

Chemical and Physical Properties of Hydrocarbons

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1. INTRODUCTION

Hydrocarbons, the principal compounds of oil and natural gas, have to be chemically altered to make useful products and materials. This is carried out by changes in the chemical and physical structure. Such differences in molecular structure, even though the empirical formula can remain the same, cause significant differences in the properties and behavior of hydrocarbons and hydrocarbon fuels.

Hydrocarbons are the simplest organic compounds and contain only carbon and hydrogen but they can be straight chain or branched chain (Stoker, 2008) with the same empirical formula but showing differences in properties.

A hydrocarbon is any chemical compound that consists only of the elements carbon (C) and hydrogen (H) (Chapter 1). All hydrocarbons contain a carbon-chain skeleton and have hydrogen atoms attached to the carbon skeleton. Most hydrocarbons are readily combustible (Chapter 10). Almost all usable supplies of hydrocarbons are currently obtained from petroleum and natural gas.

The hydrocarbons can be divided into various homologous series (Chapter 1). Each member of such a series shows a definite relationship in its structural formula to the members preceding and following it, and there is

generally some regularity in changes in physical properties of successive members of a series.

The alkanes are a homologous series of saturated aliphatic hydrocarbons. The first and simplest member of this series is methane, CH_4 ; the series is sometimes called the methane series. Each successive member of a homologous series of hydrocarbons has one more carbon and two more hydrogen atoms in its molecule than the preceding member. The second alkane is ethane, C_2H_6 , and the third is propane, C_3H_8 . Alkanes have the general formula $\text{C}_n\text{H}_{2n+2}$ (where n is an integer greater than or equal to 1). Other homologous series of hydrocarbons include the alkenes and the alkynes (Chapter 1).

Hydrocarbon mixtures are composed of hydrocarbons, benzine, and petroleum ether.

Benzine (which should not be confused with *benzene* – an aromatic hydrocarbon), also known as petroleum ether, is a hydrocarbon mixture and is a mixture of alkanes, such as pentane, hexane, and heptane.

Petroleum ether is obtained from petroleum refineries as the portion of the distillate which is intermediate between the low boiling naphtha and the higher boiling kerosene. It has a specific gravity of between 0.6 and 0.8 depending on its composition. Petroleum ether should not be confused with the class of organic compounds called *ethers*.

The *physical properties* of the unsaturated hydrocarbons are pretty much like those of the saturated hydrocarbons. The molecules are essentially *non-polar* and thus relatively *insoluble in water*. Their intermolecular bonds are the weak *van der Waals bonds*. *Melting points and boiling points* for the small molecules are fairly low. The larger and heavier the molecules are, the higher their melting and boiling points are.

Finally, the chemical and physical properties of hydrocarbons are also dictated by stereochemistry (Olah and Molnár, 2003). Both types of properties are related and the proportions of the stereoisomers serve to influence the chemical and/or physical properties.

2. STEREOCHEMISTRY

Stereochemistry, a sub-discipline of chemistry, involves the study of the relative spatial arrangement of atoms within molecules. Stereochemistry is an important facet of chemistry and the study of stereochemical effects spans the entire range of chemical and physical properties (Eliel and Wilen, 1994; Eliel et al., 2001).

Stereochemistry (molecular geometry) refers to the three-dimensional arrangement of a molecule. Organic molecules of the same chemical formula can have their atoms arranged differently in space, often leading to significantly different chemical properties.

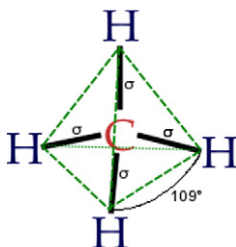
Isomers are those types of compounds which have the same chemical formula but different atomic arrangements in space. Isomers can be divided into stereoisomers and structural isomers. Stereoisomers change their atomic arrangement as a result of changes in pressure or temperature. All bonds and types of bonds (single, double, triple) are conserved in the same original fashion, however.

Structural isomers have atoms which change their position in a molecule. One example is a linear compound (where all of the carbon atoms are lined up in linear fashion), compared to the same chemical formula compound with a shorter linear structure and branching (chain isomerism). Functional groups can change their position (functional isomerism), or can differ from another isomer in the position of a double or triple bond (bond isomerism).

The number of carbon atoms in a hydrocarbon determines how many forms that compound can take. The number of possible isomers in a compound rises as the number of carbon atoms it contains rises.

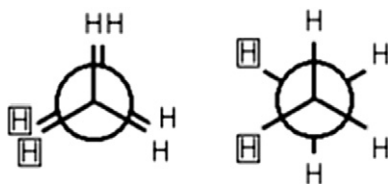
The molecular structure of the alkanes directly affects their physical and chemical characteristics. It is derived from the electron configuration of carbon (Chapter 1), which has four valence electrons. The carbon atoms in alkanes are always sp^3 hybridized, that is to say that the valence electrons are said to be in four equivalent orbitals derived from the combination of the 2s orbital and the three 2p orbitals. These orbitals, which have identical energies, are arranged spatially in the form of a tetrahedron, the angle of $\cos^{-1}(-1/3) \approx 109.47^\circ$ between them.

An alkane molecule has only C–H and C–C single bonds. The former result from the overlap of an sp^3 -orbital of carbon with the 1s-orbital of a hydrogen, the latter by the overlap of two sp^3 -orbitals on different carbon atoms. The bond lengths amount to 1.09×10^{-10} m for a C–H bond and 1.54×10^{-10} m for a C–C bond. The tetrahedral structure of methane is:

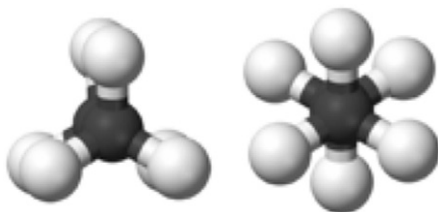


The spatial arrangement of the bonds is similar to that of the four sp^3 -orbitals – they are tetrahedrally arranged, with an angle of 109.47° between them. Structural formulas that represent the bonds as being at right angles to one another, while both common and useful, do not correspond with the reality.

The structural formula and the bond angles are not usually sufficient to completely describe the geometry of a molecule. There is a further degree of freedom for each carbon–carbon bond: the torsion angle between the atoms or groups bound to the atoms at each end of the bond. The spatial arrangement described by the torsion angles of the molecule is known as its conformation. Newman projections of the two conformations of ethane, eclipsed on the left, staggered on the right, are:



Ball-and-stick models of the two rotamers of ethane are:



Ethane forms the simplest case for studying the conformation of alkanes, as there is only one C–C bond. If one looks down the axis of the C–C bond, one will see the so-called Newman projection. The hydrogen atoms on both the front and rear carbon atoms have an angle of 120° between them, resulting from the projection of the base of the tetrahedron onto a flat plane. However, the torsion angle between a given hydrogen atom attached to the front carbon and a given hydrogen atom attached to the rear carbon can vary freely between 0° and 360° . This is a consequence of the free rotation about a carbon–carbon single bond. Despite this apparent freedom, only two limiting conformations are important: eclipsed conformation and staggered conformation.

The two conformations, also known as rotamers, differ in energy: the staggered conformation is 12.6 kJ/mol lower in energy (more stable) than the eclipsed conformation (the least stable).

This difference in energy between the two conformations, known as the torsion energy, is low compared to the thermal energy of an ethane molecule at ambient temperature. There is constant rotation about the C–C bond. The time taken for an ethane molecule to pass from one staggered conformation to the next, equivalent to the rotation of one CH₃-group by 120° relative to the other, is of the order of 10⁻¹¹ seconds.

The case of higher-molecular-weight alkanes is more complex but based on similar principles, with the anti-periplanar conformation always being the most favored around each carbon–carbon bond. For this reason, alkanes are usually shown in a zigzag arrangement in diagrams or in models. The actual structure will always differ somewhat from these idealized forms, as the differences in energy between the conformations are small compared to the thermal energy of the molecules: alkane molecules have no fixed structural form, whatever the models may suggest.

The geometry of acetylene is linear but the structure of ethylene and propylene are different because the two double-bonded carbons are sp² hybridized and therefore are trigonal planar.

There is no free rotation of a double or triple bond. Therefore, many alkenes and alkynes exhibit *geometric isomerism*. For example, *cis*-2-butene and *trans*-2-butene are geometric isomers – *cis* means *on the same side*, while *trans* means *on opposite sides* – and refer to (in the case of the butylenes) the relative position of the methyl groups.

3. MOLECULAR WEIGHT

The *molecular mass* of a substance is the mass of one molecule of that substance, in unified atomic mass units (Drews, 1998; Speight, 2001, 2002). This is distinct from the *relative molecular mass* of a molecule, frequently referred to by the term *molecular weight*, which is the ratio of the mass of that molecule to 1/12th of the mass of carbon 12 and is a dimensionless number. Thus, it is incorrect to express relative molecular mass (molecular weight) in Daltons (Da) or kilo-Daltons (kDa) (unfortunately, the terms molecular weight and molecular mass have been confused on numerous websites, which often state that molecular weight was used in the past as another term for molecular mass).

Generally, hydrocarbons of low molecular weight, e.g., methane, ethane, and propane, are gases; those of intermediate molecular weight, e.g., hexane, heptane, and octane, are liquids; and those of high molecular weight, e.g., eicosane (C₂₀H₄₂) and polyethylene, are solids. Paraffin is a mixture of high-molecular-weight alkanes.

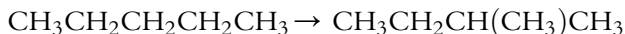
For well-defined molecular structures, such as hydrocarbons, the molecular weight is calculated from the atomic masses of the constituents. In the case of the hydrocarbon fuels, the average molecular weight can be measured by the following methods: vapor pressure osmometry, freezing point depression, boiling point elevation, gel permeation chromatography and non-fragmenting mass spectrometry (Speight, 2007). The different methods have advantages and drawbacks, which make them suitable for different molecular weight ranges.

Vapor pressure osmometry, freezing point depression, and boiling point elevation are all based on the assumption that the change in the corresponding properties (vapor pressure, freezing point, and boiling point) in a pure solvent caused by introduction of a solute at low concentration is directly proportional to the concentration of the solute. Gel permeation chromatography, also known as size exclusion chromatography, takes advantage of the difference in elution time between molecules with different sizes. Non-fragmenting mass spectrometry principally provides detailed information of the hydrocarbon types, the formulas and the concentration of all the components in a fraction.

4. CHEMICAL PROPERTIES

Chemical properties of hydrocarbons describe the *potential* of hydrocarbons to undergo chemical change or reaction by virtue of the hydrocarbon structure (Howard and Meylan, 1997; Yaws, 1999).

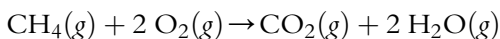
Chemical change results in the hydrocarbon yielding a product that may be entirely different in composition to the starting hydrocarbon – the exception is the isomerization reaction where a straight-chain hydrocarbon is converted to a branched-chain hydrocarbon. In such a case, the composition of the product is not changed over the composition of the starting material but the structure has been changed:



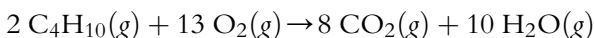
n-pentane, C₅H₁₂ isopentane, C₅H₁₂

Thus, since a chemical change alters the composition of the original matter, the expected outcome is usually the presence of different elements or compounds at the end of the chemical change. The atoms in compounds are rearranged to make new and different compounds.

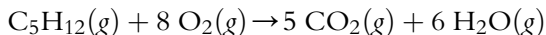
In the absence of a spark or a high-intensity light source, *alkanes* are generally inert to chemical reactions. However, anyone who has used a match to light a gas burner, or dropped a match onto charcoal coated with lighter fluid, should recognize that alkanes burst into flames in the presence of a spark. It does not matter whether the starting material is the methane found in natural gas:



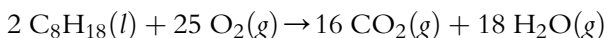
The mixture of butane and isobutane used in disposable cigarette lighters:



The mixture of C₅ to C₆ hydrocarbons in charcoal lighter fluid:

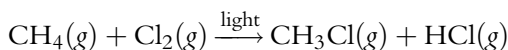


Or the complex mixture of C₆ to C₈ hydrocarbons in gasoline:

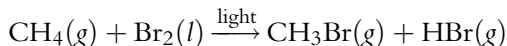


Once the reaction is ignited by a spark, these hydrocarbons burn to form CO₂ and H₂O and give off between 45 and 50 kJ of energy per gram of fuel consumed.

In the presence of light, or at high temperatures, alkanes react with halogens to form alkyl halides. Reaction with chlorine gives an alkyl chloride:



Reaction with bromine gives an alkyl bromide:



Alkenes (olefins, C_nH_{2n}) are unsaturated compounds of carbon with hydrogen which contain one or two double bonds between atoms of carbon. They burn to form carbon soot and carbon dioxide and water. They are more reactive than alkanes because of the fact that they contain double bonds.

Multiple bonds (double, triple bonds) are energetically less advantageous for atoms than corresponding single bonds. For this reason, the atoms in a compound will attempt to break multiple bonds to form single bonds, which are more advantageous energetically. This explains why compounds which contain double and triple bonds are so much more reactive than those which contain single bonds. The alkenes include ethylene (C_2H_4), propylene (C_3H_6), butylene (C_4H_8), and pentylene (pentene, C_5H_{10}). Up to butylene, the alkenes occur as gases. Up to hexadecene ($C_{16}H_{32}$) they are liquids, with higher alkenes found in the solid state of matter. Hydrocarbons with double bonds make up the *alkene* family, while hydrocarbons with triple bonds make up the *alkyne* family and there are similarities in physical properties (Table 9.1).

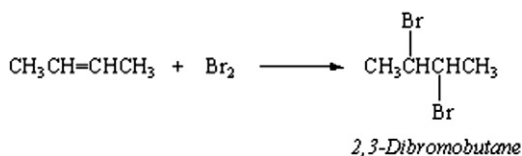
Table 9.1 General comparison of selected properties of alkanes, alkenes, and alkynes

	Alkanes	Alkenes	Alkynes
General formula	CH_nH_{2n+2}	CH_nH_{2n}	CH_nH_{2n-2}
Naming	All the members end with <i>ane</i>	All the members end with <i>ene</i>	All the members end with <i>yne</i>
Physical state	Members having 1–4 carbon atoms per molecule are gases/5–17 carbon atoms are liquids and 18 or more carbon atoms are solids at room temperature	Members having 2–4 carbon atoms per molecule are gases/5–15 carbon atoms per molecule are liquids and the higher members are solids	Members having 2–4 carbon atoms per molecule are gases/5–13 are liquids and the higher members are solids
Boiling points and melting points	The melting and boiling points increase with increase in molecular mass	The boiling point and melting point increase with the increase in molecular mass	The melting and boiling points increase with the increase in molecular mass
Combustion	Undergo complete combustion with production CO_2 , H_2O and heat	Burn with a sooty flame because of the higher percentage of carbon in them, producing CO_2 , H_2O and heat	Burn with a sooty flame because of the higher percentage of carbon in them, producing CO_2 , H_2O and heat

Open-chain alkenes with one double bond have the general formula C_nH_{2n} , where n equals the number of carbon atoms. Open-chain alkynes with one triple bond have the general formula C_nH_{2n-2} .

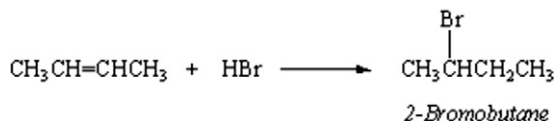
Like the alkanes and other hydrocarbons, they are insoluble in water and are flammable. The most familiar alkenes are ethylene and propylene. Ethyne (acetylene) is an important alkyne.

Unsaturated hydrocarbons such as alkenes and alkynes are much more reactive than the parent alkanes. They react rapidly with bromine, for example, to add a bromine molecule (Br_2) across the carbon-carbon double bond ($C=C$):

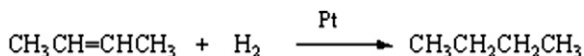


This reaction provides a way to test for alkenes or alkynes. Solutions of bromine in carbon tetrachloride have an intense red-orange color. When bromine in carbon tetrachloride is mixed with a sample of an alkane, no change is initially observed. When it is mixed with an alkene or alkyne, the color of bromine rapidly disappears.

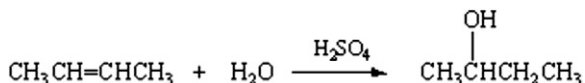
The reaction between 2-butene and bromine to form 2,3-dibromobutane is just one example of the addition reactions of alkenes and alkynes. Hydrogen bromide (HBr) adds across a carbon-carbon double bond ($C=C$) to form the corresponding alkyl bromide, in which the hydrogen ends up on the carbon atom that had more hydrogen atoms to begin with. Addition of HBr to 2-butene, for example, gives 2-bromobutane:



H_2 adds across double (or triple) bonds in the presence of a suitable catalyst to convert an alkene (or alkyne) to the corresponding alkane:

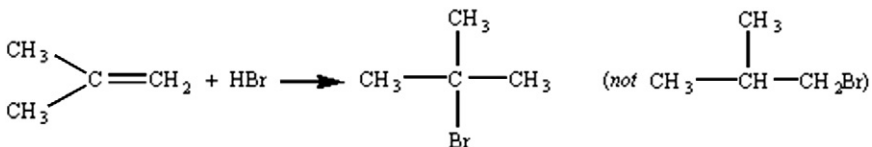


In the presence of an acid catalyst, it is even possible to add a molecule of water across a $C=C$ double bond:

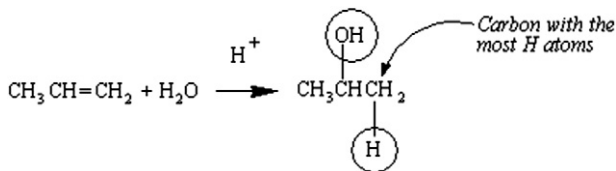


Addition reactions provide a way to add new substituents to a hydrocarbon chain and thereby produce new derivatives of the parent alkanes.

In theory, two products can form when an unsymmetrical reagent such as HBr is added to an unsymmetrical carbon-carbon double bond (C=C). In practice, only one product is obtained. When HBr is added to 2-methylpropene, for example, the product is 2-bromo-2-methylpropane, not 1-bromo-2-methylpropane:



In 1870, after careful study of many examples of addition reactions, the Russian chemist Vladimir Markovnikov formulated a rule for predicting the product of these reactions. Markovnikov's rule states that the hydrogen atom adds to the carbon atom that already has the larger number of hydrogen atoms when HX adds to an alkene. Thus, water (H-OH) adds to propene to form the product in which the OH group is on the middle carbon atom:



Alkynes (acetylenes, $\text{C}_n\text{H}_{2n-2}$) are unsaturated hydrocarbons which contain one or more triple bonds between atoms of carbon. When they burn, they tend to form carbon soot. When oxygen is present during burning, high temperatures can be reached.

The simplest (lowest-molecular-weight) alkynes are: acetylene (C_2H_2 , $\text{HC}\equiv\text{CH}$), propyne (C_3H_4 , $\text{CH}_3\text{C}\equiv\text{CH}$) and butyne (C_4H_6 , $\text{CH}_3\text{C}\equiv\text{CCH}_3$ or $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$).

Cycloalkanes (*cyclic alkanes*) are differentiated from aliphatic hydrocarbons insofar as they contain a ring structure and form a homologous group of compounds. The first member of the series is cyclopentane followed by cyclohexane. Cycloalkanes are saturated compounds and, like linear alkanes, are not very reactive.

Aromatic hydrocarbons are derived from benzene. Group members have six free valence electrons which are distributed in a circle in the form of

a charged cloud. Because of the presence of these valence electrons, we can predict that the reactivity of these aromatic compounds will be similar to other unsaturated hydrocarbons. However, benzene is much less reactive than other unsaturated hydrocarbons. Only at high temperatures and in the presence of a catalyst can benzene take on another hydrogen atom. When it does, cyclohexane is the resultant product.

5. PHYSICAL PROPERTIES

Physical properties can be observed or measured without changing the composition of matter. Physical properties are used to observe and describe matter (Howard and Meylan, 1997; Yaws, 1999). The three states of matter are: solid, liquid, and gas. The melting point and boiling point are related to changes of the state of matter. All matter may exist in any of three physical states of matter.

A physical change takes place without any changes in molecular composition. The same element or compound is present before and after the change. The same molecule is present throughout the changes. Physical changes are related to physical properties since some measurements require that changes be made.

Physical properties that are of interest in the current context include: boiling point, melting point, density, vapor density, flash point, ignition temperature, and dew point.

5.1. Boiling points and melting points

The *boiling point* of an organic compound is the temperature at which the vapor pressure of the liquid equals the environmental pressure surrounding the liquid.

The *melting point* of a solid is the temperature at which the vapor pressure of the solid and the liquid are equal. At the melting point, the solid and liquid phases exist in equilibrium.

The boiling points of organic compounds can give important clues to other physical properties and structural characteristics. A liquid boils when its vapor pressure is equal to the atmospheric pressure. Vapor pressure is determined by the kinetic energy of molecules. Kinetic energy is related to temperature and the mass and velocity of the molecules ($KE = 1/2 mv^2$). When the temperature reaches the boiling point, the average kinetic energy of the liquid particles is sufficient to overcome the forces of attraction that hold molecules in the liquid state.

Vapor pressure is caused by an equilibrium between molecules in the gaseous state and molecules in the liquid state. When molecules in the liquid state have sufficient kinetic energy they may escape from the surface and turn into a gas. Molecules with the most independence in individual motions achieve sufficient kinetic energy (velocities) to escape as gases at lower temperatures. The vapor pressure will be higher (more gas molecules are present) and therefore the compound will boil at a lower temperature.

In each homologous series of hydrocarbons, the boiling points increase with molecular weight and structure also has a marked influence since it is a general rule that branched paraffin isomers have lower boiling points than the corresponding *n*-alkane. In any given series, steric effects notwithstanding, there is an increase in boiling point with an increase in carbon number of the alkyl side chain. This particularly applies to alkyl aromatic compounds where alkyl-substituted aromatic compounds can have higher boiling points than polycondensed aromatic systems.

The boiling points of hydrocarbon fuels are rarely, if ever, distinct temperatures; it is, in fact, more correct to refer to the boiling ranges of the various fuels. To determine these ranges, the petroleum is tested in various methods of distillation, either at atmospheric pressure or at reduced pressure. In general, the limiting molecular weight range for distillation at atmospheric pressure without thermal degradation is 200–250, whereas the limiting molecular weight range for conventional vacuum distillation is 500–600.

Alkanes experience intermolecular van der Waals forces. Stronger intermolecular van der Waals forces give rise to greater boiling points of alkanes. There are two determinants for the strength of the van der Waals forces: (1) the number of electrons surrounding the molecule, which increases with the molecular weight of the alkane, and (2) the surface area of the molecule.

Under standard conditions (STP), alkanes from methane (CH_4) to butane (C_4H_{10}) are gaseous; from pentane (C_5H_{12}) to $\text{C}_{17}\text{H}_{36}$ they are liquids; and after $\text{C}_{18}\text{H}_{38}$ and higher molecular weight paraffins they are solids. As the boiling point of alkanes is primarily determined by weight, it should not be a surprise that the boiling point has almost a linear relationship with the size (molecular weight) of the molecule. As a general rule, the boiling point rises 20–30°C for each carbon added to the chain; this rule applies to other homologous series.

A straight-chain alkane will have a boiling point higher than a branched-chain alkane due to the greater surface area in contact, thus the greater van der Waals forces, between adjacent molecules. For example, compare

iso-butane (2-methylpropane) and n-butane (butane), which boil at -12 and 0°C , respectively, and 2,2-dimethylbutane and 2,3-dimethylbutane, which boil at 50 (122°F) and 58°C (136°F), respectively. For the latter case, two molecules of 2,3-dimethylbutane can associate with each other better than the cross-shaped 2,2-dimethylbutane, hence the greater van der Waals forces.

On the other hand, cycloalkanes tend to have higher boiling points than their linear counterparts due to the locked conformations of the molecules, which give a plane of intermolecular contact.

The melting points of the alkanes follow a similar trend to boiling points of alkanes (Table 9.2, Figure 9.1) for the same reason as outlined above. That is (all other things being equal), the larger the molecule the higher the melting point. There is one significant difference between boiling points and melting points. Solids have more rigid and fixed structure than liquids. This rigid structure requires energy to break down. Thus the better put together solid structures will require more energy to break apart.

For alkanes, the odd-numbered alkanes have a lower trend in melting points than even-numbered alkanes (Figure 9.1). Even-numbered alkanes pack well in the solid phase, forming a well-organized structure, which requires more energy to break apart. The odd-number alkanes pack less well and so the *looser* organized solid packing structure requires less energy to break apart.

The melting points of branched-chain alkanes can be either higher or lower than those of the corresponding straight-chain alkanes, again depending on the ability of the alkane in question to pack well in the solid phase: this is particularly true for isoalkanes (2-methyl isomers), which often have melting points higher than those of the linear analogs.

Table 9.2 Selected properties of the lower-molecular-weight alkanes

IUPAC name	Molecular formula	Structural formula	Boiling point ($^{\circ}\text{C}$)	Melting point ($^{\circ}\text{C}$)	Density (g/ml, 20°C)
Methane	CH_4	CH_4	-161.5	-182.5	
Ethane	C_2H_6	CH_3CH_3	-88.6	-183.3	
Propane	C_3H_8	$\text{CH}_3\text{CH}_2\text{CH}_3$	-42.1	-189.7	
Butane	C_4H_{10}	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	-0.5	-138.4	
Pentane	C_5H_{12}	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	36.1	-129.7	0.626
Hexane	C_6H_{14}	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	68.7	-95.3	0.659
Heptane	C_7H_{16}	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	98.4	-90.6	0.684
Octane	C_8H_{18}	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	125.7	-56.8	0.703
Nonane	C_9H_{20}	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	150.8	-53.5	0.718
Decane	$\text{C}_{10}\text{H}_{22}$	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	174.1	-29.7	0.730

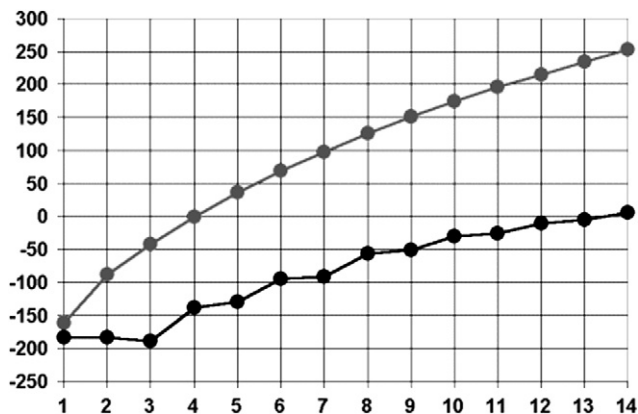


Figure 9.1 Melting points (lower line) and boiling points (upper line) of the C₁–C₁₄ alkanes

Hydrocarbon fuels are liquids at ambient temperature, and problems that may arise from solidification during normal use are not common. Nevertheless, the *melting point* is a test (ASTM D87 and ASTM D127) that is widely used by suppliers of wax and by the wax consumers; it is particularly applied to the highly paraffinic or crystalline waxes. Quantitative prediction of the melting point of pure hydrocarbons is difficult, but the melting point tends to increase qualitatively with the molecular weight and with symmetry of the molecule.

Unsubstituted and symmetrically substituted compounds (e.g., benzene, cyclohexane, *p*-xylene, and naphthalene) melt at higher temperatures relative to the paraffin compounds of similar molecular weight: the unsymmetrical isomers generally melt at lower temperatures than the aliphatic hydrocarbons of the same molecular weight.

Unsaturation affects the melting point principally by its alteration of symmetry; thus ethane (−172°C, −278°F) and ethylene (−169.5°C, −273°F) differ only slightly, but the melting points of cyclohexane (6.2°C, 21°F) and cyclohexene (−104°C, −155°F) contrast strongly. All types of highly unsymmetrical hydrocarbons are difficult to crystallize; asymmetrically branched aliphatic hydrocarbons as low as octane and most substituted cyclic hydrocarbons comprise the greater part of the lubricating fractions of petroleum, crystallize slowly, if at all, and on cooling merely take the form of glasslike solids.

Although the melting points of petroleum and petroleum products are of limited usefulness, except to estimate the purity or perhaps the composition

of waxes, the reverse process, *solidification*, has received attention in petroleum chemistry. In fact, solidification of petroleum and petroleum products has been differentiated into four categories, namely *freezing point*, *congealing point*, *cloud point*, and *pour point*.

Petroleum becomes more or less a plastic solid when cooled to sufficiently low temperatures. This is due to the congealing of the various hydrocarbons that constitute the oil. The cloud point of a petroleum oil is the temperature at which paraffin wax or other solidifiable compounds present in the oil appear as a haze when the oil is chilled under definitely prescribed conditions (ASTM D2500 and ASTM D3117). As cooling is continued, all petroleum oils become more and more viscous and flow becomes slower and slower. The pour point of petroleum or petroleum product oil is the lowest temperature at which the oil pours or flows under definitely prescribed conditions when it is chilled without disturbance at a standard rate (ASTM D97).

The solidification characteristics of a hydrocarbon or hydrocarbon fuel depend on its grade or kind. For grease, the temperature of interest is that at which fluidity occurs, commonly known as the *dropping point*. The dropping point of grease is the temperature at which the grease passes from a plastic solid to a liquid state and begins to flow under the conditions of the test (ASTM D56 and ASTM D2650). For another type of plastic solid, including petrolatum and microcrystalline wax, both *melting point* and *congealing point* are of interest.

The *melting point* of wax is the temperature at which the wax becomes sufficiently fluid to drop from the thermometer; the *congealing point* is the temperature at which melted petrolatum ceases to flow when allowed to cool under definitely prescribed conditions (ASTM D93).

For paraffin wax, the *solidification temperature* is of interest. For such purposes, the *melting point* is the temperature at which the melted paraffin wax begins to solidify, as shown by the minimum rate of temperature change, when cooled under prescribed conditions. For pure or essentially pure hydrocarbons, the solidification temperature is the freezing point, the temperature at which a hydrocarbon passes from a liquid to a solid state (ASTM D118).

The relationship of *cloud point*, *pour point*, *melting point*, and *freezing point* to one another varies widely from one hydrocarbon fuel to another. Hence, their significance for different types of product also varies. In general, cloud, melting, and freezing points are of more limited value and each is of narrower range of application than the pour point.

The *cloud point* of hydrocarbon fuel is the temperature at which paraffin wax or other solidifiable compounds present in the oil appear as a haze when the sample is chilled under definitely prescribed conditions (ASTM D2500, ASTM D3117).

To determine the *cloud point* and the *pour point* (ASTM D97, ASTM D512, ASTM D1835, ASTM D524, ASTM D5501, ASTM D975) the oil is contained in a glass test tube fitted with a thermometer and immersed in one of three baths containing coolants. The sample is dehydrated and filtered at a temperature 20°C (45°F) higher than the above the anticipated cloud point. It is then placed in a test tube and cooled progressively in coolants held at -1 to +2°C (30–35°F), -18 to -20°C (-4 to 0°F) and -32 to -35°C (-26 to -31°F), respectively. The sample is inspected for cloudiness at temperature intervals of 1°C (2°F). If conditions or oil properties are such that reduced temperatures are required to determine the pour point, alternate tests are available that accommodate the various types of samples.

Related to the *cloud point*, the wax appearance temperature or wax appearance point is also determined (ASTM D3117).

The *pour point* of petroleum hydrocarbons or a petroleum product is determined using this same technique (ASTM D97) and it is the lowest temperature at which the oil pours or flows. It is actually 2°C (3°F) above the temperature at which the oil ceases to flow under these definitely prescribed conditions when it is chilled without disturbance at a standard rate. To determine the pour point, the sample is first heated to 46°C (115°F) and cooled in air to 32°C (90°F) before the tube is immersed in the same series of coolants as used for the determination of the *cloud point*. The sample is inspected at temperature intervals of 2°C (3°F) by withdrawal and holding horizontal for 5 seconds until no flow is observed during this time interval.

Cloud and pour points are useful for predicting the temperature at which the observed viscosity of oil deviates from the true (Newtonian) viscosity in the low-temperature range. They are also useful for identification of oils or when planning the storage of oil supplies, as low temperatures may cause handling difficulties with some oils.

The pour point of a crude oil was originally applied to crude oil that had a high wax content. More recently, the pour point, like the viscosity, is determined principally for use in pumping arid pipeline design calculations. Difficulty occurs in these determinations with waxy crude oils that begin to exhibit irregular flow behavior when wax begins to separate. These crude oils possess viscosity relationships that are difficult to predict in pipeline

operation. In addition, some waxy crude oils are sensitive to heat treatment that can also affect their viscosity characteristics. This complex behavior limits the value of viscosity and pour point tests on waxy crude oils. At the present time, long crude oil pipelines and the increasing production of waxy crude oils make an assessment of the pumpability of a wax-containing crude oil through a given system a matter of some difficulty that can often only be resolved after field trials.

Alkenes contain a carbon–carbon double bond ($C=C$), which affects the physical properties of alkenes relative to the physical properties of alkanes. At room temperature, alkenes exist in all three phases, solid, liquids, and gases. Melting and boiling points of alkenes are similar to those of alkanes; however, isomers of *cis* alkenes have lower melting points than those of *trans* isomers. Alkenes display weak dipole–dipole interactions due to the electron-attracting sp^2 carbon. The physical properties of alkenes are comparable with those of alkanes. The physical state depends on the molecular weight. The lower-molecular-weight alkenes (ethylene, propylene, and butylene) are gases, while linear alkenes of approximately five to 16 carbons are liquids, and higher alkenes are waxy solids.

The boiling points of alkenes, like the boiling points of the alkanes, increase with molecular weight (Table 9.3). Branched-chain alkenes have lower boiling points than the corresponding straight-chain alkenes. However, the boiling point of each alkene is very similar to that of the alkane with the same number of carbon atoms (Tables 9.2 and 9.3). Ethylene, propylene, and the various butenes are gases at room temperature. The higher boiling alkenes are liquids.

Table 9.3 Boiling points of alkenes

Alkene	Boiling points (°C)
Ethylene	−104
Propylene	−47
<i>Trans</i> -2-Butene	0.9
<i>Cis</i> -2-butene	3.7
1-Pentene	30
<i>Trans</i> -2-Pentene	36
<i>Cis</i> -2-Pentene	37
1-Heptene	115
3-Octene	122
3-Nonene	147
5-Decene	170

In each case, the alkene has a boiling point which is slightly lower than the boiling point of the corresponding alkane. The only attractions involved are Van der Waals dispersion forces, and these depend on the shape of the molecule and the number of electrons it contains. Each alkene has two fewer electrons than the alkane with the same number of carbons.

Cis isomers and *trans* isomers often have different physical properties. Differences between isomers, in general, arise from the differences in the shape of the molecule or the overall dipole moment of the molecule. This difference can be small as in the case of the boiling point of straight-chain alkenes, such as 2-pentene which is 37°C (98°F), in the *cis* isomer and 36°C (96°F) in the *trans* isomer.

The melting points of alkenes also increase with molecular weight (Table 9.4). Generally, alkenes have similar melting points to those of corresponding alkanes. However, melting points of alkenes depend on the packaging of the molecules – *cis* isomers are packaged in a U-bending shape and, therefore, display lower melting points compared to those of the respective *trans* isomers.

In keeping with the general trend of alkanes and alkenes (and to no one's surprise), the boiling points and melting points of *alkynes* increase as the number of carbon atoms (i.e., molecular weight) increases (Table 9.5).

However, alkynes have higher boiling points than alkanes or alkenes, because the electric field of an alkyne, with its increased number of weakly held π electrons, contain the triple bond. Because of these weakly held electrons, its electric field is more easily distorted, producing stronger attractive forces between molecules. This holds the molecules together at higher temperatures, preventing vaporization.

Table 9.4 Melting points of alkenes

Compound	Melting points (°C)
Ethene	−169
Propene	−185
Butene	−138
1-Pentene	−165
<i>Trans</i> -2-Pentene	−135
<i>Cis</i> -2-Pentene	−180
1-Heptene	−119
3-Octene	−101.9
3-Nonene	−81.4
5-Decene	−66.3

Table 9.5 Physical properties of alkynes

Name	Formula	Melting point (°C)	Boiling point (°C)	Density (20°C)
Acetylene	HCCH	-82	-75	
Propyne	HCCCH ₃	-101.5	-23	
1-Butyne	HCCCH ₂ CH ₃	-122	91	
2-Butyne	CH ₃ CCCH ₃	-24	27	0.694
1-Pentyne	HCC(CH ₂) ₂ CH ₃	-98	40	0.695
2-Pentyne	CH ₃ CCCH ₂ CH ₃	-101	55	0.714
1-Hexyne	HCC(CH ₂) ₃ CH ₃	-124	72	0.719
1-Heptyne	HCC(CH ₂) ₄ CH ₃	-80	100	0.733
1-Octyne	HCC(CH ₂) ₅ CH ₃	-70	126	0.747
1-Nonyne	HCC(CH ₂) ₆ CH ₃	-65	151	0.763
1-Decyne	HCC(CH ₂) ₇ CH ₃	-35	182	0.770

Cycloalkanes are similar to alkanes in their general physical properties, but they have higher boiling points, melting points, and densities than alkanes. This is due to stronger London forces because the ring shape allows for a larger area of contact. Containing only carbon-carbon single (C-C) bonds and carbon-hydrogen (C-H) single bonds, unreactivity of cycloalkanes with little or no ring strain (see below) is comparable to non-cyclic alkanes.

The London dispersion force is the weakest intermolecular force. The London dispersion force is a temporary attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. This force is sometimes called a dipole-induced attraction. London forces are the attractive forces that cause non-polar substances to condense to liquids and to freeze into solids when the temperature is lowered sufficiently.

Because of the constant motion of the electrons, an atom or molecule can develop a temporary (instantaneous) dipole when its electrons are distributed unsymmetrically about the nucleus. A second atom or molecule, in turn, can be distorted by the appearance of the dipole in the first atom or molecule (because electrons repel one another), which leads to an electrostatic attraction between the two atoms or the two molecules.

5.2. Density and specific gravity

Specific gravity (*relative density*) is the ratio of the density (mass of a unit volume) of a substance to the density of a given reference material. Specific gravity usually means relative density with respect to water.

If the specific gravity of a hydrocarbon or hydrocarbon fuel is less than one then it is less dense than water, or the reference chemical. Conversely,

if the specific density is greater than one, it is denser than the reference. If the relative density is exactly one then the densities are equal; that is, equal volumes of the two substances have the same mass. If the reference material is water then a substance with a relative density (or specific gravity) less than one will float in water.

Temperature and pressure must be specified for both the sample and the reference. Pressure is nearly always 14.7 psi (1 atmosphere). Where it is not it is more usual to specify the density directly. Temperatures for both sample and reference vary from industry to industry. In British brewing practice the specific gravity as specified above is multiplied by 1,000. Specific gravity is commonly used in industry as a simple means of obtaining information about the concentration of solutions of various materials such as brine, sugar solutions, and acids.

The *density* and *specific gravity* of crude oil and hydrocarbon fuels (ASTM D70, ASTM D71, ASTM D287, ASTM D941, ASTM D1217, ASTM D1298, ASTM D1480, ASTM D1481, ASTM D1555, ASTM D1657, ASTM D4052) are two properties that have found wide use in the industry for preliminary assessment of the character and quality of crude oil.

Density is the mass of a unit volume of material at a specified temperature and has the dimensions of grams per cubic centimeter (a close approximation to grams per milliliter). *Specific gravity* is the ratio of the mass of a volume of the substance to the mass of the same volume of water and is dependent on two temperatures, those at which the masses of the sample and the water are measured. When the water temperature is 4°C (39°F), the specific gravity is equal to the density in the centimeter–gram–second (cgs) system, since the volume of 1 g of water at that temperature is, by definition, 1 ml. Thus the density of water, for example, varies with temperature, and its specific gravity at equal temperatures is always unity. The standard temperatures for a specific gravity in the petroleum industry in North America are 60/60°F (15.6/15.6°C).

In the early years of the petroleum industry, density was the principal specification for petroleum and refinery products; it was used to give an estimation of the gasoline and, more particularly, the kerosene present in the crude oil. However, the derived relationships between the density of petroleum and its fractional composition were valid only if they were applied to a certain type of petroleum and lost some of their significance when applied to different types of petroleum. Nevertheless, density is still used to give a rough estimation of the nature of petroleum and petroleum

products. Although density and specific gravity are used extensively, the API (American Petroleum Institute) gravity is the preferred property. This property was derived from the Baum scale:

$$\text{Degrees Baum} = (140/\text{sp gr at } 60/60^\circ\text{F}) - 130$$

However, a considerable number of hydrometers calibrated according to the Baum scale were found at an early period to be in error by a consistent amount, and this led to the adoption of the equation:

$$\text{Degrees API} = (141.5/\text{sp gr at } 60/60^\circ\text{F}) - 131.5$$

The specific gravity of petroleum usually ranges from about 0.8 (45.3 API) for the lighter crude oils to over 1.0 (less than 10 API) for heavy crude oil and bitumen.

Specific gravity is influenced by the chemical composition of petroleum, but quantitative correlation is difficult to establish. Nevertheless, it is generally recognized that increased amounts of aromatic compounds result in an increase in density, whereas an increase in saturated compounds results in a decrease in density. Indeed, it is also possible to recognize certain preferred trends between the density of petroleum and one or another of the physical properties. For example, an approximate correlation exists between the density (API gravity) and sulfur content, Conradson carbon residue, viscosity, and nitrogen content (Speight, 2000).

Density, specific gravity, or API gravity may be measured by means of a hydrometer (ASTM D287, ASTM D1298, ASTM D1657, IP 160), a pycnometer (ASTM D70, ASTM D941, ASTM D1217, ASTM D1480, and ASTM D1481), by the displacement method (ASTM D712), or by means of a digital density meter (ASTM D4052) and a digital density analyzer (ASTM D5002).

The pycnometer method (ASTM D70, ASTM D941, ASTM D1217, ASTM D1480, ASTM D1481) for determining density is reliable, precise, and requires relatively small test samples. However, because of the time required, other methods such as using the hydrometer (ASTM D1298), the density meter (ASTM D4052), and the digital density analyzer (ASTM D5002) are often preferred. However, surface tension effects can affect the displacement method and the density meter method loses some of its advantage when measuring the density of heavy oil and bitumen.

The pycnometer method (ASTM D70, ASTM D941, ASTM D1217, ASTM D1480, and ASTM D1481) is routinely used to measure the density of samples being charged to a distillation flask, where volume charge is

needed, but the volume is not conveniently measured. The volume may be found by weighing the sample and determining the sample density. It is also used in routine measurements of material properties. It is worthy of note that even a small amount of solids in the sample will influence its measured density. For example, 1% by weight solids in the sample can raise the density by 0.007 g/cm^3 .

The densimeter method (ASTM D4052) uses an instrument that measures the total mass of a tube by determining its natural frequency of vibration. This frequency is a function of the dimensions and the elastic properties of the tube, and the weight of the tube and contents. Calibration with water and air provides data for the determination of the instrument constraints, which allow conversion of the natural frequency of vibration to sample density.

The variation of density with temperature (Table 9.3), effectively the coefficient of expansion, is a property of great technical importance, since most petroleum products are sold by volume and specific gravity is usually determined at the prevailing temperature (21°C , 70°F) rather than at the standard temperature (60°F , 15.6°C). The tables of gravity corrections (ASTM D1555) are based on an assumption that the coefficient of expansion of all petroleum products is a function (at fixed temperatures) of density only.

However, not all of these methods are suitable for measuring the density or specific gravity of heavy oil and bitumen, although some methods lend themselves to adaptation.

The API gravity of a feedstock (ASTM D287) is calculated directly from the specific gravity. The specific gravity of bitumen shows a fairly wide range of variation. The largest degree of variation is usually due to local conditions that affect material close to the faces, or exposures, occurring in surface oil sand beds. There are also variations in the specific gravity of the bitumen found in beds that have not been exposed to weathering or other external factors. The range of specific gravity usually varies over the range of the order of 0.995–1.04.

A very important property of the Athabasca bitumen (which also accounts for the success of the hot water separation process) is the variation in density (specific gravity) of the bitumen with temperature. Over the temperature range $30\text{--}130^\circ\text{C}$ ($85\text{--}265^\circ\text{F}$) the bitumen is lighter than water. Flotation of the bitumen (with aeration) on the water is facilitated, hence the logic of the hot water separation process (Speight, 2007).

The density of the *alkanes* usually increases with increasing number of carbon atoms, but remains less than that of water (Table 9.1). Hence, alkanes form the upper layer in an alkane–water mixture.

The density of the *alkenes* is higher than the density of the corresponding alkanes. Again, density usually increases with increasing number of carbon atoms, but all alkenes have density smaller than 1. The density of the cycloalkanes is higher than the density of the corresponding alkanes (Table 9.6).

5.3. Vapor density

Vapor density is the density of a vapor in relation to that of air – hydrogen may also be used as the standard of comparison.

In the case of air (which is commonly used in relation to hydrocarbons and hydrocarbon fuels), the vapor density is the mass of a specified volume of the substance divided by mass of the same volume of air and air is given an arbitrary vapor density of one. With this definition, the vapor density would indicate whether a gas is denser (greater than one) or less dense (less than one) than air.

The vapor density has implications for container storage and personnel safety – if a container can release a dense gas, its vapor could sink and, if flammable, collect until it is at a concentration sufficient for ignition. Even if

Table 9.6 Physical properties of alkanes and cycloalkanes

Compounds	Bp, °C	Mp, °C	Density, d_4^{20} , g / ml
Propane	−42	−187	0.580 ^a
Cyclopropane	−33	−127	0.689 ^a
Butane	−0.5	−135	0.579 ^b
Cyclobutane	13	−90	0.689 ^b
Pentane	36	−130	0.626
Cyclopentane	49	−94	0.746
Hexane	69	−95	0.659
Cyclohexane	81	7	0.778
Heptane	98	−91	0.684
Cycloheptane	119	−8	0.810
Octane	126	−57	0.703
Cyclooctane	151	15	0.830
Nonane	151	−54	0.718
Cyclononane	178	11	0.845

^aAt −40°.

^bUnder pressure.

not flammable, it could collect in the lower floor or level of a confined space and displace air, possibly presenting a smothering hazard to individuals entering the lower part of that space.

5.4. Flash point and ignition temperature

The flash point of a volatile liquid is the lowest temperature at which it can vaporize to form an ignitable mixture in air (Table 9.7). At the flash point, the vapor may cease to burn when the source of ignition is removed.

The flash point is often used as a descriptive characteristic of liquid fuel, and it is also used to describe liquids that are not normally used as fuels but are flammable liquids and/or combustible liquids. There are various international standards for defining each, but most agree that liquids with a flash point less than 43°C (109°F) are flammable, while those having a flash point above this temperature are combustible.

The *fire point* is a slightly higher temperature and is the temperature at which the vapor continues to burn after being ignited. Neither the flash point nor the fire point is related to the temperature of the ignition source or of the burning liquid, which are much higher. The flash point is not to be confused with the auto-ignition temperature, which does not require an ignition source.

The *ignition temperature* is the minimum temperature to which a substance must be heated before it will spontaneously burn independently of the source of heat.

Table 9.7 Flash points, auto-ignition temperatures, and flammability limits for various hydrocarbons

Hydrocarbon	Flash point (°C)	Auto-ignition temperature (°C)	Flammable limits	
			upper (vol % at 25°C)	lower
Methane	-188	630	5.0	15.0
Ethane	-135	515	3.0	12.4
Propane	-104	450	2.1	9.5
n-Butane	-74	370	1.8	8.4
n-Pentane	-49	260	1.4	7.8
n-Hexane	-23	225	1.2	7.4
n-Heptane	-3	225	1.1	6.7
n-Octane	14	220	0.95	6.5
n-Nonane	31	205	0.85	—
n-Decane	46	210	0.75	5.6
n-Dodecane	74	204	0.60	—
n-Tetradecane	99	200	0.50	—

The auto-ignition temperature (*kindling point*) of a substance (Table 9.7) is the lowest temperature at which it will spontaneously ignite in a normal atmosphere without an external source of ignition, such as a flame or spark. This temperature is required to supply the activation energy needed for combustion. The temperature at which a chemical will ignite decreases as the pressure increases or oxygen concentration increases. It is usually applied to a combustible fuel mixture.

Auto-ignition temperatures of liquid chemicals are typically measured using a 500-milliliter flask placed in a temperature-controlled oven in accordance with a standard test procedure (ASTM E659).

The flash point of a volatile liquid is the lowest temperature at which the liquid can vaporize to form an ignitable mixture in air. Measuring a liquid's flash point requires an ignition source. At the flash point, the vapor may cease to burn when the source of ignition is removed. The flash point is not to be confused with the auto-ignition temperature, which does not require an ignition source.

The fire point, a slightly higher temperature than the flash point, is the temperature at which the vapor continues to burn after being ignited. Neither the flash point nor the fire point is related to the temperature of the ignition source or of the burning liquid, which are much higher.

The flash point is often used as a descriptive characteristic of hydrocarbons (Table 9.7) and hydrocarbon fuels (Table 9.8) and it is also used to describe other liquids, including those that are not normally used as fuels. Flash point refers to both flammable liquids and combustible liquids. There are various international standards for defining each, but most agree that liquids with a flash point less than 43°C (109°F) are flammable, while those having a flash point above this temperature are combustible.

There are two basic types of flash point measurement: open cup and closed cup. The best known example of the open cup method is the Cleveland Open Cup (COC).

In open cup devices the sample is contained in an open cup which is heated, and at intervals a flame is brought over the surface. The measured

Table 9.8 Examples of flash points of hydrocarbon fuels

Fuel	Flash point	Auto-ignition temperature
Gasoline	<−40°C (−40°F)	246°C (475°F)
Diesel fuel	>62°C (143°F)	210°C (410°F)
Jet fuel	>60°C (140°F)	210°C (410°F)
Kerosene	>38–72°C (100–162°F)	220°C (428°F)

flash point will actually vary with the height of the flame above the liquid surface, and at sufficient height the measured flash point temperature will coincide with the fire point.

There are two types of closed cup testers: non-equilibrium, such as Pensky-Martens, where the vapors above the liquid are not in temperature equilibrium with the liquid; and equilibrium, where the vapors are deemed to be in temperature equilibrium with the liquid. In both these types the cups are sealed with a lid through which the ignition source can be introduced. Closed cup testers normally give lower values for the flash point than open cup (typically 5–10°C) and are a better approximation to the temperature at which the vapor pressure reaches the lower flammability limit (LFL).

The flash point is an empirical measurement rather than a fundamental physical parameter. The measured value will vary with equipment and test protocol variations, including temperature ramp rate (in automated testers), time allowed for the sample to equilibrate, sample volume and whether the sample is stirred.

Methods for determining the flash point of a liquid are specified in many standards. For example, testing by the Pensky-Martens closed cup method is detailed in ASTM D93. Determination of flash point by an alternate closed cup method is detailed in ASTM D3828 and ASTM D3278.

Gasoline is designed for use in an engine which is driven by a spark and the fuel should be premixed with air within its flammable limits and heated above its flash point, then ignited by the spark plug. The fuel should not pre-ignite in the hot engine. Therefore, gasoline is required to have a low flash point and a high auto-ignition temperature (Table 9.7).

Diesel fuel flash points vary between 52°C and 96°C (126°F to 204°F). Diesel is designed for use in a high compression engine in which air is compressed until it has been heated above the auto-ignition temperature of the fuel. The diesel fuel is then injected as a high-pressure spray, keeping the fuel-air mix within the flammable limits of diesel. There is no ignition source and, therefore, diesel is required to have a high flash point and a low auto-ignition temperature (Table 9.8).

The flash point of jet fuel also varies considerably. Both Jet A and Jet A-1 have flash points between 38 and 66°C (100–150°F).

5.5. Dew point

The hydrocarbon dew point (HDP) is a function of the composition of the gas mixture and is strongly influenced by the concentration of the

higher-molecular-weight hydrocarbons, especially C_{6+} . The presence of higher-molecular-weight hydrocarbons will increase the hydrocarbon dew point and failure to include them in a hydrocarbon dew point calculation will underpredict the hydrocarbon dew point.

For most pipeline conditions, the hydrocarbon dew point temperature at a given pressure increases as the concentration of heavier hydrocarbons increases. Thus, the potential to form liquids at certain pipeline conditions exists for gases rich in C_{6+} . Processing of the gas stream primarily removes or extracts higher-molecular-weight hydrocarbons and thus reduces the hydrocarbon dew point of a given mixture. The level of hydrocarbon removal directly impacts the hydrocarbon dew point.

The hydrocarbon dew point curve is plotted as a function of gas pressure (P) and temperature (T) (Figure 9.2). The left-hand side of the curve is the bubble point line and divides the single-phase liquid region from the two-phase gas-liquid region. The right-hand side of the curve is the dew point line and divides the two-phase gas-liquid region and the single-phase gas region. The bubble point and dew point lines intersect at the critical point, where the distinction between gas and liquid properties disappears. Note that two dew point temperatures are possible at a given pressure (P_3) and two dew point pressures are possible at a given temperature (T_3). This phase envelope phenomenon provides for behavior

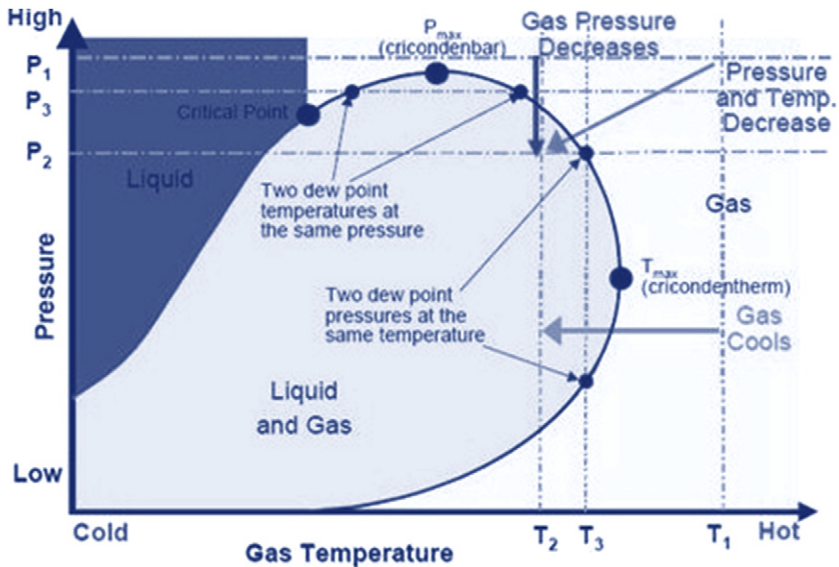


Figure 9.2 Hydrocarbon dew point curve for a natural gas

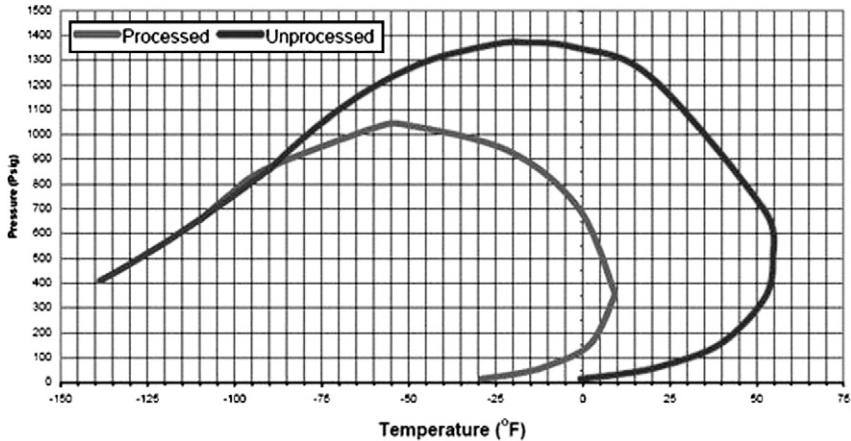


Figure 9.3 Contrast between unprocessed (black line) and processed (gray line) natural gas

known as retrograde condensation. The retrograde phenomenon occurs when liquids form at a given temperature when the pressure is lowered (see red arrow).

The word *retrograde* indicates a phenomenon that is contradictory to the phase behavior of pure components, which condense with increasing pressure and/or decreasing temperature. The maximum pressure at which phase change occurs (P_{\max}) is called the cricondenbar, and the maximum temperature (T_{\max}) at which phase change occurs is called the cricondentherm.

For unprocessed and processed gas mixtures there are variations in the hydrocarbon dew point (Figure 9.3). The unprocessed hydrocarbon dew point curve has a higher cricondentherm temperature than the processed hydrocarbon dew point curve and illustrates the impact of processing on the hydrocarbon dew point.

The significance of the hydrocarbon dew point curve for gas transmission and distribution operations lies in the potential transition from the single-phase gas region to the two-phase gas-liquid region.

REFERENCES

- ASTM, 2009. Annual Book of Standards. American Society for Testing and Materials, West Conshohocken, Pennsylvania.
- Drews, A.W., 1998. In: Manual on Hydrocarbon Analysis. American Society for Testing and Materials, West Conshohocken, Pennsylvania.

- Eliel, E.L., Wilen, S.H., 1994. *Stereochemistry of Organic Compounds*. John Wiley & Sons Inc., New York.
- Eliel, E.L., Wilen, S.H., Doyle, M.P., 2001. *Basic Organic Stereochemistry*. John Wiley & Sons Inc., New York.
- Howard, P.H., Meylan, W.M., 1997. *Handbook of Physical Properties of Organic Chemicals*. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Olah, G.A., Molnár, A., 2003. *Hydrocarbon Chemistry*, second ed. John Wiley & Sons Inc., Hoboken, New Jersey.
- Speight, J.G., 2001. *Handbook of Petroleum Analysis*. John Wiley & Sons Inc., New York.
- Speight, J.G., 2002. *Handbook of Petroleum Product Analysis*. John Wiley & Sons Inc., Hoboken, New Jersey.
- Speight, J.G., 2005. *Lange's Handbook of Chemistry*, sixteenth ed. McGraw Hill, New York.
- Speight, J.G., 2007. *The Chemistry and Technology of Petroleum*, fourth ed. CRC Press, Taylor & Francis Group, Boca Raton, Florida.
- Stoker, H.S., 2008. *General, Organic, and Biological Chemistry*. Florence, Kentucky.
- Yaws, C.L., 1999. *Chemical Properties Handbook*. McGraw-Hill, New York.