# Glycerine: an overview

terms
technical data
properties
performance



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# Introduction

Glycerine is an material of outstanding utility with many areas of application. The key to glycerine's technical versatility is a unique combination of physical and chemical properties, ready compatibility with many other substances, and easy handling. Glycerine is also virtually nontoxic to human health and to the environment.

Physically, glycerine is a water-soluble, clear, almost colorless, odorless, viscous, hygroscopic liquid with a high boiling point. Chemically, glycerine is a trihydric alcohol, capable of being reacted as an alcohol yet stable under most conditions. With such an uncommon blend of properties, glycerine finds application among a broad diversity of end uses. In some, glycerine is the material of choice because of its physical characteristics, while other uses rely on glycerine's chemical properties.

Glycerine has over 1500 known end uses. Major, or large volume, applications include some dozen different categories that range from foods to urethane foams. About 300 million pounds of glycerine are used annually in the United States. Other leading areas of consumption are the European Community (ca. 350 million (pounds) and Japan (ca. 100 million pounds). Worldwide consumption is estimated at about 1.1-1.2 billion pounds per year and is expected to rise as industrialization progresses in less developed countries.<sup>1</sup>

The origin, chemical structure, and utility of glycerine have been known for little more than two centuries. Glycerine was accidentally discovered in 1779 by K. W. Scheele, the Swedish chemist, while he was heating a mixture of olive oil and litharge (lead monoxide). Scheele called glycerine the "sweet principle of fat."<sup>2</sup> Scheele later established that other metals and glycerides produce the same chemical reaction which yields glycerine and soap and, in 1783, he published a description of his method of preparation in *Transactions of the Royal Academy of Sweden*. Scheele's method was used to produce glycerine commercially for some years.<sup>3</sup>

The immense potential of glycerine went largely untapped until M. E. Chevreul, the French pioneer investigator of fats and oils, studied it early in the 19th Century. Chevreul named Scheele's "sweet principle of fat" glycerine in 1811 after the Greek word, *glykys*, meaning sweet.<sup>4</sup> In 1823 Chevreul obtained the first patent for a new way to produce fatty acids from fats treated with an alkali, which included the recovery of glycerine released during the process.<sup>5</sup> Thirteen years later, Pelouze, another French investigator, announced the empirical formula as  $C_3H_8O_3$ .<sup>5</sup> The accepted structural formula,  $C_3H_5(OH)_3$ , was established by Berthelot and Lucca almost fifty years later in 1883.<sup>5</sup>

Glycerine did not become economically or industrially significant until Alfred Nobel invented dynamite in 1866 after twenty years of experimentation. Nobel's invention successfully stabilized trinitroglycerin, a highly explosive compound, by absorption on kieselguhr, which permitted safe handling and transportation.<sup>6</sup>

The invention of dynamite and the later invention of blasting gelatin, also by Nobel, thrust glycerine into economic and military importance. Dynamite became

discovered in 1779

#### technical history

the first worldwide technical application for glycerine and through it, glycerine had an enormous influence on industrial development. Dynamite unlocked immense underground deposits of minerals and fuels from which much chemical<sup>a</sup> and technical progress later sprang. Huge amounts of dynamite were also consumed in building railroads and in other construction projects. A notable example is the Panama Canal, which required about 8,000 tons of the explosive, an amount equivalent to about 4,000 tons of glycerine.<sup>7</sup>

Glycerine plays an important role in nature, too. It is one of nature's wonders and is closely linked to the life processes themselves, being a component of all living cells. It occurs naturally in wines, beers, bread, and other fermentation products of grains and sugars. Glycerine is found abundantly in nature in the form of triglycerides, the chemical combinations of glycerine and fatty acids which are the principal constituents of almost all vegetable and animal fats and oils. Triglycerides in plants originate from carbohydrates produced photosynthetically from water and carbon dioxide. In animals, they appear to be formed through assimilation of triglycerides present in foods and through biosynthesis from other food substances, especially carbohydrates. The chemistry of triglyceride synthesis in both plants and animals is highly complex and still not completely understood.

Industrially, glycerine is a product of fats and oils that have been saponified, hydrolysed, or transesterified, which is recovered in a crude state and then purified by distillation or ion exchange, or it is synthesized from propylene. Glycerine may also be produced by fermentation or hydrogenolysis of carbohydrates, but these routes currently are not utilized industrially; however, they were used during World Wars I and II in Europe.<sup>8</sup>

Glycerine, whether recovered from triglycerides or synthesized, is almost always consumed as a refined or purified substance. Producers of glycerine, whether natural or synthetic, strictly monitor each stage of processing from pretreatment of crude or precursor materials to finishing to assure high purity and uniform quality.

abundant

# production methods

# **Glycerine Definitions and Grades**

#### glycerine

glycerin

#### glycerol

terminology product types GLYCERINE is the most commonly used commercial name in the United States for products whose principal component is glycerol, but it is frequently spelled *GLYCERIN*. More precisely, however, *glycerin* applies to *purified* commercial products containing 95% or more of glycerol. GLYCEROL (CAS registry No. 56-81-5; NIOSH No. MA8050000) refers to the chemical compound 1,2,3-propanetriol, CH<sub>2</sub> OHCHOHCH<sub>2</sub>OH, and to the anhydrous content in a glycerine product or in a formulation. Concentration is by weight, normally obtained by conversion from specific gravity measurements made at either 20/20°C or 25/25°C.

Outside the United States, especially in Europe, *glycerol* is a much more broadly applied term, being employed much in the same manner as *glycerine* is in the United States. *Glycerol* in European usage may pertain to any grade of glycerine, including crude.

Glycerine is an important article of domestic and international commerce. The designations for the various grades of glycerine used in the United States and in Europe are prevalent worldwide because these areas are the leaders in glycerine production and consumption. Accordingly, reference is made to European nomenclature for similar U.S. grades or types of commercially available glycerine where possible in the discussion that follows.

USP GLYCERIN(E) is a clear, almost colorless product for uses requiring glycerine of high purity with taste and odor characteristics desirable for pharmaceutical and food purposes. Its glycerol content in aqueous solution is "not less than 95%," as defined by a specific gravity of not less than 1.249 at 25/25°C. The designation USP is an abbreviation of U.S. Pharmacopeia and signifies that the glycerine thus designated meets or exceeds the standards established in U.S. Pharmacopeia (USP XXII, 1990) monograph, Glycerin. The USP designation has official legal status in the United States since the U.S. Pharmacopeia has been incorporated by reference in various statutes and regulations governing drug and medical practices, of which the federal Food, Drug, and Cosmetic Act is the most significant. USP glycerine is commonly available commercially at anhydrous glycerol content levels of 96%, 99.0% and 99.5%. Concentrations above 99.5% are also available commercially. The European equivalent of USP in the United States is *PH.EUR.*, commonly followed by a percentage indicating glycerol content (e.g., PH.EUR.99.5%). The PH.EUR label signifys that the glycerine so designated meets the specifications of the European Pharmacopoeia II (1986), as determined by analytical methods given in the same compendium. The European Pharmacopeia obtains in the European Economic Community (EEC), i.e., it supersedes the national pharmacopeias of member countries.

CP GLYCERINE or chemically pure glycerine is generally understood to be of the same quality or grade as USP glycerine, but this term is considered generic in the United States because it does not reflect compliance with any official quality requirements or specifications as does the USP designation. In Europe, the term CP glycerine is understood to conform with the standard specification for CHEMICALLY PURE GLYCEROL, BS 2625:1979 issued by the British Standards Institution. A notation in this standard states that glycerol meeting the criteria of BS 2625:1979 will also comply with the requirements of the European Pharmacopeia.

FOOD GRADE GLYCERINE in the United States meets the requirements outlined in the monograph *Glycerin* contained in the *Food Chemicals Codex* prepared by the Committee on Food Protection of the National Research Council. Food grade requirements are similar to USP standards. Within the European Economic Community, glycerine for use in food products must comply with Council Directive 78/663/EEC which specifies the standards of purity for emulsifiers, stabilizers, thickeners, and gelling agents for use in foods.

HIGH GRAVITY GLYCERINE is a designation used in the United States for a commercial grade of glycerine that is clear, almost colorless and conforms to Federal Specification 0-G-491C issued November 14, 1983 by the General Services Administration. This product also conforms to *Standard Specification for High-Gravity Glycerin, D-1257*, issued by the American Society for Testing and Materials (ASTM). This grade must contain not less than 98.7% glycerol based on specific gravity of 1.2587 minimum at 25/25°C. It is commonly supplied at not less than 99.0% concentration (specific gravity minimum 1.2595 at 25/25°C). ASTM Standard Specification D-1257 is also recognized in Europe to define a grade of glycerine for industrial purposes.

DYNAMITE GLYCERINE in the United States meets all the High Gravity grade specifications except color, but it cannot be darker than the Federal Color Standard. In Europe, glycerine for use in explosives is defined by *Specification 21D* for dynamite glycerine issued by the Nobel Explosives Company Ltd. The British Standards Institution has also issued a standard specification for this grade of glycerine as *British Standard Specification for Dynamite Glycerol, BS 2624: 1979.* 

SAPONIFICATION (88%) CRUDE AND SOAP LYE (80%) CRUDE are generic terms used in the United States to designate grades of crude glycerine recovered from triglycerides. The percentages refer to the glycerol content of the crudes. Saponification crude is a concentrate of the "sweetwater" from fat hydrolysis or "splitting." In Europe, the term for this type of crude is HYDROLYSER CRUDE GLYCEROL. Hydrolyser crude glycerol contains not less than 88% glycerol and conforms to British Standard Specification BS 2622: 1979. Soap lye crude is the product of the spent lye of the soap kettle, after concentration in a desalting evaporator. In Europe, crude glycerine of this derivation is called SOAP LYE CRUDE GLYCEROL. It contains not less than 80.0% glycerol and meets the requirements given in British Standard Specification for Soap Lye Crude Glycerol BS 2621: 1979. Although important articles of commerce, these grades of glycerine are almost never consumed in any process except refining.

## **Glycerine Properties and Performance**

Industrial consumption of glycerine in the United States per year is in the neighborhood of 300 million pounds, mainly in such large volume applications as urethane foams, alkyd resins, drugs, foods, tobacco, dentifrices, and cosmetics. Products requiring smaller quantities of glycerine, but in which glycerine's function is equally essential, number in the hundreds. Among them are such diverse materials as antifreeze solutions, soldering fluxes, cements, textiles, and waxes. Glycerine's versatility is a tribute to its unique combination of chemical and physical properties.

Chemically, glycerine is a trihydric alcohol which is very stable under most conditions, but which can be reacted to form many derivatives. Physically, it is a clear, almost colorless, viscous, high-boiling liquid miscible with water and alcohol, and like these materials, a good solvent. At low temperatures, glycerine tends to supercool, rather than crystallize. Water solutions of glycerine resist freezing, a property responsible for glycerine's use as a permanent antifreeze in cooling systems. Among its most valuable attributes are hygroscopicity, or the ability to absorb moisture from the atmosphere, and low vapor pressure, a combination that produces outstanding permanent humectancy and plasticity.

Glycerine is virtually nontoxic<sup>9</sup> in the digestive system and non-irritating to the skin and sensitive membranes, except in very high concentrations when a dehydrating effect is noted. It is also odorless and has a warm sweet taste.

Some of glycerine's uses depend on its chemical properties, one such example being the manufacture of urethane polymers. Others make use of one or more of its physical characteristics, such as toothpaste and moisturizing cream. Quite often, however, the choice of glycerine in either type of application may depend upon secondary factors such as virtual nontoxicity and freedom from disagreeable odor or taste. Esters used as food emulsifiers are outstanding examples of chemical applications for glycerine where nontoxicity of reactants is essential. Similarly, food wraps and bottle cap liners in intimate contact with food and beverages require a plasticizer-humectant that cannot be a source of contamination, and hence glycerine is a common choice.

The ability to meet a nontoxicity requirement plus the availability of bonus properties in addition to those associated with its principal function in a product make glycerine a prized ingredient among chemists and formulators. In a hand cream, for example, glycerine may be incorporated as an ingredient because of its outstanding humectancy. Simultaneously, glycerine's emollient qualities may improve the efficacy of the formulation, its viscosity may give the product a very desirable body, its antifreeze qualities may afford necessary protection in shipping and storage—all in addition to the main function of maintaining the moisture content of the product at the proper level.

Glycerine is a trihydric alcohol and, like other alcohols, forms esters, ethers, amines, aldehydes, and compounds analogous to metallic alcoholates. But, because of its multiple hydroxyl groups, it can be reacted to form an unusually large number

trihydric alcohol

clear liquid, almost colorless

of derivatives. One, two or three of these hydroxyls can be replaced with other chemical groups, thus permitting the synthesis of many different derivatives with properties designed for specific applications.

Structurally, glycerine has two primary and one secondary hydroxyl groups. The primary hydroxyl groups generally are more reactive than the secondary group and, of the two primary groups, the first to react usually does so more readily than the second. In any reaction, however, the second and third hydroxyls will react to some extent before all the most reactive groups are exhausted. Reaction mixtures thus contain isomers and products of different degrees of reaction, with the relative amounts of each reflecting their ease of formation.

Glycerine is stable to atmospheric oxidation under ordinary conditions, but can be readily oxidized by other oxidants. Partial oxidation is generally difficult to control to give a large yield of a single product.

Applications in which glycerine's versatility as a chemical is exploited account for approximately half of the glycerine consumed by industry. The most important industrial class of derivatives is esters, which are formed by reacting glycerine with acids, usually at high temperatures. Among these are alkyd resins of long chain fatty acids.

Glycerine possess a unique combination of physical properties. Although chemical reactivity and versatility make glycerine one of the basic building blocks of the chemical industry, each year large volumes go into non-chemical uses. In these processes and products, glycerine's function—as a plasticizer, humectant, solvent, bodying agent, lubricant, etc.—is based on one or more of its physical properties, some of which properties are summarized in Table I. Generally, no chemical combination should take place in such applications; thus, chemical stability is a prerequisite in the choice of a material to impart specific physical properties. Glycerine meets this requirement, for it is highly stable under ordinary conditions of storage and use, remaining free from objectionable color, odor or taste with the passage of time. Glycerine solutions subject to heat, however, should *not* be processed or stored in iron- or copper-containing vessels unless inhibitors are present, since iron and copper salts will catalyze oxidation of glycerine under such conditions.

HYGROSCOPICITY, the ability to attract moisture from the air and hold it, is one of the most valuable properties of glycerine. It is the basis for its use as a humectant and as a conditioning agent in many applications where both the glycerine and the water it holds act as plasticizers. The net effect is to give products the desired softness, flexibility, creaminess, and shelf life.

On exposure to air, glycerine at a given concentration gains or loses moisture until it reaches another concentration that is in equilibrium with the moisture (relative humidity) in the surrounding atmosphere. The equilibrium concentration is relatively independent of temperature change within normal atmospheric limits

#### three hydroxyl groups

attracts and holds water from air

#### Table I Properties of Glycerine

Molecular Weight 92.09 1.2636 (20°C); 1.2620 (25°C) Specific Gravity (in air) Vapor Pressure 0.0025 mm (50°C) 290°C (760 mm) **Boiling** Point Boiling Points at Low Pressure: 152.0°C (5 mm) 166.1°C (10 mm) 181.3°C (20 mm) 190.9°C (30 mm) 198.0°C (40 mm) Melting Point 18.17°C Freezing Point (eutectic) (66.7% glycerol solution) -46.5°C Viscosity 1499 centipoises (20°C) Specific Heat 0.5795 cal pr gm deg (26°C) **Refractive Index** (N<sub>d</sub><sup>20</sup>)1.47399 Flash Point (99% glycerol) 177°C (99% glycerol) 204°C Fire Point Auto Ignition Point 523°C (on platinum) (on glass) 429°C Heat of Combustion 397.0 Kcal per mole Food-Energy Value 4.32 Kcal per gram Surface Tension 63.4 dynes cm (20°C) 58.6 dynes cm (90°C) 51.9 dynes cm (150°C) Sound Transmission 1923 m/sec (20°C) Coefficient of Thermal Expansion 0.0006115 (15-25°C Temperature interval) (Gravimetric) 0.000610 (20-25°C Temperature interval) Thermal Conductivity 0.000691 cal cm deg/sec (0°C) Molar Heat of Solution 1381 cal  $0.07 \times 10^{-12}$ **Dissociation Constant** Dielectric Constant 42.48 (25°C; current frequency =  $0.57 \times 10^6$  cycles sec) Specific Conductivity  $5.6 \times 10^{-8}$  reciprocal ohms (11.7°C) Compressibility  $21.1 \times 10^{-6}$  cc per atm pr cc (28.5°C)

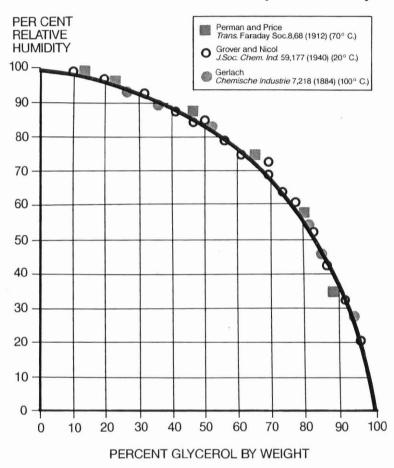
provided that a constant relative humidity is maintained. A number of determinations have been made of the relative humidity maintained over glycerine solutions, as shown plotted in Figure 1. The curve in Figure 1 can be used to determine the relationship between relative humidity and the equilibrium concentration of glycerol (or water) expressed as a percent held by an aqueous solution of glycerine when the transfer of water vapor between air and the solution is in balance.

How soon equilibrium between glycerine and the surrounding atmosphere is attained depends largely on the character of the exposed product—its area, viscosity, gel structure, and other factors affecting the rate of migration of the water within it—as well as on the relative humidity of the surrounding atmosphere.

It may take several days for equilibrium to be reached when glycerine is distributed in a mass such as a glue or gelatin, which is also true of other humectants as well. However, if glycerine is present as a thin film as it is when used to soften textile or paper fibers, equilibrium is reached within a few minutes.

Figure 1

# RELATIVE HUMIDITY OVER AQUEOUS GLYCERIN (20°-10° C)

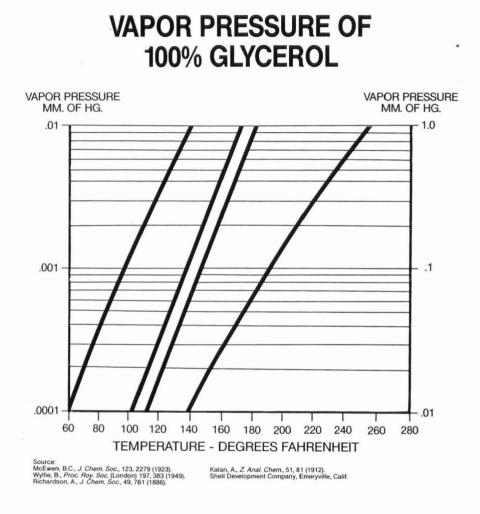


LOW VOLATILITY or low vapor pressure allows for the permanency of glycerine in products. Low vapor pressure is closely allied to hygroscopicity in glycerine's effectiveness as a humectant. As is apparent in Figures 2 and 3, glycerine is practically nonvolatile at normal use temperatures. Moreover, between 0°C and 70°C, changes in temperature have little effect on the relative vapor pressure of glycerine solutions.

In common with other alcohols, glycerine has a lower vapor pressure than might be expected from its molecular weight. The relatively low vapor pressure is characteristic of alcohols, water, and other polar compounds, and is the result of molecular association. Glycerine causes a greater reduction in the vapor pressure of water than can be accounted for by its molecular concentration, an effect that is attributable to the formation of hydrates.

remains permanent in products

Figure 2



The ability of glycerine to persist or "stay put" in products is particularly important when large areas are exposed for long periods of time. Such conditions can result in significant losses of relatively volatile humectants and occur most generally with films and fibers.

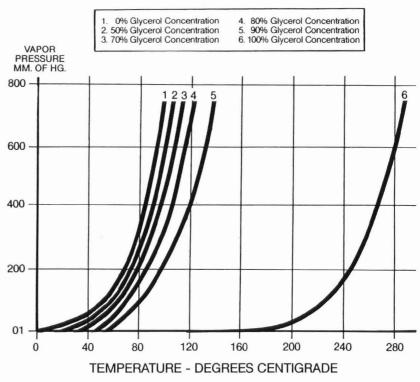
A DIRECT PLASTICIZING EFFECT is produced in most applications for glycerine as a humectant-plasticizer because glycerine and water act together to promote softness and flexibility and to prevent drying out. These applications include personal products such as cosmetic creams, lotions, capsules, and dentifrices, edibles such as candy and cough drops, cigarette tobacco, and industrial materials such as cellophane, paper products, cork and gasket compounds, glues, textiles, and printing supplies.

The plasticizing effect, however, is *more* than merely the result of glycerine's holding water. Even when conditions are such that little or no water is present, the glycerine itself may perform a direct plasticizing function. This action is in part a

#### promotes softness and flexibility

Figure 3

# VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF GYCERINE



Data by Mayer-Bugstron, Z. Oel.-Fette-Ind., 44, 417-8 (1920)

consequence of a combination of properties such as solvent power, low volatility, and noncrystallinity as well as hygroscopicity. It depends, too, on the molecular size and structure of glycerine relative to the molecular structure or space lattice of the material that is being treated. The lubricating action of glycerine on the materials can also be a factor. For these reasons, glycerine will frequently have a much greater conditioning effect on materials than equal concentrations of other compounds with similar hygroscopic characteristics, but with different molecular orientation.

SOLVENT POWER and SOLUBILITY have caused glycerine to be regarded as one of the most valuable compounding ingredients for the formulator. Besides functioning as a suitable solvent for the active principles in a formulation, the easy compatibility of glycerine with many other substances affords the formulator a wide choice of ingredients.

Because of its hydroxyl groups, glycerine has solubility characteristics similar to those of water and simple aliphatic alcohols. It is a good solvent for many

solubility characteristics

# Table IISolubility of Various Compounds in Glycerol

	Glycerol		Sol. In	
	Concen-	Tempera-	Parts per	
	tration	ture	100 Parts	
Substance	% Weight	°C.	of Solvent	Ref. No.
Alum	•	15	40	5
Ammonium carbonate		15	20	6
Ammonium chloride	•	15	20.06	6
Atropine	•	15	3	4
Benzoic acid	98.5		2	3
Boric acid	98.5	20	24.80	3
Calcium hydroxide	35	25	1.3	1
Calcium hypophosphite	99.04	20	2.5	7
Calcium sulfate	•	15	5.17	6
Codeine hydrochloride	99.04	20	11.1	7
Ethyl ether	99.04	20	0.65	7
Ferrous sulfate		15	25	5
Guaiacol	99.04	20	13.1	7
Iodine	95	15	2	6
Iodoform	+	15	0.12	2
Iron and potassium tartrate		15	8	4
Iron lactate	*	15	16	4
Morphine acetate	99.04	15	20	4
Novocaine	99.04	20	11.2	7
Phenacetin	99.04	20	0.47	7
Phenol	*	20	276.4	7
Potassium iodide	98.5	15	39.72	4
Quinine sulfate	*		1.32	3
Salicin	*	15	12.5	4
Sodium bicarbonate	*	15	8.06	6
Sodium tetraborate (borax)	*	15	60	6
Sodium carbonate (crystals)		15	98.3	6
Tannic acid	*	15	48.8	5
Tartar emetic	*	15	5.5	4
Urea	*	15	50	4
Zinc chloride	*	15	49.87	6
Zinc iodide	+	15	39.78	6

\*Glycerol concentration not specified, probably 95 to 100 per cent.

1. Cameron F.K., and Patten, H.E., J. Phys. Chem. 15, 67-72 (1911).

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7. Roborgh, J.A., Pharm. Weekblad, 64, 1205-1209 (1927).

industrial compounds, pharmaceutical preparations, and flavor extracts as shown in Table II. Many substances such as iodine, bromine, tannin, alkaloids, thymol, phenol, mercuric chloride, and boric acids are more soluble in glycerine than in water, and thus glycerine is used to prepare highly concentrated solutions of these materials. With vanillin and some similar materials, glycerine forms supersaturated solutions, thus making possible solutions of high concentrations.

Commonly used substances with which glycerine is completely miscible include methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, secondary butyl alcohol, tertiary amyl alcohol, ethylene glycol, propylene glycol, trimethylene glycol, and phenol. It is also completely miscible with ethylene glycol monomethyl ether.

Glycerine's solubility in acetone is 5% by weight, and in ethyl acetate, 9%. It is only sparingly soluble in dioxane and ethyl either, and is practically insoluble in higher alcohols, fatty oils, and hydrocarbons and chlorinated solvents such as hexane, benzene and chloroform.

The miscibility of aliphatic and aromatic hydrocarbons with glycerine is increased by introducing hydroxyl and amine groups into their structure, but is decreased by the introduction of alkyl groups. Heterocyclic compounds such as pyridine, quinoline, piperidine, and alpha-picoline, which contain a nitrogen atom in the ring, are generally miscible with glycerine.<sup>10</sup>

Detailed studies of multi-component systems containing glycerine have been made over a long history of use in formulations. Micibility and solubility data for such systems as glycerine-tertiary amyl alcohol-water, glycerine-phenol-water, glycerine-alcohol-water, glycerine-sucrose-water and glycerine-benzene-ethyl alcohol have been published.<sup>11</sup> The availability of such information greatly helps simplify the work of the chemist in incorporating glycerine in formulations.

COMPATIBILITY, while not strictly a scientific concept, is an important consideration for formulators who require assurance that an ingredient added to a mixture or solution for one purpose will not interfere with the stability or activity of the other constituents. In general, the ability to act together harmoniously with other materials can be expected in a chemical like glycerine with its related properties of high solvent power, solubility, micibility, and stability.

The compatibility of glycerine with a wide range of other materials has been established through long use and empirical tests. Glycerine has been shown to be a highly compatible material, especially in cosmetic and pharmaceutical products which may incorporate many compounds of varying chemical structure and properties.

Pure glycerine is stable to atmospheric oxygen under normal conditions of use or storage. However, at higher temperatures, oxidation may be promoted by iron and copper catalysts. For this reason, processing or storing glycerine solutions in iron- or copper-containing vessels without the use of inhibitors should be avoided.

HIGH VISCOSITY is one of the most distinctive characteristics of glycerine. This quality is of value in a number of mechanical applications for glycerine such as a hydraulic fluid or a special lubricant, in laboratory studies of fluid flow phenomena, and in viscosimeter calibrations, where aqueous solutions of glycerine are used as standards. But, by far, the most important commercial use for glycerine on the basis of its viscosity is as thickening or bodying agent for liquid preparations,

#### very miscible

highly compatible

thickener

syrups, emulsions, and gels.

At normal temperatures, glycerine remains a viscous liquid up to 100% concentration. Thus, it is available for use over a wide range of viscosities without crystallization difficulties. Likewise, at low temperatures, concentrated glycerine solutions tend to supercool as high-viscosity fluids. When glycerine supercools, its viscosity increases slowly at first, and then rapidly, until it becomes glassy at about  $-89^{\circ}$ C.

Viscosities of various concentrations of glycerine in water at various temperatures are shown in Table III. In addition to these values, data on the viscosity of glycerine-alcohol-water solutions and of glycerine in combination with glucose, sugar solutions, and various salts are available in the literature.<sup>12</sup>

The results of using glycerine for bodying action in a formulation may not always be proportional to the amount of glycerine added or to its viscosity in a pure state because the other ingredients present may also be exerting an influence. The effect of glycerine on the viscosity of a liquid cream, for example, is likely to be proportional to the amount added, and increases progressively with additions. But, in the case of a semisolid cream, the addition of glycerine may increase body up to a certain concentration beyond which further additions result in a decrease in viscosity.

Glyc. %					Temperatu	ıre (°C)					
Wt.	0	10	20	30	40	50	60	70	80	90	100
0*	1.792	1.308	1.005	0.8007	0.6560	0.5494	0.4688	0.4061	0.3565	0.3165	0.2838
10	2.44	1.74	1.31	1.03	0.826	0.680	0.575	0.500			_
20	3.44	2.41	1.76	1.35	1.07	0.879	0.731	0.635		_	
30	5.14	3.49	2.50	1.87	1.46	1.16	0.956	0.816	0.690		_
40	8.25	5.37	3.72	2.72	2.07	1.62	1.30	1.09	0.918	0.763	0.668
50	14.6	9.01	6.00	4.21	3.10	2.37	1.86	1.53	1.25	1.05	0.910
60	29.9	17.4	10.8	7.19	5.08	3.76	2.85	2.29	1.84	1.52	1.28
65	45.7	25.3	15.2	9.85	6.80	4.89	3.66	2.91	2.28	1.86	1.55
67	55.5	29.9	17.7	11.3	7.73	5.50	4.09	3.23	2.50	2.03	1.68
70	76	38.8	22.5	14.1	9.40	6.61	4.86	3.78	2.90	2.34	1.93
75	132	65.2	35.5	21.2	13.6	9.25	6.61	5.01	3.80	3.00	2.43
80	255	116	60.1	33.9	20.8	13.6	9.42	6.94	5.13	4.03	3.18
85	540	223	109	58	33.5	21.2	14.2	10.0	7.28	5.52	4.24
90	1310	498	219	109	60.0	35.5	22.5	15.5	11.0	7.93	6.00
91	1590	592	259	127	68.1	39.8	25.1	17.1	11.9	8.62	6.40
92	1950	729	310	147	78.3	44.8	28.0	19.0	13.1	9.46	6.82
93	2400	860	367	172	89	51.5	31.6	21.2	14.4	10.3	7.54
94	2930	1040	437	202	105	58.4	35.4	23.6	15.8	11.2	8.19
95	3690	1270	523	237	121	67.0	39.9	26.4	17.5	12.4	9.08
96	4600	1580	624	281	142	77.8	45.4	29.7	19.6	13.6	10.1
97	5770	1950	765	340	166	88.9	51.9	33.6	21.9	15.1	10.9
98	7370	2460	939	409	196	104	59.8	38.5	24.8	17.0	12.2
99	9420	3090	1150	500	235	122	69.1	43.6	27.8	19.0	13.3
100	12070	3900	1410	612	284	142	81.3	50.6	31.9	21.3	14.8

#### Table III Viscosity of Aqueous Glycerol Solutions Centipoises

\*Viscosity of water taken from Properties of Ordinary Water-Substance, N.E. Dorsey, p. 184, New York (1940)

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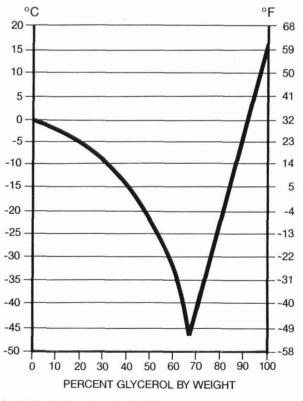
bodying agent

Glycerine is EASY-TO-USE. Glycerine is a liquid at high concentrations and at the temperatures generally encountered in storage and use. That undesirable crys-tallization which adversely affects the appearance of a product cannot occur with glycerine at room temperature. If, for example, glycerine is exposed on the threads of a bottle or cap even in a dry atmosphere, it will not become "gritty" like a crystallizing sugar.

The freezing points of various concentrations of glycerine are shown in Figure 4. These values explain why pure glycerine, with a freezing point of approximately 18°C, is seldom seen in the crystalline state. As is evident from these data, even the small amounts of water usually present in most formulations depress the freezing point of glycerine. A combination of two parts of glycerine to one part of water forms a eutectic mixture which freezes at  $-46.5^{\circ}$ C.

#### Figure 4

# FREEZING POINTS OF GLYCEROL-WATER SOLUTIONS



Lane, L. B., Ind. Eng. Chem., 17, 924 (1925).

#### presents no crystallization problems

#### antifreeze properties

Because of such antifreeze properties, glycerine was the first permanent-type antifreeze for automobile radiator cooling systems. Although later replaced by ethylene glycol in this application, combinations of an alcohol or a glycol and glycerine are still employed for this purpose. Glycerine-water and glycerine-alcohol solutions, however, are used in some refrigeration systems and in quick freezing of foods. Here glycerine's virtual nontoxicity combines with its antifreeze properties to make it the coolant of choice.

Since glycerine is a liquid, it is convenient to handle, which is another bonus quality of particular advantage to many industrial consumers who use glycerine in large quantities. In some applications, glycerine is easily pumped from the tank car to the storage tank, and from there metered to the reactor as required, compared to the handling required when solid polyols are used. Glycerine also has an added advantage in that it can be measured either by volume or by weight. Therefore, systems using other liquid ingredient materials can stay entirely in the "liquid phase."

The virtual NONTOXICITY of glycerine as an ingredient in foods and pharmaceuticals has been established through generations of safe use and by supporting data.<sup>13,14</sup>

Glycerine occurs naturally in foods, both in a combined form as in fats and in a free state as in fermentation products like beer and wine. With a diet of 100 grams of fat per day, the human body would absorb and metabolize 10 grams of glycerine as glycerides. When metabolized, glycerine yields roughly the same caloric food value

as glucose or starch.<sup>15</sup>

#### **GRAS** substance

virtually nontoxic

Glycerine, i.e., *glycerin*, was initially accorded GRAS status (generally recognized as safe) as a miscellaneous substance by the U.S. Food and Drug Administration (FDA) in 1959. Subsequently, in 1961, it was reclassified as a miscellaneous and general purpose food additive. Under a regulation FDA promulgated in 1977, it was reclassified and recodified as a multiple purpose GRAS food substance. Glycerine was also first listed as GRAS as a substance migrating to food from paper and paperboard products used in food packaging in a regulation published in 1961. Glycerine is currently listed as GRAS in the *Code of Federal Regulations* (CFR) as a multiple purpose GRAS food substance (21CFR 182.1320) and as a substance migrating from paper and paperboard products: (21CFR 182.90) for use in certain food packaging materials.<sup>16</sup>

The FDA proposed reaffirmation of glycerine as GRAS as a direct human food ingredient in February 1983 as part of a comprehensive review of human food ingredients classified as GRAS or subject to prior sanction.<sup>17</sup> There has been no official FDA action with respect to the proposed reaffirmation of the GRAS status of glycerine since it was promulgated. The FDA review of the GRAS list is, by its very nature, a lengthy procedure and one that involves many food ingredients. Glycerine

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has demonstrated over many years that it is essentially nontoxic as an ingestive substance and thus, it apparently has *not* been accorded a high priority in the FDA GRAS review process.

Glycerol is also virtually nontoxic to the environment, which is another plus factor with respect to ordinary plant operations and the kinds of problems usually associated with accidental spills. Its aquatic toxicity is insignificant. Glycerine's TLm96 value, or the concentration that will kill 50% of the exposed organisms in 96 hours, is over 1000 mg/L.<sup>18</sup>

Glycerine may be used on every part of the epidermis, including mucous membranes. When diluted to a concentration below 50%, it acts as an emollient and demulcent, finding important applications in ointments and lotions. Preparations for the most sensitive areas of the body—antiseptic, vaginal, nasal, analgesic, dermatological, and burn ointments and jellies—are commonly made of watersoluble bases compounded with glycerine. Glycerine, too, is one of the most widely used ingredients in medical prescriptions. Only water may exceed glycerine in its range of applications.

A predominantly sweet taste producing a pleasant sensation of warmth in the mouth is another of glycerine's assets. Studies have shown that it is from 55 to 75 percent as sweet as sucrose, with the relative sweetness depending on the concentration tested.<sup>19</sup>

As a sweetening agent, glycerine makes many medicinal preparations palatable, which ordinarily would be unpleasant or less pleasant to swallow. In cough remedies, for example, it makes the mixture more pleasing to the taste while simultaneously soothing the mucous membranes.

In such products as dentrifices and chewing gum, glycerine imparts a desirable degree of sweetness without clashing with the other flavor elements. Perfumes or flavors remain "true to type," with no fragrance or flavor change resulting from the presence of glycerine. It also tends to offset the harshness or bite of alcoholic (ethyl) content.

sweet-tasting

emollient

# Applications

#### Food and Beverages

In foods and beverages, glycerine functions as a humectant, solvent, sweetener, and preservative. It acts as a solvent for flavors and food colors in soft drinks and confections and as a humectant and softening agent in candy, cakes, and casings for meats and cheese. Glycerine is also used in dry pet foods to help retain moisture and enhance palatability.

Another important, but indirect, use of glycerine in food processing is represented by *monoglycerides*, the glycerol esters of fatty acids, which are emulsifiers and stabilizers for many products. Edible monoglycerides help maintain moisture balance in a product and permit richer formulations with longer shelf life when added to margarine to increase plasticity and to dough mixes to promote dispersion of fat. Monoglycerides are also used in salad dressings, frozen desserts, candy, and food coatings.

#### Drugs

Glycerine is one of the most widely used ingredients in drugs and pharmaceuticals. It functions as a solvent, moistener, humectant, and bodying agent in tinctures, elixirs, ointments, and syrups.<sup>20</sup> Capsules for medicinal use, which are plasticized with glycerine, are another important application. Other well known uses include suppositories, ear infection remedies, anesthetics, cough remedies, lozenges, gargles, and vehicles for antibiotics and antiseptics.

Medically, glycerine serves as an emollient and demulcent in preparations used on the skin and as an osmotic diuretic to manage cerebral edema, reduce cerebrospinal pressure, and lower intraocular pressure.<sup>20</sup> A derivative, nitroglycerine, is a coronary vasodilator used to treat angina.

In veterinary medicine, glycerine has been used as a source of glucose in bovine ketosis and nitroglycerine as a treatment for bronchial asthma in dogs.<sup>21</sup>

#### **Cosmetics and Toiletries**

Glycerine is widely used in cosmetics and other toiletry applications, being virtually nontoxic, non-irritating, and odorless. It functions as a humectant, vehicle, and emollient. Glycerine is a major toothpaste ingredient, preventing drying out and hardening in the tube and around the cap threads or at the opening of the pumptype dispenser. Other uses include skin creams and lotions, shaving preparations, deodorants, and make up. Glycerol esters of fatty acids, an important class of glycerine derivatives, are utilized as emulsifiers in creams and lotions and as replacements for waxes in lipstick, in mascara, and in other non-greasy emulsions.

properties in action

#### Tobacco

A glycerine content of about 3% keeps tobacco moist and soft to prevent breaking and crumbling during processing and to ensure freshness in packaged cigarettes and other tobacco products. Sheet-formed cigar tobacco is plasticized with glycerine. It also adds flavor to chewing and pipe tobaccos. Triacetin (glycerol triacetate) acts as a plasticizer for cellulose acetate in the manufacture of cigarette filter-tips.

#### **Surface Coating Resins**

Alkyds are an important class of resins used in surface coatings. Glycerine, because of its chemical versatility and process advantages, is a standard component in the manufacture of these resins. Alkyd resins produced from glycerine may readily be modified to meet a wide range of coating applications and demanding conditions.

#### **Paper and Printing**

Glycerine is used in the manufacture of papers as a plasticizer/humectant and lubricant. In addition to the softening effect of retained moisture, it also reduces shrinkage. It is likewise useful with other ingredients in specialty treatments such as grease-proofing. Since many papers are used as food wrappers or in sanitary products, glycerine's essential nontoxicity, freedom from odor, and stability meet other important quality requirements. Glycerine also finds extensive use in ink manufacture, especially the alkyd resins which are an important constituent of many printing inks.

#### Lubrication

Glycerine plays an important role in the lubricants used in many applications because of its stability over a broad range of temperatures and pressures. In addition, the virtually nontoxic character of glycerine makes it suitable for lubrication of food and other machinery where product purity is of paramount importance.

#### **Textiles**

Glycerine is a textile conditioning agent used widely in lubricating, sizing, and softening yarn and fabric. Its effectiveness in these and similar applications is due mainly to its viscosity and hygroscopicity. Glycerine is also successfully used to lubricate many kinds of fibers in spinning, twist setting, knitting, and weaving operations.

#### **Rubber and Plastics**

Glycerine's main use in the rubber industry is for its lubricating action on rubber. In the plastics industry, glycerine is used as a plasticizer and lubricant.

#### **Urethane Polymers**

In this application, glycerine serves as the fundamental building block in polyethers for urethane foams. The flexible foams resulting from the processes utilizing glycerine have superior properties with respect to humid aging and resilience. Glycerine-based polyethers have also found some application in rigid foams and, particularly, in urethane coatings.

#### **Electrical and Electronics**

Glycerine is widely employed for the manufacture of electrolytes for electrolytic condensers used in radios and neon lights and in processes for electrodeposition and treatment of metals. Electronic applications are mostly of a proprietary nature, although one use in this field is associated with the production of computers.

#### Nitration

The nitration of glycerol to yield nitroglycerine is probably the most well-known application. Dynamite, as it is manufactured today, is a mixture based on an explosive compound, usually nitroglycerine, mixed with an absorbent, usually diatomaceous earth, in a proportion of about 3:1 nitroglycerine to the absorbent.<sup>22</sup>

Nitroglycerine is also used as a cardiovascular agent, functioning as a vasodilator in coronary spasm and as an antianginal agent.<sup>22</sup> It has also been used therapeutically for canine bronchial asthma.<sup>22</sup>

#### **Other Uses**

There are many other applications for glycerine. These uses are small in volume and include such applications as photography, laboratory use, cell preservation, and gas drying among many others too numerous to list. Applications for some glycerine derivatives have also been discussed. It is worth noting that they include ethers, esters, acetates, and alcohol substitution products. New uses, many proprietary, for glycerine and its derivatives come under constant development as technology progresses.

Producers of glycerine are excellent sources of information about applications for glycerine. They stand ready to provide technical assistance to formulators and others regarding current and new applications.

# Specifications

Specifications are precise, written descriptions of the physical and chemical quality requirements of a particular grade or type of glycerine product and of the analytical methods to be used in determining product compliance with designated parameters.

Specifications deal with product quality issues in various ways, depending upon the grade or kind of crude or refined glycerine being addressed and the kinds of materials that may be associated with it. Quality requirements may include parameters for glycerol content, specific gravity or relative density, characteristics of color, odor, and flavor, fatty acid and ester content, chlorinated compounds, chloride, sulfate, arsenic, heavy metals, ignition residue, and other aspects of the product as appropriate. Likewise, the specifications stipulate the analytical methods which are to be used in assaying each given requirement. The test methods may be incorporated in the specifications directly or by reference.

Standard specifications for various grades of glycerine have been issued by some national standards institutions and professional and industry organizations. The organized, definitive character of standard specifications makes them very useful in commerce. Specifications involved in a commercial transaction are basically subject to agreement between buyer and seller. While standard specifications have proven very helpful commercially, the parties to a transaction sometimes prefer to develop their own criteria or adapt existing ones to their needs.

In the United States, the specifications used in commerce include the requirements of the *U.S. Pharmacopoeia* (USP) monograph, *Glycerin*, and those of the *Foods Chemicals Codex*, prepared by the National Academy of Science (National Academy Press, Third Edition, 1981). Also important are the specifications for reagent grade glycerine issued by the American Chemical Society (ACS) and those of the Cosmetic, Toiletry, and Fragrance Association (CTFA) for glycerine in cosmetic and toiletry applications. The American Society for Testing and Materials (ASTM) and the General Services Administration (GSA) have both issued standard specifications for high gravity glycerine.

In the international area, specifications for various grades of glycerine are available from national standards institutions and from national pharmacopoeias in the case of refined glycerine. Within the European Economic Community (EEC), the counterpart of USP glycerine is provided for by the glycerine specifications included in the *European Pharmacopoeia II* (1986). The *European Pharmacopoeia* is published in accordance with the *Convention on the elaboration of a European Pharmacopoeia*, under the auspices of the Council of Europe (Partial Agreement) (European Treaty Series No. 50). It supercedes the national pharmacopoeias in the EEC member countries. Glycerine for use in foods within the EEC is governed by *Directive 78/663/EEC*, issued by the Council of Europe, which mandates the quality criteria for emulsifiers, stabilizers, thickeners, and gelling agents. The main source of information on European standard specifications for glycerine is the Association Europeenne des Producteurs d'Acides Gras (APAG), an international organization of

describes product quality requirements

stipulates analytical methods

sources of standard specifications

and in steam tracing of piping. Storage tanks may have insulated external steam coils or may have internal coils for circulation of low pressure steam or hot water.

PIPING should be stainless steel, aluminum or galvanized iron. Valves and pumps should be all bronze, cast iron and bronze trim, or stainless steel. Piping should also be self-draining.

The SIZE OF PUMPS for unloading process feed and circulating stored glycerine to maintain it at desired temperatures depends upon individual requirements. A 50-gpm pump will unload a tank car of warm glycerine in about four hours.

## Safety

safety tips

Long experience in research, development, and production has demonstrated that glycerine is one of the safest industrial chemical materials. Despite an enviable safety record, the only appropriate way to handle glycerine is in accordance with sound industrial, maintenance, and safety practices.

#### Human Exposure

Glycerine is essentially nontoxic by ingestion and harmless to the skin. In the event of eye contact, the eye should immediately be rinsed gently with tepid (body temperature) water. However, accidents involving splash burns of hot liquor to the eye or skin should be treated by a physician.

#### Fire and Explosion

Glycerine has a high flash point  $(350^{\circ}\text{F or } 177^{\circ}\text{C at } 99.0\% \text{ glycerol concentration})$  and a fire point of glycerine of  $400^{\circ}\text{F}$  ( $204^{\circ}\text{C}$  at 99.0% concentration). Fire hazard is low even when exposed to heat or flame, but glycerine is still combustible.

Glycerine can react violently in contact with certain strong oxidizing agents such as acetic anhydride, (aniline + nitrobenzene), calcium hypochlorite, chromium peroxide, chromium trioxide, ( $F_2$  + PbO), (HClO<sub>4</sub> + PbO), potassium chlorate, potassium permanganate, potassium peroxide, silver perchlorate, and sodium hydride.<sup>23</sup>

If glycerine catches fire, it should be treated with water, dry powder or carbon dioxide fog.<sup>24</sup> The toxic hazard from the products of combustion is slight, but use of a canister mask is suggested.<sup>25</sup>

#### Environmental

Glycerine has no harmful impact on the environment due to a massive release or spill. In water, it does not appear to have any effect other than an oxygen demand arising from biodegradation which occurs at a moderate rate.<sup>26</sup> Aquatic toxicity as measured by TLm96, defined as the concentration that will kill 50% of the exposed organisms in 96 hours, is over 1000 mg/L,<sup>27</sup> a level which is insignificant.

CAUTION strong oxidizing agents

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#### Appendix

Sources of Standard Specifications and/or Test Methods for Glycerine

AMERICAN CHEMICAL SOCIETY 1155 16th Street, N.W. Washington, D.C. 20036 USA Tel: (202) 872-4600

AMERICAN OIL CHEMISTS' SOCIETY Box 3489 1608 Broadmoor Drive Champaign, Illinois 61826-3489 USA Fax: (217) 351-8091 Telex: 4938651 AOCS UI

AMERICAN SOCIETY FOR TESTING AND MATERIALS 1916 Race Street Philadelphia, Pennsylvania 19103-1187 USA Tel: (215) 299-5400 Fax: (215) 977-9679

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THE UNITED STATES PHARMACOPEIAL CONVENTION, INC. 12601 Twinbrook Parkway Rockville, MD 20852 USA

# Specific Gravity and Per Cent Glycerol by Weight

### Apparent Specific Gravity

#### Apparent Specific Gravity

	15/15°C	15.5/15.5°C	20/20°C	25/25°C		15/15°C	15.5/15.5°C	20/20°C	25/25°C
Chusanal 9/					Chucanal 9/				
Glycerol %	1 00557	1 00500	1 00000	1 00001	Glycerol %	1 10005	4 40070	4 400 45	4 40700
100	1.26557	1.26532	1.26362	1.26201	50	1.12985	1.12970	1.12845	1.12720
99	1.26300	1.26275	1.26105	1.25945	49	1.12710	1.12695	1.12570	1.12450
98	1.26045		1.25845	1.25685	48	1.12440	1.12425	1.12300	1.12185
97	1.25785	1.25760	1.25585	1.25425	47	1.12165	1.12150	1.12030	1.11915
96	1.25525	1.25500	1.25330	1.25165	46	1.11890	1.11880	1.11760	1.11650
05	1 05070	1.05045	1 05075	1 04010	45	1 11000	4 4 4 0 0 5	4 44 400	1 11000
95	1.25270	1.25245 1.24980	1.25075	1.24910	45	1.11620	1.11605	1.11490	1.11380
94	1.25005		1.24810	1.24645	44	1.11345	1.11335	1.11220	1.11115
93	1.24740	1.24715	1.24545	1.24380	43	1.11075	1.11060	1.10950	1.10845
92	1.24475	1.24450	1.24280	1.24115	42	1.10800	1.10790	1.10680	1.10575
91	1.24210	1.24185	1.24020	1.23850	41	1.10525	1.10515	1.10410	1.10310
90	1.23950	1.23920	1.23755	1.23585	40	1.10255	1.10245	1.10135	1.10040
89	1.23680	1.23655	1.23490	1.23320	39	1.09985	1.09975	1.09870	1.09775
88	1.23415	1.23390	1.23220	1.23055	38	1.09715	1.09705	1.09605	1.09510
87	1.23150	1.23120	1.22955	1.22790	37	1.09445	1.09435	1.09335	1.09245
86	1.22885	1.22855	1.22690	1.22520	36	1.09175	1.09165	1.09070	1.08980
85	1.22620	1.22590	1.22420	1.22255	35	1.08905	1.08895	1.08805	1.08715
84	1.22355	1.22325	1.22155	1.21990	34	1.08635	1.08625	1.08535	1.08455
83	1.22090	1.22055	1.21890	1.21720	33	1.08365	1.08355	1.08270	1.08190
82	1.21820	1.21790	1.21620	1.21455	32	1.08100	1.08085	1.08005	1.07925
81	1.21555	1.21525	1.21355	1.21190	31	1.07830	1.07815	1.07735	1.07660
80	1.21290	1.21260	1.21090	1.20925	30	1.07560	1.07545	1.07470	1.07395
79	1.21015	1.20985	1.20815	1.20655	29	1.07295	1.07285	1.07210	1.07135
78	1.20740	1.20710	1.20540	1.20380	28	1.07035	1.07025	1.06950	1.06880
77	1.20465	1.20440	1.20270	1.20110	27	1.06770	1.06760	1.06690	1.06625
76	1.20190	1.20165	1.19995	1.19840	26	1.06510	1.06500	1.06435	1.06370
75	1.19915	1.19890	1.19720	1.19565	25	1.06250	1.06240	1.06175	1.06115
74	1.19640	1.19615	1.19450	1.19295	24	1.05985	1.05980	1.05915	1.05860
73	1.19365	1.19340	1.19175	1.19025	23	1.05725	1.05715	1.05655	1.05605
72	1.19090	1.19070	1.18900	1.18755	22	1.05460	1.05455	1.05400	1.05350
71	1.18815	1.18795	1.18630	1.18480	21	1.05200	1.05195	1.05140	1.05095
	1.10010	1.10700	1.10000	1.10400		1.00200	1.00100	1.00140	1.00000
70	1.18540	1.18520	1.18355	1.18210	20	1.04935	1.04935	1.04880	1.04840
69	1.18260	1.18240	1.18080	1.17935	19	1.04685	1.04680	1.04630	1.04590
68	1.17985	1.17965	1.17805	1.17660	18	1.04435	1.04430	1.04380	1.04345
67	1.17705	1.17685	1.17530	1.17385	17	1.04180	1.04180	1.04135	1.04100
66	1.17430	1.17410	1.17255	1.17110	16	1.03930	1.03925	1.03885	1.03850
65	1.17155	1.17130	1.16980	1.16835	15	1.03675	1.03675	1.03635	1.03605
64	1.16875	1.16855	1.16705	1.16560	14	1.03425	1.03420	1.03390	1.03360
63	1.16600	1.16575	1.16430	1.16285	13	1.03175	1.03170	1.03140	1.03110
62	1.16320	1.16300	1.16155	1.16010	12	1.02920	1.02920	1.02890	1.02865
61	1.16045	1.16020	1.15875	1.15735	11	1.02670	1.02665	1.02640	1.02620
60	1.15770	1.15745	1.15605	1.15460	10	1.02415	1.02415	1.02395	1.02370
59	1.15490	1.15465	1.15325	1.15185	9	1.02175	1.02175	1.02155	1.02135
58	1.15210	1.15190	1.15050	1.14915	8	1.01935	1.01930	1.01915	1.01900
57	1.14935	1.14910	1.14775	1.14640	7	1.01690	1.01690	1.01675	1.01660
56	1.14655	1.14635	1.14500	1.14365	6	1.01450	1.01450	1.01435	1.01425
0			1 1 1 2 2 2 2	4 4 4 4 4 4 4 4		1 0 1 0 1 0			
55	1.14375	1.14355	1.14220	1.14090	5 4	1.01210	1.01205	1.01195	1.01185
54	1.14100	1.14080	1.13945	1.13815	4	1.00965	1.00965	1.00955	1.00950
53	1.13820	1.13800	1.13670	1.13540	3	1.00725	1.00725	1.00720	1.00710
52	1.13540	1.13525	1.13395	1.13265	2	1.00485	1.00485	1.00480	1.00475
51	1.13265	1.13245	1.13120	1.12995	1	1.00240	1.00240	1.00240	1.00235

SOURCE: Bosart, L.W., and Snoddy, A.O., Ind. Eng. Chem., 19, 506-510 (1927).