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INTRODUCTION

Scope

This Engineering Fundamenal covers the basic elements of thermodynamic and transport properties in sufficient detail to allow an engineer to estimate thermodynamic properties with the suitable accuracy.

The thermodynamic properties are important to know for the characteristic of substances. The physical properties of process materials are needed in all stages of design, from the initial screening of possible processes to the plant startup and production. Thermodynamic data is also required in most calculations such as sizing vessels, process pipeline sizing, and separation of multi-components, gas absorption, and chemical reactor design. Physical property data of compounds are frequently required for pilot plant studies or for the design of large process plants.

When building a simulation, it is important to ensure that the properties of pure components and mixtures are being estimated appropriately. In fact, selecting the proper method for estimating properties is one of the most important steps that will affect the rest of the simulation. There for, it is important to carefully consider the choice of methods to estimate the different properties.

Intensive and extensive properties are discussed in this guideline. In this section, there are tables that assist in making these thermodynamic properties from the vary reference sources. All the important parameters use in the guideline are explained in the definition section which help the reader more understand the meaning of the parameters or the term used.

The theory section explained about kind of thermodynamic properties in some methods, equation of state as a base to estimate some thermodynamic properties, and Joback methods. The examples of application will make the engineer easier to study. This guideline also provide an excel spreadsheet to make easier to calculate.

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General Design Consideration

From the initial screening of possible processes to the plant startup and production, information on manufacturing processes, equipment parameters, and materials of construction, costs, and the physical properties of process materials are needed in all stages of design. Thermodynamic data is also required in most calculations such as sizing vessels, process pipeline sizing, and separation of multi-components, gas absorption, and chemical reactor design.

The collection and assembly of physical property data for the components of the system is important but time-consuming factor in practically every design situation and in development of flowsheets. When a project is largely a repeat of a previous project, the data and information required for the design will be available in the company's process files, if proper detailed records are kept.

For a new project or process, the design data must be obtained from the literature, or by experiment (research laboratory and pilot plant), or purchased from other companies. Often it is not sufficient to obtain single data points from various tables, since many designs cover rather wide ranges of temperature and pressure, and the effects of these temperature and pressure changes on the properties must be taken into account

The information on manufacturing processes available in the general literature can be of use in the initial stages of process design, for screening potential processes, but is usually mainly descriptive and too superficial to be of much use for detailed design and evaluation. Data may be located in many useful handbooks as well as published technical papers and company compilations.

The literature on the physical properties of elements and compounds is extensive, and reliable values for common materials can usually be found. Physical property data of compounds are frequently required for pilot plant studies or for the design of large process plants. These data are not readily available except in some simulation design packages or in the largest libraries.

The data can, of course, be obtained by conducting experiments to measure the properties of individual substances or of mixtures, which may exhibit non-ideal behavior.

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However, this is often time-consuming and expensive. Therefore the process engineer may resort to correlations and interpolations to obtain data of sufficient accuracy for design purposes.

Tables and graphs of physical properties are given in many handbooks and textbooks on chemical engineering and related subjects. Many of the data given are duplicated from book to book, but the various handbooks do provide quick, easy access to data on the more commonly used substances. The values of some properties are dependent on the method of measurement; for example, surface tension and flash point, and the method used should be checked, by reference to the original paper if necessary, if an accurate value is required.

The accuracy needed depends on the use to which the data will be put. This will depend on several factors:

- 1. The level of design: Less accuracy is obviously needed for rough screening calculations made to sort out possible alternative designs than in the final stages of design, when money will be committed to purchase equipment.
- 2. The reliability of the design methods: If there is some uncertainty in the techniques to be used, it is clearly a waste of time to search out highly accurate physical property data that will add little or nothing to the reliability of the final design.
- 3. The sensitivity to the particular property: How much will a small error in the property affect the design calculation? The sensitivity of a design method to errors in physical properties and other data can be checked by repeating the calculation using slightly altered values.

Techniques are available for the prediction of most physical properties with sufficient accuracy for use in process and equipment design. A detailed review of some the different methods available is beyond the scope of this guideline, selected methods are given for the more commonly needed properties.

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Group contribution techniques are based on the concept that a particular physical property of a compound can be considered to be made up of contributions from the constituent atoms, groups, and bonds, the contributions being determined from experimental data. They provide the designer with simple, convenient methods for physical property estimation, requiring only a knowledge of the structural formula of the compound.

Also useful, and convenient to use, are prediction methods based on the use of reduced properties (corresponding states), providing that values for the critical properties are available or can be estimated with sufficient accuracy

The easiest way to estimate mixture properties is usually to set up a stream with the desired temperature, pressure, and composition in one of the simulators. If no experimental data is available, then it is usually a good idea to make an independent estimate of any parameters that have a strong influence on the design, to be satisfied that the results from the simulator are credible. If the independent estimate does not agree with the simulation result, then it may be worthwhile to conduct some experiments to collect real data.

Phase Diagram

A phase diagram is a plot of pressure versus temperature, indicating conditions at which the solid, liquid, or gas is the thermodynamically stable form, and at which two or even all three phases are in equilibrium. Figure 1 shown vapor–liquid phase diagram of a material. The vapor pressure curve extends from the triple point, where solid, liquid, and gas are in equilibrium, to the critical point. Liquid and gas are in equilibrium along this line. Liquid is the stable phase above the curve, and gas is the stable phase below.

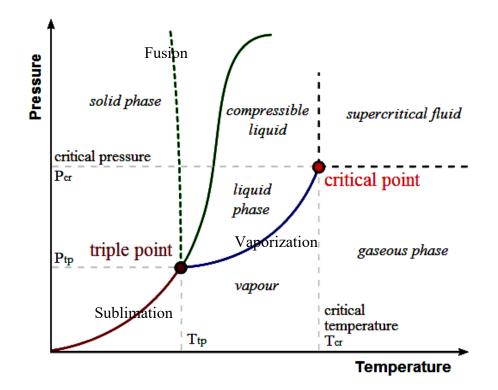
The triple point is merely the point of intersection of sublimation and vaporization curves. It must be understood that only on p-T diagram is the triple point represented by a point. On p-V diagram it is a line, and on a U-V diagram it is a triangle. The pressure and temperature at which all three phases of a pure substance coexist may be measured with the apparatus that is used to measure vapor pressure. Triple-point data for some interesting substances are given in Table 1.

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Solid and gas are in equilibrium along the curve from the origin to the triple point. This curve can be regarded as indicating the vapor pressure above solid as a function of temperature, or the change in sublimation temperature with pressure. The straight line up from the triple point marks the conditions of equilibrium between solid and liquid, showing how the melting point changes with pressure.

The positive slope of all three of these curves is predictable by Le Chatelier's principle. An increase in pressure favors denser phase. The molar volume of the liquid is greater than of the solid, and that of the gas is greater than either. Hence the temperature of sublimation, melting, and boiling all increase as pressure increase, since more energy is required to bring molecules into the less dense phase.





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As shown in the phase diagram, this is the point at which the phase boundary between liquid and gas terminates. As the substance approaches critical temperature, the properties of its gas and liquid phases converge, resulting in only one phase at the critical point: a homogeneous supercritical fluid. The heat of vaporization (or enthalpy of vaporization - the energy required to transform a given quantity of a substance from a liquid into a gas at a given pressure) is zero at and beyond this critical point, and so no distinction exists between the two phases.

The heat of vaporization diminishes with increasing temperature and it vanishes completely at the critical temperature (Tr=1) because above the critical temperature the liquid and vapor phases no longer co-exist. (The reduced temperature Tr of a fluid is its actual temperature, divided by its critical temperature). On the PT diagram, the point at which critical temperature and critical pressure meet is called the critical point of the substance. Above the critical temperature, a liquid cannot be formed by an increase in pressure, even though a solid may be formed under sufficient pressure. The critical pressure is the vapor pressure at the critical temperature. The critical molar volume is the volume of one mole of material at the critical temperature and pressure. Critical properties vary from material to material, and for many pure substances are readily available in the literature.

Substance	Temp, K	Pressure, mm Hg
Hydrogen	13.96	54.1
Deuterium	18.63	128
Neon	24.57	324
Nitrogen	63.18	94
Oxygen	54.36	1.14
Ammonia	195.40	45.57
Carbon dioxide	216.55	3.88
Sulphur dioxide	197.68	1.256
Water	273.16	4.58

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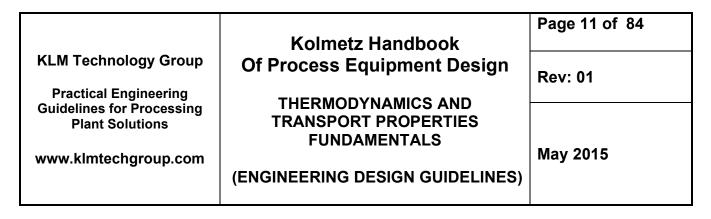
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The composition of a one-component system is fixed so that the state of the system may therefore be defined by specifying the value of any two of the pressure, volume and temperature. The state of the system may therefore be represented as a surface on a three-dimensional pressure, volume and temperature plot. Areas on the surface represent regions where only one phase is stable. The lines drawn between the regions represent the values of these variables at which two phases coexist in equilibrium. Points at the intersection between two lines represent the values at which three phases coexist in equilibrium.

When heat is transferred to the ice, the pressure remains constant, the specific volume increases slightly, and the temperature increases until it reaches 32°F, at which point the ice melts while the temperature remains constant. In this state the ice is called a saturated solid. For most substances, the specific volume increases during this melting process, but for water the specific volume of the liquid is less than the specific volume of the solid. This causes ice to float on water. When all the ice is melted, any further heat transfer causes an increase in temperature of the liquid. The process of melting is also referred to as fusion.

The ice passes directly from the solid phase to the vapor phase in the process known as sublimation. Sublimation is a special term used for cases in which the transition between the solid phase and the vapor phase occurs directly, without passing through the liquid phase. A heat addition at a constant pressure to a saturated liquid will cause the liquid to evaporate (change phase from liquid to vapor). If heat is removed at a constant pressure from a saturated vapor, condensation will occur and the vapor will change phase to liquid. So the processes of vaporization and condensation are the exact opposite of each other

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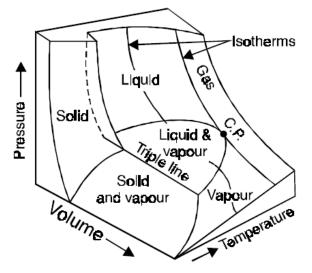


Figure 2: A pressure-volume-temperature (p-V-T) surface.

All the equilibrium states lie on the surface of the model. States represented by the space above or below the surface are not possible. It may be seen that the triple point appears as a line in this representation. The point C.P. is called the critical point and no liquid phase exists at temperatures above the isotherms through this point. The term evaporation is meaningless in this situation. At the critical point the temperature and pressure are called the critical temperature and the critical pressure respectively and when the temperature of a substance is above the critical value, it is called a gas. It is not possible to cause a phase change in a gas unless the temperature is lowered to a value less than the critical temperature. Oxygen and nitrogen are examples of gases that have critical temperatures below normal atmospheric temperature.

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Thermodynamic properties

Thermodynamics basically refers to flow of heat and it deals with the quantitative relationship between heat and other forms of energy observed in physio-chemical transformations. Thermodynamics is based on three fundamental laws. These are applicable to the entire phenomenon that takes place in nature. These laws are not theoretical but are based on experimental outcomes. Thermodynamics deals only with state of the system and makes no mention of the mechanism of how the change is accomplished and it will provide answer to why a change occurs but not how it occurs.

The standard state pressure is 100 kPa (1 bar). The standard states are defined for different phases by:

- The standard state of a pure gaseous substance is that of the substance as a (hypothetical) ideal gas at the standard state pressure.
- The standard state of a pure liquid substance is that of the liquid under the standard state pressure.
- The standard state of a pure crystalline substance is that of the crystalline substance under the standard state pressure

Thermodynamics deals with the changes that occur during a chemical reaction. Thermodynamics is not based on any theoretical hypothesis. It is based on practical observations and measurable properties. Thermodynamic system depending upon interactions between system and surroundings can be classified as open systems, closed systems and isolated systems. Measurable properties of a system may be divided into two classes:

- 1. Extensive property
- 2. Intensive property

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Extensive property

Extensive property is one that is additive for independent, non-interacting subsystems. The property is proportional to the amount of material in the system. An extensive property of a system depends upon the total amount of material in the system. Mass, volume, internal energy, heat contents, free energy, entropy, and heat capacity are all extensive properties. (9)

- Mass: This gives the idea of how much of the initial matter was contained in the system and how much is left after the process is complete.
- Volume: This gives an idea of the dimension of the matter contained in and what will be the final dimension after the process is over.
- Internal energy: It is the total energy contained in to create the thermodynamic system but excludes the energy to displace the system's surroundings. It has two major components of kinetic energy and potential energy due to the movement of particles and the static electric energy of the atoms contained in.
- Heat contents: Under a given pressure, the heat content or Enthalpy is a measure of total energy of a thermodynamic system. It includes internal energy which is required to create a system and establish its volume and pressure.
- Free energy: It is the energy in the physical system which can be converted into work.
- Entropy: It is a thermodynamic property which is used to determine the energy available for useful work in a thermodynamic process.
- Heat capacity: Heat capacity or thermal capacity is the measurable physical quantity that gives an idea of the amount of heat required to change a substance's temperature by a given range.

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Intensive property

An intensive property is intensive property is a bulk property, meaning that it is a physical property of a system that does not depend on the system size or the amount of material in the system. Density, molar property, surface tension, viscosity, specific heat, thermal conductivity, refractive index, pressure, temperature, boiling point, freezing point, and vapor pressure of a liquid are all intensive properties. (9)

- Density: Density of a material is defined as a ratio between its volume and the matter contained in or mass.
- Molar property: Molar property mainly consists the detailing of molar volume, molar energy, molar entropy, molar heat capacity and all these are quantified from the point of moles of the substance involved in.
- Surface tension: It is a property of a liquid surface which helps in resisting any kind of external force applied on it.
- Viscosity: It is a measurable internal quantity of a fluid which resists its flow.
- Specific heat: It is the amount of heat per unit mass required to raise the temperature by one degree Celsius.
- Thermal conductivity: Thermal conductivity (λ) is the intrinsic property of a material which relates its ability to conduct heat.
- Refractive index: The measure of the speed of light in a medium is referred as refractive index of that medium.
- Pressure: It is the perpendicular force acting per unit area on the surface of an object.
- Temperature: It is the property of the matter which quantitatively expresses the coldness or hotness of substance.
- Boiling point: It is the temperature of the substance at which the vapor pressure of the liquid equals environmental pressure.

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- Freezing point: It is the temperature at which a liquid composition solidifies under a given pressure.
- Vapor pressure of a liquid: It is defined as the equilibrium pressure above its liquid resulting due to the evaporation of liquid

Boiling Point

The boiling point is defined as the temperature at which the vapor pressure of a liquid is equal to the pressure of the atmosphere on the liquid. For pure compounds, the normal boiling point is defined as the boiling point at one standard atmosphere of pressure on the liquid. If the pressure on the liquid differs from one atmosphere, the boiling point observed for the compound differs from that estimated for the pure compound. The normal boiling point (i.e. the boiling point at 1 atm) is one of the major physicochemical properties used to characterize and identify a compound. Besides being an indicator for the physical state (liquid or gas) of a compound, the boiling point also provides an indication of its volatility.

The degree of volatility is particularly important in industrial applications, as the hazardous nature of a chemical is usually closely related to its volatility. Boiling point is one of the most important thermal properties. Almost all other thermo chemical properties are predictable from boiling point and critical constants with using corresponding state theory.

Moreover, boiling points can be used to predict or estimate other physical properties, such as critical temperatures, flash points, enthalpies of vaporization, etc. The boiling point is often the first property measured for a new compound and one of the few parameters known for almost every volatile compound. Normal boiling points are easy to determine; however, when a chemical is unavailable, as yet unknown, or hazardous to handle, a reliable procedure for estimating its boiling point is required.

Furthermore, the rapid growth of combinatorial chemistry, where literally millions of new compounds are synthesized and tested without isolation, could render such a procedure

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very useful. So precise forecast of boiling point is needed. Impurities in the liquid, or mixed solvent boiling point will become different from normal boiling point.

It can be said

- Molecular size become larger, boiling point become larger.
- Compared with spherical structure and stick type structure, spherical structure become lower boiling point. (Possibly because of accessible surface area?)
- hydrogen bond make boiling point rise dramatically
- Dipole moment make boiling point (maybe) raise
- Halogen atom make boiling point bring down

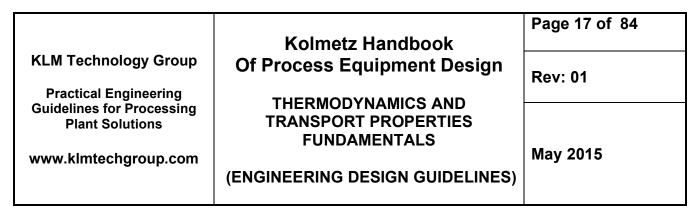
Critical Point

A critical point, also known as a critical state, occurs under conditions (such as specific values of temperature, pressure or composition) at which no phase boundaries exist. The errors in ideal gas predictions become most striking as you approach the gases critical conditions. At higher temperatures and/or higher pressures the difference between a gas and a liquid eventually disappears and a supercritical fluid is formed.

The point at which this happens is called the critical point. The highest temperature at which a species can coexist as a liquid and a vapor is termed its critical temperature, Tc. The highest pressure at which a species can coexist as a liquid and a vapor is termed its critical pressure, Pc

Values of the critical temperature and pressure are needed for prediction methods that correlate physical properties with the reduced conditions. It is also important to know the critical conditions when applying equation of state methods, as some of the equation of state models are unreliable close to the critical point. The critical point is reached when the molar volumes of liquid and gas become the same, so the distinction between the two separate phases vanishes.

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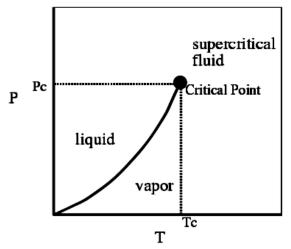


Figure 3: Critical point

There some method to estimated the critical properties

Joback Method

The Joback method is based on the Lydersen method, except it uses a larger database and has fewer functional groups. Joback tested approximately 400 organic compounds. The average relative error is 2.3% for Vc, 0.8% for Tc and 5.2% for Pc. The average error is 7.5 cc/mole, 4.8 K and 2.1 bar

Lydersen Method

The Lydersen method is one of the first successful methods for estimating critical parameters. The estimated error for T_c is usually 4% for Vc, less than 2% for Tc and 4% for Pc. For high molecular weight nonpolar compounds (MW >> 100), the errors are 5% or higher

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Simple Method

The Simple method does not depend on molecular structure, but requires MW and TB as input. This method was developed by Klincewicz and Reid. The average error for about 200 diverse organic compounds tested is 2.3%.

Ambrose Method

The Ambrose method yields smaller errors than the Joback and Lydersen methods, but is more difficult to use. The errors for approximately 400 organic compounds are: average relative error 2.8% for Vc, 0.7% for Tc and 4.6% for Pc. Average error 8.5 cc/mole, 4.3K and 1.8 bar

Gani Method

The Gani method uses contributions from both first-order and second-order groups. The second order groups account for the effect of neighboring atoms. Estimation accuracy is generally superior to other methods. For 400 compounds tested, the average relative error is 1.79 % for Vc, 0.85% for Tc and 2.89% for Pc. The average error is 6 cc/mole, 4.85 K and 1.13 bar.

Every these methods need normal boiling point to predict critical temperature and the accuracy of Tc estimated value is strongly depend on inputted normal boiling point. So for completely unknown molecule case, it needs to estimate of boiling point, then to calculate Tc, this means multiply two errors.

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							Vc
No	Substance	Mw	Ω	Tc (K)	Pc (bar)	Zc	(cm³/mol)
1	Methane	16.043	0.012	190.6	45.99	0.286	98.6
2	Ethane	30.07	0.1	305.3	48.72	0.279	145.5
3	Propane	44.097	0.152	369.8	42.48	0.276	200
4	n-Butane	58.123	0.2	425.1	37.96	0.274	255
5	n-Pentane	72.15	0.252	469.7	33.7	0.27	313
6	n-Hexane	86.177	0.301	507.6	30.25	0.266	371
7	n-Heptane	100.204	0.35	540.2	27.4	0.261	428
8	n-Octane	114.231	0.4	568.7	24.9	0.256	486
9	n-Nonane	128.258	0.444	594.6	22.9	0.252	544
10	n-Decane	142.285	0.492	617.7	21.1	0.247	600
11	Isobutane	58.123	0.181	408.1	36.48	0.282	262.7
12	Ethylene	28.054	0.087	282.3	50.4	0.281	131
13	Propylene	42.081	0.14	365.6	46.65	0.289	188.4
14	1-Butene	56.108	0.191	420	40.43	0.277	239.3
15	1 -Hexene	84.161	0.28	504	31.4	0.265	354
16	1,3-Butadiene	54.092	0.19	425.2	42.77	0.267	220.4
17	Cyclohexene	82.145	0.212	560.4	43.5	0.272	291
18	Acetylene	26.038	0.187	308.3	61.39	0.271	113
19	Benzene	78.114	0.21	562.2	48.98	0.271	259
20	Toluene	92.141	0.262	591.8	41.06	0.264	316
21	Ethylbenzene	106.167	0.303	617.2	36.06	0.263	374
22	o-Xylene	106.167	0.31	630.3	37.34	0.263	369
23	m-Xylene	106.167	0.326	617.1	35.36	0.259	376
24	p-Xylene	106.167	0.322	616.2	35.11	0.26	379
25	Styrene	104.152	0.297	636	38.4	0.256	352
26	Naphthalene	128.174	0.302	748.4	40.51	0.269	413
27	Formaldehyde	30.026	0.282	408	65.9	0.223	115

Table 2: Critical properties for some substances

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							Vc
No	Substance	Mw	Ω	Тс (К)	Pc (bar)	Zc	(cm³/mol)
28	Acetaldehyde	44.053	0.291	466	55.5	0.221	154
29	Acetone	58.08	0.307	508.2	47.01	0.233	209
30	Diethyl ether	74.123	0.281	466.7	36.4	0.263	280
31	Methanol	32.042	0.564	512.6	80.97	0.224	118
32	Ethanol	46.069	0.645	513.9	61.48	0.24	167
33	1-Propano1	60.096	0.622	536.8	51.75	0.254	219
34	1-Butanol	74.123	0.594	563.1	44.23	0.26	275
35	Phenol	94.113	0.444	694.3	61.3	0.243	229
36	Ethylene glycol	62.048	0.487	719.7	77	0.246	191
37	Acetic acid	60.053	0.467	592	57.86	0.211	179.7
38	n-Butyric acid	88.106	0.681	615.7	40.64	0.232	291.7
39	Benzoic acid	122.123	0.603	751	44.7	0.246	344
40	Methylamine	31.057	0.281	430.1	74.6	0.321	154
41	Ethylamine	45.084	0.285	456.2	56.2	0.307	207
42	Carbon tetrachloride	153.822	0.193	556.4	45.6	0.272	276
43	Chloroform	119.377	0.222	536.4	54.72	0.293	239
44	Methyl chloride	50.488	0.153	416.3	66.8	0.276	143
45	Ethyl chloride	64.514	0.19	460.4	52.7	0.275	200
46	Chlorobenzene	112.558	0.25	632.4	45.2	0.265	308
47	Argon	39.948	0	150.9	48.98	0.291	74.6
48	Krypton	83.8	0	209.4	55.02	0.288	91.2
49	Xenon	131.3	0	289.7	58.4	0.286	118
50	Helium 4	4.003	-0.39	5.2	2.28	0.302	57.3
51	Hydrogen	2.016	-0.216	33.19	13.13	0.305	64.1
52	Oxygen	31.999	0.022	154.6	50.43	0.288	73.4
53	Nitrogen	28.014	0.038	126.2	34	0.289	89.2
54	Air+	28.851	0.035	132.2	37.45	0.289	84.8
55	Chlorine	70.905	0.069	417.2	77.1	0.265	124
56	Carbon monoxide	28.1	0.048	132.9	34.99	0.299	93.4

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No	Substance	Mw	Ω	Tc (K)	Pc (bar)	Zc	Vc (cm³/mol)
57	Carbon dioxide	44.01	0.224	304.2	73.83	0.274	94
58	Carbon disulfide	76.143	0.111	552	79	0.275	160
59	Hydrogen sulfide	34.082	0.094	373.5	89.63	0.284	98.5
60	Sulfur dioxide	64.065	0.245	430.8	78.84	0.269	122
61	Sulfur trioxide	80.064	0.424	490.9	82.1	0.255	127
62	Nitric oxide (NO)	30.006	0.583	180.2	64.8	0.251	58
63	Nitrous oxide (NzO)	44.013	0.141	309.6	72.45	0.274	97.4
64	Hydrogen chloride	36.461	0.132	324.7	83.1	0.249	81
65	Hydrogen cyanide	27.026	0.41	456.7	53.9	0.197	139
66	Water	18.015	0.345	647.1	220.55	0.229	55.9
67	Ammonia	17.031	0.253	405.7	112.8	0.242	72.5

Where,

- Mw = Molecular weight
- ω = Acentric factor
- Tc = Critical temperature
- Pc = Critical pressure
- Zc = Critical compressibility factor

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Equation of State

Equations of state have appeal for predicting thermodynamic properties because they provide internally consistent values for all properties in convenient analytical form. An equation of state is an algebraic expression that relates temperature, pressure, and molar volume for a real fluid. Any thermodynamic property, such as fugacity coefficients and enthalpies, can be calculated from the equation of state. Equation-of-state properties are calculated relative to the ideal gas properties of the same mixture at the same conditions.

Many equations of state of varying complexity have been developed. The equations of state most frequently used in the design of multi-component separation processes are Van de Waals, Redlich-Kwong, Soave Redlich-Kwong (SRK), Peng Robinson, etc.

1. Van de Waals

In 1873, J. D. van der Waals introduced the first equation of state derived by the assumption of a finite volume occupied by the constituent molecules. His new formula revolutionized the study of equations of state, and was most famously continued via the Redlich-Kwong equation of state and the Soave modification of Redlich-Kwong.

2. Redlich-Kwong

Introduced in 1949, the Redlich-Kwong equation of state was a considerable improvement over other equations of the time. It is still of interest primarily due to its relatively simple form. While superior to the van der Waals equation of state, it performs poorly with respect to the liquid phase and thus cannot be used for accurately calculating vapor–liquid equilibria. The Redlich-Kwong equation is adequate for calculation of gas phase properties when the ratio of the pressure to the critical pressure (reduced pressure) is less than about one-half of the ratio of the temperature to the critical temperature (reduced temperature).

The Redlich-Kwong equation has the advantage of a simple analytical form which permits direct solution for density at specified pressure and temperature. The equation

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uses two parameters for each mixture component, which in principle permits parameter values to be determined from critical properties.

3. Soave Redlich Kwong

The Soave Redlich-Kwong (SRK) is a modified version of the Redlich-Kwong equation. In 1972 G. Soave replaced the $1/\sqrt{(T)}$ term of the Redlich-Kwong equation with a function $\alpha(T,\omega)$ involving the temperature and the acentric factor (the resulting equation is also known as the Soave-Redlich-Kwong equation). It is expressed as a function of the acentric factor. The α function was devised to fit the vapor pressure data of hydrocarbons and the equation does fairly well for these materials.

The SRK correlation has improved accuracy in predicting the saturation conditions of both pure substances and mixtures. It can also predict phase behavior in the critical region, although at times the calculations become unstable around the critical point. Less accuracy has been obtained when applying the correlation to hydrogen-containing mixtures.

This property method is comparable to the PR property method. It is recommended for gas-processing, refinery, and petrochemical applications. Example applications include gas plants, crude towers, and ethylene plants. Use the SRK property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen.

4. Peng Robinson

Peng and Robinson similarly developed a two-constant Redlich-Kwong equation of state in 1976. In this correlation, the attractive pressure term of the semi-empirical van der Waals equation has been modified. It accurately predicts the vapor pressures of pure substances and equilibrium ratios of mixtures. In addition to offering the same simplicity as the SRK equation, the Peng-Robinson equation is more accurate in predicting the liquid density. The Peng-Robinson equation was developed in 1976 at The University of Alberta in order to satisfy the following goals:

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- 1. The parameters should be expressible in terms of the critical properties and the acentric factor.
- 2. The model should provide reasonable accuracy near the critical point, particularly for calculations of the compressibility factor and liquid density.
- 3. The mixing rules should not employ more than a single binary interaction parameter, which should be independent of temperature pressure and composition.
- 4. The equation should be applicable to all calculations of all fluid properties in natural gas processes.

It is recommended for gas-processing, refinery, and petrochemical applications. Sample applications include gas plants, crude towers, and ethylene plants. The Peng-Robinson model has been extended to handle polar components and non-ideal chemical systems. For mixture, use the PR property method for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen.

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DEFINITIONS

Acentric Factor - A parameter which helps to specify the VP curve which in turn correlates the rest of the thermodynamic variables. A factor frequently used in correlating thermodynamic properties defined by $\omega = \log Pvr - 1.00$ where Pvr = reduced vapor pressure at Tr = 0.7.

Boiling point - the temperature corresponding to equilibrium between the liquid and vapor phases at 101.325 kPa (or 14.696 psia).

Closed system - A System in which the exchanges of energy with the surroundings is possible, and the transfer of matter to and from the surroundings does not take place.

Corresponding States - The theory that proposes pure components and mixtures have the same relative thermodynamic properties when at the same relative thermodynamic state.

Critical point - the set of physical conditions at which the physical properties of the liquid and gas become identical. The critical temperature, Tc, critical pressure, Pc, and the critical volume, Vc, define the physical conditions of the critical point

Critical Pressure - The vapor pressure at the critical temperature.

Critical Temperature - The temperature above which a component cannot be liquefied. For mixtures, the temperature above which all of the mixture cannot be liquid.

Density - Mass per unit volume of a substance.

Enthalpy - Heat content, H, composed of internal energy, E, and flow energy, PV. Usually expressed as H = E + PV.

Enthalpy (heat) of formation of an ideal gas - the increment in enthalpy associated with the reaction of forming the given compound in its ideal gas state from the elements

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in their standard state defined as the existing phase at a temperature of 298.15 K and a pressure of 101325 Pa.

Thermodynamic property - A quantity which is either an attribute of an entire system or is a function of position which is continuous and does not vary rapidly over microscopic distances, except possibly for abrupt changes at boundaries between phases of the system; examples are temperature, pressure, volume, concentration, surface tension, and viscosity. Also known as macroscopic property.

Entropy - A measure of the inability to do work for a given heat transferred. A thermodynamic quantity, S, defined by the equation - dS = dQ/T where Q is the amount of heat entering or leaving the system at absolute temperature, T.

Freezing point - the temperature corresponding to equilibrium between the crystal phase and the air-saturated liquid at 101.325 kPa (or 14.696 psia).

Gibbs energy of formation of an ideal gas - the increment in Gibbs free energy associated with the reaction of forming the given compound in its ideal gas state from the elements in their standard state defined as the existing phase at a temperature of 298.15 K and a pressure of 101325 Pa.

Heat - Energy in transit. This transfer occurs on a molecular level as a result of temperature differences. The unit of heat is the British thermal unit (Btu).

Heat of vaporization - the enthalpy of the saturated vapor minus the enthalpy of the saturated liquid at the boiling temperature.

Ideal Gas - A gas which follows the equation PV = nRT where n = number of moles.

Irreversibility - The degree of heat or work that is lost when a system is taken from one pressure and temperature to another pressure and/or temperature and returned to its original condition.

Isolated system - It is a system that prevents any interactions between the system and the surroundings.

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Latent heat - the amount of heat added or removed to produce only a phase change.

Melting point - the temperature at which melting occurs under 101325 Pa (1 atmosphere

Mole(s) - A mass of substance corresponding to its molecular weight, expressed usually either as lb-moles or gm-moles.

Normal boiling point - the temperature at which the vapor pressure equals 101325 Pa (1 atmosphere).

Open systems - A system which can exchange both matter and energy with the surroundings.

Phase Envelope - The boundaries of an area on the P-T diagram for the material which encloses the region where both vapor and liquid coexist.

Reduced Pressure - The ratio of the absolute pressure to the critical pressure.

Reduced Temperature - The ratio of the absolute temperature to the critical temperature.

Saturated Water - Water at its boiling temperature for the pressure exerted on it.

Saturated Steam - Steam at the boiling temperature of water for the pressure exerted on it but containing no liquid water.

Saturation - combination of temperature and pressure at which a mixture of vapor and liquid can exist at equilibrium

Sensible heat - the heat added or removed that causes a temperature change.

Specific Volume - The volume of a substance per unit mass. (Inverse of density)

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Thermodynamics - The science which deals with the energy of systems and its changes and effects.

NOMENCLATURE

Ar	Weight of atomic relative
B∟	Thermal expansion coefficient of liquid, 1/°C
Ср	Specific heat capacity, kJ/kgºC;
Cpg	Heat capacity of ideal gas, J/(mol K)
Ср	Heat capacity of saturated liquid, J/(mol K)
Dab	Diffusion coefficient for a binary mixture of gases A and B, cm ² /s
D ^о ав	Diffusion coefficient of solute A in solvent B, cm ² /s
Н	Henry's law constant at pressure of 1 atm (101.325 kPa), atm/mol
k	Thermal conductivity of liquid or solid, W/(m K)
K	Watson characterization factor,
kg	Thermal conductivity of gas, W/(m K)
ki,	Thermal conductivity of components;
ΚL	Thermal conductivity of liquid, W/(m K)
k _m	Thermal conductivity of mixture;
Μ	Molecular mass.
m	Viscosity, mNs/m2;
Mw	Relative molecular mass;
Mwi	Molecular weight of component i.
n	Moles of gas;
Na	Number of atom
Р	Absolute pressure N/m2 (Pa);
Р	Pressure,
Pc	Critical pressure, psia or atm
Pv	Vapor pressure, mm Hg
R	Universal gas constant, J /K mol
S	Solubility, ppm (wt)
Sg	Specific gravity
Sg_{60F}	specific gravity at 60 F
Т	Absolute temperature, K

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T _{abs}	The absolute temperature at which the heat was transferred (°R)
Tb	Normal boiling point, K;
T _{bi}	Normal boiling point of component i. Either Fahrenheit or Rankine units
Тс	Critical temperature, K or R
Tf	Flash point, (K
Tr	Reduced temperature,
V	Volume m3;
VA	Molal volume of solute A at its normal boiling point, cm ³ /mol
Vc	Molar volume at the critical conditions, m ³ /kmol;
Х	Concentration of salt (NaCl) in water, ppm (wt)
Xi	Mole fraction of component
Xvi	Volume fraction of component i
Xwi	Weight fraction of component i
xwt	Solubility in water at pressure of 1 atm, weight fraction
Zc	Critical compressibility factor calculated

Greek Leters

ΔGf	Gibbs energy of formation	on of ideal gas, kJ/mol
-----	---------------------------	-------------------------

- ΔHf Enthalpy of formation of ideal gas, kJ/mol
- ΔHv Enthalpy of vaporization, kJ/mol
- Δ Hvi Latent heats of the components kJ/kmol;
- ΔP Critical pressure increments
- ΔQ The amount of heat transferred during the process (Btu)
- ΔS The change in entropy of a system during some process (Btu/°R)
- ΔT Critical temperature increments,
- ΔV Molar volume increments,
- μ_B Viscosity of solvent B, cP
- μg Iscosity of gas, (μP)
- μ_{gm} Gas mixture viscosity, (μP)
- μ_i Gas viscosity of component i, , (μ P)
- μL Viscosity of liquid, (cP)
- ρ Density
- σ Surface tension, dyn/cm

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Φ Association factor of solvent B, dimensionless

 ω Acentric factor,

Superscript

- CABP Cubic Average Boiling Point
- MABP Molal average boiling point
- MeABP Mean average boiling point
- VABP Volumetric average boiling point
- WABP Weight average boiling point

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