation. It is a very important quantity for characterizing a substance in solution.[3,4]

From the above equations alone, one might expect a substance would completely settle out of the solution even with very weak centrifugal fields or gravity alone if the field is applied for sufficient time. This, of course, is not the case because of thermal agitation or BROWNIAN MOTION of the molecules or particles, which gives rise to back diffusion. It can be shown[5] that the average displacement of a particle in time τ due to Brownian motion is $\bar{\Delta}X = \sqrt{2D\tau}$ and for a spherical particle of radius a the average velocity for a time τ is

$$v_\tau = \frac{\bar{\Delta}X}{\tau} = \left(\frac{RT}{N}\frac{1}{3\pi\eta a\tau}\right)^{1/2}$$

where N is the avogadro number. It is clear that when v_τ becomes very much larger than the settling velocity v nothing can sediment out of the solution. When this is the case, it can be shown[3,4] that when equilibrium is reached between sedimentation and back diffusion

$$\log_e\frac{C_1 f_1}{C_2 f_2} = \frac{M(1 - \rho\bar{V})\omega^2(r_2^2 - r_1^2)}{2RT} \qquad (4)$$

where C_1 and f_1 are the concentration and activity coefficient, respectively, at the radius r_1 and C_2 and f_2 are the corresponding quantities at the radius r_2. If the substance is in dilute solution in a sector-shaped centrifuge cell, the weight-average molecular weight M_w is given by[3,4]

$$M_w = \frac{2RT}{(1 - \bar{V}\rho)\omega^2(r_b^2 - r_a^2)}\frac{C_b - C_a}{C_0} \qquad (5)$$

where C_a is the concentration at the radius of the miniscus r_a, C_b is the concentration at the peripheral radius r_b and C_0 is the average concentration.

In deriving the above equations, the effect of electrical charges has been neglected. Usually, the solutions are kept near the isoelectric point, but in many important cases this is not possible. The effects of charges on the above equations have been investigated and in some cases found to be quite large.[3,4,6]

For the separation, purification, or concentration of materials in solution or suspension in a liquid, the centrifugal field is made high enough so that the sedimentation velocity v is appreciable. Equations (1), (2) and (3) are used for estimating the sedimentation. However, these equations hold strictly only when the sedimentation is radial and no turbulence, radial flow, or re-mixing occurs. In most centrifuges used commercially (the cream separator, for example), the liquid flows through the machine during the sedimentation. Any radial flow stream is acted upon by coriolis forces which usually produce mixing. Also, the temperature may not be uniform throughout the sedimenting column. This gives rise to convection if the temperature change produces greater densities near the axis. The driving force which generates thermal convection is roughly proportional to the density gradient times the centrifugal field. Since the latter is large in most centrifuges, the temperature gradient must be small. For a detailed discussion of commercial type centrifuges, both flow-through and batch-type and their operation, reference should be made to Keith and Lavanchy[2] and others.[7] In addition to the use of the centrifuge in industry, it is widely used in research and testing laboratories for the purification and preparation of many different substances. As should be expected from theory, high speed centrifuges do not deactivate most molecular species. Even molecular species such as are often encountered in biology and medicine which are stable only over a few degrees of temperature and a small range of pH are not appreciably effected by a comparatively large centrifugal field. For this reason, high speed centrifuges are widely used in biochemistry and molecular biophysics. The rotors of these high speed centrifuges usually spin in a good vacuum (below 10^{-5} torr) to avoid heating and thermal gradients in the rotor. Such centrifuges with push-button control are readily obtainable commercially.

Analytical Centrifuges. The centrifuge is employed as an analytical tool in one of two general methods.[3,4] The first method makes use of Eqs. (1), (2) and (3), while the second is based upon Eqs. (4) and (5). Sometimes combinations of these two methods are used.[3,4] When a centrifuge is employed in analytical work, it is usually called an ultracentrifuge.[3] The first method has been more widely used, at least, until recently. In this method, comparatively high rotor speeds with the resulting high centrifugal fields are employed in order to produce an easily measurable rate of sedimentation v. The value of v is usually measured by optical means and s is computed. The high centrifugal field quickly produces a small density gradient across the centrifuge cell which stabilizes the sedimenting column. As a result, very high accuracy in rotor temperature and speed control are not mandatory, although desirable. Another important factor is that the time of centrifugation is comparatively short (~hours). Furthermore, if the solution contains a number of molecular species, each species sediments at its characteristic rate and the value of its sedimentation constant s is easily determined. The effect of ionic charge and the pH of the solution on the values of s and the effect of concentration of one species on the other during sedimentation, etc., have been quantitatively investigated, both theoretically and experimentally, by a number of workers.[3,4,7,8] The rate-of-sedimentation method has the disadvantage of not being an absolute method and requiring a knowledge of the diffusion constant D as well as the shape of the sedimenting particle or molecule. Often these factors introduce large uncertainties in the value of M.

The second method, known as the equilibrium method, is based upon Eqs. (4) and (5). It is a reliable, absolute method since it is based upon equilibrium thermodynamics. Also, it is not necessary to know the value of the diffusion constant or the shape of the molecule to get the value of M. As pointed out above, no actual sedimentation on the walls of the centrifuge cell occurs in the equilibrium method so that the rotor speed and resulting centrifugal field are relatively low. Consequently, if the concentration of the solute in the solvent is low, the density gradient in the cell is small which in turn makes the sedimenting column sensitive to small rotor temperature and rotor speed variations. Recently, considerable effort has gone into designing and adapting ultracentrifuges to equilibrium measurements and the centrifuging time has been reduced from several days to several hours.[1,3,4,9] An over-all precision in the measurement of the molecular weights of between 0.1 and 1 per cent over the molecular weight range from 100 to 10^8 has been obtained.[9] The determination of molecular weight distributions, etc., can be carried out.

Gas Centrifuging. The centrifuge has been used for removing fine particles suspended in gases and for the separation of gaseous mixtures. The fine particles sediment on the inner wall of the centrifuge where they are removed while the centrifuge is spinning or when it is stopped. In the separation of gases and vapors a tubular type centrifuge is usually used in which the gases flow out of the centrifuge in a light and heavy fraction. Such tubular centrifuges have been used for the separation of isotopes.[7,10-12]

When a centrifugal field is applied to a gas it sets up a pressure gradient

$$dp/dr = M\rho\omega^2 r = \frac{Mp}{RT}\omega^2 r$$

where ρ is the molar density and p the pressure. In a binary mixture of two ideal gases with molecular weights M_1 and M_2 and with mole fraction N of the lighter gas of molecular weight M_1, it has been shown both theoretically and experimentally that at equilibrium where r_2 is the radius of the inside periphery of the centrifuge tube

$$\left(\frac{N}{1-N}\right)_{r=r_2} = \left(\frac{N}{1-N}\right)_{r=0} \exp\frac{(M_2 - M_1)\omega^2 r_2^2}{2RT}$$

In order to determine the value of a centrifuge or cascade of centrifuges for separating isotopes or gases, it is customary to calculate the separative work or separative power which is a measure of separation produced by a single centrifuge or a number of centrifuges used in a cascade. Cohen[13] has shown that the separative power of a single centrifuge is

$$\delta U = \frac{Dp}{RT}\left[\frac{(M_2 - M_1)\omega^2 r_2^2}{2RT}\right]^2 \frac{\pi Z f}{2} \text{ moles/sec}$$

where Z is the centrifuge tube length, D the diffusion constant, and f the flow factor which depends upon the flow pattern in the centrifuge and has a maximum value of one. The number of centrifuges required to carry out a given amount of separation in a time t is $\frac{U}{t\delta U}$ where U is the total separative work and is defined as[14]

$$U = W(2N_w - 1)\log_e\frac{N_w}{1-N_w} P(2N_p - 1)$$
$$\log_e\frac{N_p}{1-N_p} - F(2N_F - 1)\log_e\frac{N_F}{1-N_F}$$

where F is the number of moles of feed material of mole fraction N_F and W and N_w and P and N_p are the corresponding values for the waste and the product. It will be observed that the effectiveness of a centrifuge for gaseous or isotope separation increases directly as the fourth power of the peripheral speed, as the length of the centrifuge, and as $(M_2 - M_1)^2$.

J. W. BEAMS

References

1. Beams, J. W., *Science*, 120, 619 (1954); *Physics Today*, 12, 20 (1959) (see for other references).
2. Keith, F. W., Jr., and Lavanchy, A. C., in Kirk-Othmen's "Encyclopedia of Chemical Technology," second edition, New York, Interscience Publishers, 1964.
3. Svedberg, T., and Pederson, K. O., "The Ultracentrifuge," Clarendon Press, 1940.
4. Schachman, H. K., "Ultracentrifugation in Biochemistry," New York, Academic Press, 1959.