chapter two

Thermodynamics

Introduction

The thermodynamic approach was developed in the nineteenth century for a better understanding of the change in the energy in steam engines. Certain principles were developed, known as the first and second laws of thermodynamics, to mathematically correlate the changes in heat and energy during a particular process. An understanding of the above is extremely important for all branches of science and engineering. The mathematical correlations developed help us to understand how the physical properties and energies are changed during operations such as compression, expansion, and so on.

Heat, work, and energy

From our experience, we know that if two bodies of different temperatures are brought into contact with each other, the heat is transferred from the hot body to the cold body. In fact, the transfer of heat is directly proportional to the difference in temperatures between the two bodies. A popular unit of heat is the calorie, which is defined as the heat required to increase the temperature of 1 g of water by 1°C. The calorie is now recognized as a unit of energy. In the SI unit, the unit of energy is the joule, which is equal to 1 Nm or the mechanical work done when a force of 1 N acts through a distance of 1 m. Thus, mathematically, the work can be defined as a product of force (N) and displacement (m).

Force

Force is derived from Newton's second law as a product of mass and acceleration. The SI unit of force is N. Mathematically

$$F = ma \tag{2.1}$$

While the mass of a body is a scalar quantity that is independent of location, force is a vector quantity that depends on the acceleration due to gravity at any particular location. For example, if an astronaut weighs

750 N on Earth ($a = 9.81$ m/s^2), his mass on Earth will be 76.45 kg and his weight on the moon will be 127.67 N (assuming that the acceleration on the moon is 1.67 m/s^2).

Kinetic and potential energy

The concept of work, kinetic energy, and potential energy was developed through Newton's laws of motion. The work done is defined as

$$dW = madl \tag{2.2}$$

Considering the definition of acceleration as velocity over time and velocity as length over time, Equation 2.2 can be modified as

$$dW = mvdv \tag{2.3}$$

Integrating

$$W = m\left(\frac{v_2^2 - v_1^2}{2}\right) = \Delta\left(\frac{mv^2}{2}\right) \tag{2.4}$$

The term ½ mv^2 is called the kinetic energy.

$$E_K = \frac{1}{2}mv^2 \tag{2.5}$$

If a body of mass m is raised by a distance z, the work done can be defined as

$$W = \Delta(mzg) \tag{2.6}$$

The term mzg is called the potential energy:

$$E_P = mzg \tag{2.7}$$

First law of thermodynamics

The first law of thermodynamics defines the relationship between heat and work. According to the first law, if heat is produced from work, there will be a relationship between the work done and heat produced or vice versa. Alternatively, energy can exist in different forms and the total quantity of energy is always constant. If energy disappears in one form, it will appear in some other form simultaneously.

According to the first law of thermodynamics, the relationship among internal energy, heat, and work in a closed system can be expressed mathematically as

$$dU = dQ + dW \tag{2.8}$$

Phase rule

In a heterogeneous system, phase rule defines how the degree of freedom (F) relates to the number of components (C) and the number of phases (P), such as

$$F = C - P + 2 \tag{2.9}$$

As an example, water exists in two phases (liquid and vapor) at 101.3 kPa and 100°C. In this case, the degree of freedom is 1, meaning that when water exists in the vapor and liquid phases and at 101.3 kPa pressure, the temperature cannot be changed from 100°C. If we add another component, say, glycol, the degree of freedom will be 2. This means that even at 101.3 kPa pressure and under a two-phase condition, the temperature can be a variable depending on the composition.

Reversible process

A system can change from one state to another through either a reversible or an irreversible process. In a reversible process, the change occurs slowly in minute quantities till the total specified change happens.

If an expansion is carried out from an initial pressure P_1 to a final pressure P_2 (volume from V_1 to V_2), the reversible work (W_r) and irreversible work (W_{ir}) done at constant temperature are

$$W_r = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2} \tag{2.10}$$

$$W_{ir} = P_2 (V_2 - V_1) = RT \left(1 - \frac{P_2}{P_1} \right) \tag{2.11}$$

The difference between reversible work and irreversible work can be defined as

$$W_r - W_{ir} = \frac{RT}{P_1 P_2}(P_1 - P_2)^2 \tag{2.12}$$

The right-hand side of Equation 2.12 is a positive quantity, meaning that the work done in a reversible process is always greater than the work done in an irreversible process.

Example 2.1

1 mol air at 300 K is expanded from 500 to 100 kPa. Estimate the work done in both reversible and irreversible processes.

SOLUTION

Reversible work

$W_r = 8.314 * 300 * \ln(5) = 4014.3$ J

Irreversible work

$W_{ir} = 8.314 * 300 * (1 - 0.2) = 1995.4$ J

Heat content or enthalpy

The enthalpy of a system is defined as

$$H = U + PV \tag{2.13}$$

In differential form

$$dH = dU + PdV + VdP \tag{2.14}$$

Heat capacity at constant volume and constant pressure

The heat capacity at constant volume is defined as the change in internal energy with the temperature at constant volume, and the heat capacity at contact pressure is defined as the change in enthalpy with the temperature at constant pressure. Mathematically [1]

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{2.15a}$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.15b}$$

The values of two specific heats are not the same, and the relationship between the two values can be expressed as

$$\begin{aligned} C_P - C_V &= \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \\ &= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \\ &= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \end{aligned}$$

(Since $U = f(T,V)$)

$$= \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

For ideal gas, $(\partial U/\partial V)_T = 0$
Therefore

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = P * \frac{R}{P} = R \tag{2.16}$$

Isothermal process

An isothermal process is a process when the temperature remains constant. The work done to increase an ideal gas pressure from P_1 to P_2 is defined as

$$PV = \text{constant}$$

$$W = RT \ln\frac{P_2}{P_1} \tag{2.17}$$

Adiabatic process

An adiabatic process is the process when there is no heat transfer between the system and the surrounding area ($dQ = 0$). For this case, the work done to increase the system pressure from P_1 to P_2 is defined as [1]

$$PV^{\gamma} = \text{constant}$$

$$W = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] \tag{2.18}$$

Example 2.2

1 kmol air is compressed from 100 kPa and 25°C to 500 kPa. Calculate the work done if the compression is (a) isothermal and (b) adiabatic. The ratio of specific heats for air is 1.4.

SOLUTION

a. The work done for an isothermal process

$$W = RT\ln\frac{P_2}{P_1} = 8.314 * 298 * 1.609 = 3987.5\ \text{kJ}$$

b. The work done for an adiabatic process

$$W = \frac{8.314 * 298}{0.4}(1.584 - 1) = 3616.1\ \text{kJ}$$

Equation of state

Boyle's law and Charles's law

We can assume a cubical box with each side of length l (as shown in Figure 2.1) and whose three axes are x, y, and z. The velocity v can be defined as

$$v^2 = x^2 + y^2 + z^2 \tag{2.19}$$

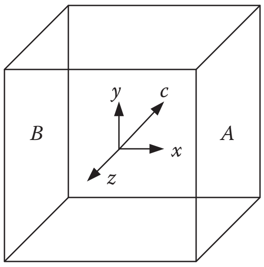


Figure 2.1 Pressure in a cube.

The momentum of a gas particle, with mass m, in the x-direction will be mx, and if we assume that the gas molecule rebounds in an elastic manner, the change in momentum will be $2mx$.

Now, with the distance between the two opposite walls equal to l, the number of collisions per unit time will be x/l. The change in momentum per unit time will be $2mx^2/l$. Considering all the sides, the total momentum imparted per unit time will be

$$\frac{2m(x^2 + y^2 + z^2)}{l} = \frac{2mv^2}{l}$$

Now, considering N number of molecules, the total force exerted on all the walls will be

$$F = \frac{2mNv^2}{l} \tag{2.20}$$

Again, pressure P can be defined as

$$P = \frac{F}{6l^2} = \frac{1}{3}\frac{mNv^2}{V} \tag{2.21a}$$

or

$$PV = \frac{1}{3}mNv^2 \tag{2.21b}$$

where

V = volume of the cube

Now

$$PV = \frac{2}{3}N * \frac{1}{2}mv^2$$

For a given mass of gas, 2/3 N and ½ mv^2 (kinetic energy) are constant if the temperature is constant. Otherwise, PV is constant when the temperature is constant. This is Boyle's law.

Again, at constant pressure, V/T is constant, which is Charles's law. Combining Boyle's and Charles's laws

$$PV = RT \tag{2.22}$$

where

R = universal gas constant

Equation of state for real gas

Equation 2.22 is valid for a perfect gas. In practice, the equation is required to be modified to represent the actual world. There are large numbers of semi-empirical correlations available in the literature, and they are generally developed following identical logics. A gas molecule experiences uniform attraction in all directions when located at the center of a container. However, the gas molecule close to the wall will experience an unbalanced attraction (pulling inward). This will reduce the momentum of the gas molecule. If this decrease in pressure is denoted as $p^{/}$, then the ideal pressure will be $P + p^{/}$, where P is the actual observed pressure.

Similarly, the gas molecule will occupy some space within the container and the actual volume will be reduced to some extent. If the reduction in volume is b, the actual volume will be $V - b$. With these modifications, the general equation is modified as

$$(P + a)(V - b) = RT \tag{2.23}$$

The first equation of state (EOS) was developed by J.D. van der Waals in 1873 and presented as [1]

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{2.24}$$

where the values of a,b typically depend on the pressure and temperature conditions. Changing the values to zero, the equation will modify into the equation of an ideal gas.

Various EOSs were developed to establish calculation procedures for a and b. Out of a large number of EOSs, the following two are extensively used in process engineering calculations:

- Peng–Robinson (PR) [2]
- Soave–Redlich–Kwong (SRK) [3]

Comparison between PR and SRK EOSs

The comparison between PR and SRK EOSs is presented in Table 2.1.

Acentric factor

One important parameter presented in the EOS is the acentric factor ω. The acentric factor is used to correlate physical and thermodynamic properties. Mathematically, the acentric factor is defined as [4]

$$\omega = -\log p_r^{*} - 1.000 \tag{2.26}$$

Table 2.1 Comparison between PR and SRK EOSs

PR	SRK	Equation number
$P = \dfrac{RT}{V-b} - \dfrac{a}{V(V+b)+b(V-b)}$	$P = \dfrac{RT}{V-b} - \dfrac{a}{V(V+b)}$	(2.25a)
$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z$ $-(AB - B^2 - B^3) = 0$	$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$	(2.25b)
where		
$b = \sum_{i=1}^{N} x_i b_i$	$\sum_{i=1}^{N} x_i b_i$	(2.25c)
$b_i = 0.077796 \dfrac{RT_{ci}}{P_{ci}}$	$0.08664 \dfrac{RT_{ci}}{P_{ci}}$	(2.25d)
$a = \left(\sum_{i=1}^{N} x_i a_i^{0.5}\right)^2$	$\left(\sum_{i=1}^{N} x_i a_i^{0.5}\right)^2$	(2.25e)
$a_i = a_{ci}\alpha_i$	$a_{ci}\alpha_i$	(2.25f)
$a_{ci} = 0.457235 \dfrac{(RT_{ci})^2}{P_{ci}}$	$0.42747 \dfrac{(RT_{ci})^2}{P_{ci}}$	(2.25g)
$\alpha_i^{0.5} = 1 + m_i(1 - T_{ri}^{0.5})$	$1 + m_i(1 - T_{ri}^{0.5})$	(2.25h)
$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$	$0.48 + 1.574\omega_i - 0.176\omega_i^2$	(2.25i)
$A = \dfrac{aP}{(RT)^2}$	$\dfrac{aP}{(RT)^2}$	(2.25j)
$B = \dfrac{bP}{RT}$	$\dfrac{bP}{RT}$	(2.25k)

Note: T = absolute temperature, P = absolute pressure, V = specific volume, Z = compressibility, T_c = critical temperature, P_c = critical pressure, T_r = reduced temperature, ω = acentric factor, a,b = parameters used in the equations, $a(T)$ = parameter used in the equations, a_c = value of $a(T)$ at $T = T_c$, α = correction factor, a/a_c, m = slope of $\alpha^{0.5}$ against $Tr^{0.5}$, i = component i in the mixture, N = number of components.

where

p_r^* = reduced vapor pressure, p^*/p_c
p^* = vapor pressure at $T = 0.7T_c$, kPaA
p_c = critical pressure, kPaA
T = temperature, K
T_c = critical temperature, K

For hydrocarbon mixtures, the acentric factor is calculated as

$$\omega = \sum_{i=1}^{N} x_i \omega_i \tag{2.27}$$

where

N = number of components
ω_i = acentric factor of component i
x_i = mole fraction of component i

Other important factors used to establish the physical and thermodynamic properties of hydrocarbon mixtures are the Watson characterization factor K and the critical compressibility factor z_c. Table 2.2 presents the values of the acentric factor, the Watson characterization factor, and the critical compressibility factor. A complete list is available in the API Technical Data Book [4].

Vapor pressure of pure components

The vapor pressure of pure components can be calculated using the Antoine equation. The Antoine equation defines the vapor pressure of pure components as [5]

$$\ln(P) = A - \frac{B}{T + C} \tag{2.28}$$

where

P = vapor pressure, mmHg
T = temperature, K
A,B,C = constants in the Antoine equation

For the commonly used hydrocarbon vapor, the values of constants A, B, and C along with critical pressures and temperatures are presented in Table 2.3. A more complete list is available in the literature [1,5].

Table 2.2 Acentric Factors, Watson Characterization Factors, and Critical Compressibility Factors of Pure Substances

Components	Acentric factor (ω)	Watson characterization factor (K)	Critical compressibility factor (z_c)
	Nonhydrocarbons		
Hydrogen	–0.2153		0.305
Nitrogen	0.04		0.292
Oxygen	0.0218		0.288
Carbon monoxide	0.0663		0.295
Carbon dioxide	0.23894		0.274
Sulfur dioxide	0.2451		0.269
Hydrogen sulfide	0.081		0.284
Water	0.344		0.229
Ammonia	0.252		0.242
	Paraffins		
Methane	0.011498	19.54	0.288
Ethane	0.0986	19.49	0.284
Propane	0.1524	14.69	0.280
n-Butane	0.201	13.50	0.274
i-Butane	0.18479	13.78	0.282
n-Pentane	0.25389	13.03	0.269
i-Pentane	0.2224	13.01	0.270
2,2-Dimethylpropane	0.1964	13.36	0.269
n-Hexane	0.3007	12.78	0.264
i-Hexane	0.2781	12.82	0.267
3-Methylpentane	0.2773	12.65	0.273
2,2-Dimethylbutane	0.2339	12.77	0.272
2,3-Dimethylbutane	0.2476	12.62	0.269
n-Heptane	0.3494	12.68	0.263
i-Heptane	0.3282	12.72	0.261
3-Methylhexane	0.3216	12.55	0.255
3-Ethylpentane	0.3094	12.36	0.268
2,2-Dimethylpentane	0.2879	12.60	0.267
2,3-Dimethylpentane	0.2923	12.35	0.256
2,4-Dimethylpentane	0.3018	12.72	0.265
3,3-Dimethylpentane	0.2672	12.42	0.273
2,2,3-Trimethylbutane	0.2503	12.38	0.266
n-Octane	0.3962	12.68	0.259

continued

Table 2.2 (continued) Acentric Factors, Watson Characterization Factors, and Critical Compressibility Factors of Pure Substances

Components	Acentric factor (ω)	Watson characterization factor (K)	Critical compressibility factor (z_c)
i-Octane	0.3768	12.64	0.261
n-Nonane	0.4368	12.64	0.255
n-Decane	0.4842	12.64	0.249
	Napthenes		
Cyclopropane	0.1348	11.93	0.274
Cyclobutane	0.1866	11.45	0.274
Cyclopentane	0.1943	10.94	0.273
Methylcyclopentane	0.2302	11.32	0.272
Ethylcyclopentane	0.2715	11.39	0.269
Cyclohexane	0.2149	11.00	0.273
Methylcyclohexane	0.2350	11.31	0.269
Ethylcyclohexane	0.2455	11.36	0.270
Cyclooctane	0.2536	10.89	0.270
	Olefins		
Ethylene	0.0852		0.277
Propylene	0.1424	14.21	0.275
1-Butene	0.1867	13.04	0.276
cis-2-Butene	0.2030	12.61	0.272
trans-2-Butene	0.2182	12.93	0.274
i-Butylene	0.1893	13.01	0.275
1-Pentene	0.2330	12.65	0.270
cis-2-Pentene	0.2406	12.48	0.279
trans-2-Pentene	0.2373	12.61	0.279
1-Hexene	0.2800	12.50	0.265
cis-2-Hexene	0.2722	12.30	0.266
trans-2-Hexene	0.2613	12.45	0.267
1-Heptene	0.3310	12.41	0.262
trans-2-Heptene	0.3389	12.39	0.256
1-Octene	0.3747	12.40	0.256
trans-2-Octene	0.3384	12.36	0.260
1-Nonene	0.4171	12.42	0.249
1-Decene	0.4645	12.46	0.247

Table 2.2 (continued) Acentric Factors, Watson Characterization Factors, and Critical Compressibility Factors of Pure Substances

Components	Acentric factor (ω)	Watson characterization factor (K)	Critical compressibility factor (z_c)
Diolefins			
Propadiene	0.1594	12.58	0.271
1,2-Butadiene	0.2509	12.16	0.267
1,3-Butadiene	0.1932	12.51	0.270
1,2-Pentadiene	0.2235	11.90	0.256
1,3-Pentadiene	0.0837	12.21	0.285
2,3-Pentadiene	0.2194	11.91	0.253
Acetylenes			
Acetylene	0.1873	16.72	0.271
Methylacetylene	0.2161	12.34	0.276
Ethylacetylene	0.0500	12.14	0.270
Aromatics			
Benzene	0.2108	9.74	0.271
Toluene	0.2641	10.11	0.264
Ethylbenzene	0.3036	10.33	0.263
o-Xylene	0.3127	10.27	0.263
m-Xylene	0.3260	10.41	0.259
p-Xylene	0.3259	10.44	0.260
n-Propylbenzene	0.3462	10.59	0.265
i-Propylbenzene	0.3377	10.54	0.262
n-Butylbenzene	0.3917	10.82	0.261
i-Butylbenzene	0.3811	10.84	0.256
Napthalene	0.3019	9.32	0.269

Source: Adapted from *Technical Data Book—Petroleum Refining*, 4th ed., American Petroleum Institute, Washington, D.C., 1982.

Vapor pressure of water

A much better correlation can be developed for the estimation of water vapor pressure by using the following equation:

$$P = 10^{(7.97 - 1668.2/(T - 45.2))} \tag{2.29}$$

where

P = vapor pressure of water, mmHg
T = temperature, K

Table 2.3 Values of Antoine Constants and Critical Pressures and Temperatures

	Constant in Antoine equation			Temperature limits (°C)		Critical conditions	
Components	*A*	*B*	*C*	Min	Max	Pressure (kPa)	Temperature (K)
Methane	15.2243	597.84	−7.16	−180	−153	4640.7	190.7
Ethane	15.6637	1511.42	−17.16	−143	−74	4883.9	305.4
Propane	15.726	1872.46	−25.16	−109	−24	4256.7	369.9
n-Butane	15.6782	2154.9	−34.42	−78	17	3796.6	425.2
i-Butane	15.5381	2032.73	−33.15	−86	7	3647.6	408.1
n-Pentane	15.8333	2477.07	−39.94	−53	57	3375.1	469.6
n-Hexane	15.8366	2697.55	−48.78	−28	97	3031.6	507.9
n-Heptane	15.8737	2911.32	−56.51	−3	127	2736.8	540.2
n-Octane	15.9426	3120.29	−63.63	19	152	2490	568.7
n-Nonane	15.9671	3291.45	−71.33	39	179	2290	594.6
n-Decane	16.0114	2456.8	−78.67	57	203	2110	617.7
Carbon monoxide	14.3686	530.22	−13.15	−210	−165	3499	132.9
Carbon dioxide	22.5898	3103.39	−0.16	−119	−69	7370	304.1
Hydrogen sulfide	16.1040	1768.69	−26.06	−83	−43	9007.8	373.6
Nitrogen	14.9542	588.72	−6.6	−219	−183	3394.4	126.2
Oxygen	15.4075	734.55	−6.45	−210	−173	5043	154.6
Hydrogen	13.6333	164.9	3.19	−259	−248	1313	33.19
Water	18.3036	3816.44	−46.13	11	168	22,120	647.3

Vapor pressure calculation using EOSs

The vapor pressure of pure components can be calculated by estimating the fugacity of the component. The general equation of fugacity for pure components

SRK EOS

$$\ln\frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{B}\ln\left(\frac{Z + B}{Z}\right) \tag{2.30}$$

PR EOS

$$\ln\frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\ln\frac{Z + 2.414B}{Z - 0.414B} \tag{2.31}$$

Vapor pressure is the equilibrium pressure, where

$$f^L = f^V \tag{2.32}$$

where

f^L = fugacity of the liquid phase
f^V = fugacity of the vapor phase
P = pressure
Z = compressibility
B = parameter defined in Table 2.1

Example 2.3

Estimate the vapor pressure of *n*-hexane at 31.6°C (304.75 K).

SOLUTION

Use the Antoine equation

$A = 15.8366$
$B = 2697.55$
$C = -48.78$

$$\ln(P) = 15.8366 - \frac{2697.55}{304.75 - 48.78} = 5.29806$$

or

$$P = 199.95 \text{ mmHg} = 26.66 \text{ kPa}$$

Use PR EOS

Critical pressure = 3025 kPa
Critical temperature = 507.6 K
Acentric factor = 0.3047
Temperature = 304.75 K

Parameters are calculated as

$$a_c = 0.457235\frac{(8.314 * 507.6)^2}{3025} = 2692.04$$

$$m_i = 0.37464 + 1.54226 * 0.3047 - 0.26992 * 0.3047^2 = 0.8195$$

$$T_{ri} = 304.75/507.6 = 0.6$$

$$\alpha = (1 + 0.8195 * (1 - 0.6^{0.5}))^2 = 1.4031$$

$$a = a_c * \alpha = 3777.15$$

$$b = 0.077796\frac{8.314 * 507.6}{3025} = 0.1085$$

The vapor pressure will be the pressure at which the fugacity of the liquid and vapor phases will be the same. This is calculated by assuming an initial value and then modifying the value suitably. This calculation converges very rapidly.

Assumption 1: Vapor pressure is 1 kPa

$$A = \frac{3777.15 * 1}{(8.314 * 304.75)^2} = 0.0005884$$

$$B = \frac{0.1085 * 1}{304.75 * 8.314} = 0.000043$$

Using the above values of A and B, the cubic equation will be

$$Z^3 - 0.99996Z^2 + 0.000503Z - 2.337 * 10^{-8} = 0$$

The above equation has three real roots; the highest value is the compressibility of the vapor phase and the lowest one is the compressibility of the liquid phase:

Compressibility of vapor phase = 0.99945
Compressibility of liquid phase = 0.000052

The fugacity can be calculated as

Liquid-phase fugacity = 26 kPa
Vapor-phase fugacity = 1 kPa

Since the values are not the same, the initial pressure is to be modified and recalculated.

This calculation is repeated till the liquid and vapor phase fugacity difference is <0.00001.

The estimated vapor pressure is 26.7 kPa (200.3 mmHg).

The calculated vapor pressure of hexane at 31.6°C:

Using the Antoine equation = 26.66 kPa (199.95 mmHg)
Using PR EOS = 26.7 kPa (200.3 mmHg)
Literature value [6] = 200 mmHg

Second law of thermodynamics

The first law of thermodynamics states that the energy is interchangeable, but it did not provide any indication whether change will occur at all or to what extent it will occur. The second law provides the essential conditions to make a change possible.

- The change from heat to work is possible through a thermodynamic engine, which works in a reversible cyclic process.

- The thermodynamic engine must work between two temperatures, taking up heat from the higher-temperature source, converting a portion into work, and giving up the rest of the heat to the lower-temperature sink.

Carnot's cycle

Carnot's cycle (Figure 2.2) can be used to explain how and to what extent work is obtained from heat. In this cycle, the engine starts at a point A and comes back to the same point. Alternatively, the engine must operate in a complete cycle. Also, maximum work can be obtained when every step operates in a reversible fashion.

In the above cycle, the following operations can be analyzed.

Operation 1: Gas is allowed to expand, isothermally and reversibly, from point A to point B (volume changes from V_1 to V_2). For an ideal gas, the heat absorbed is equal to the work done.

$$Q_1 = RT_1 \ln \frac{V_2}{V_1} \tag{2.33}$$

Operation 2: The gas is then allowed to expand from V_2 to V_3 adiabatically and reversibly till the temperature drops to the temperature of the sink. Owing to the adiabatic process, the heat exchange is 0. The work done (W_1) by the gas can be calculated as

$$W_1 = C_V (T_1 - T_2) \tag{2.34}$$

Operation 3: The gas is compressed isothermally and reversibly from V_3 to V_4. For an ideal gas, the heat given out is equal to the work done by the gas:

$$Q_2 = RT_2 \ln \frac{V_4}{V_3} \tag{2.35}$$

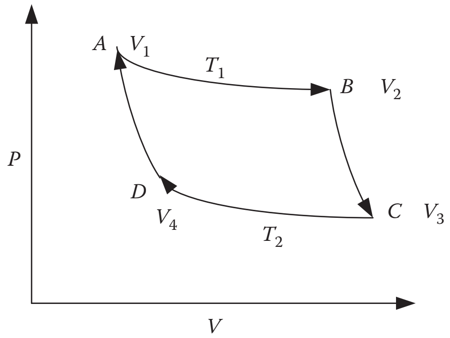


Figure 2.2 Carnot's cycle.

Operation 4: The gas is compressed adiabatically and reversibly from V_4 to V_1 and comes back to the initial state.

$$W_2 = -C_V\,(T_1 - T_2) \tag{2.36}$$

The net work (W) done by the gas in the complete cycle

$$W = RT_1 \ln\frac{V_2}{V_1} + C_V\,(T_1 - T_2) + RT_2 \ln\frac{V_4}{V_3} - C_V\,(T_1 - T_2) \tag{2.37}$$

or

$$W = RT_1 \ln\frac{V_2}{V_1} + RT_2 \ln\frac{V_4}{V_3} \tag{2.38}$$

Now, from the first law

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Therefore, the net work done can be defined as

$$W = R(T_1 - T_2)\ln\frac{V_2}{V_1} \tag{2.39}$$

The efficiency (η) of the process is given as

$$\eta = \frac{W}{Q_1} = 1 - \frac{T_2}{T_1} \tag{2.40}$$

And the work is given as

$$W = Q_1\left(1 - \frac{T_2}{T_1}\right) \tag{2.41}$$

This relationship is the mathematical form of the second law.

Entropy

With some extension of the above analysis, it can be concluded that a thermodynamic change defined as dQ/T is independent of the path of the transformation of the system. This function is called entropy and is normally denoted by S.

Mathematically, the change in entropy is measured by the ratio of the heat change and temperature at which the heat change occurs and is defined as

$$dS = \frac{dQ_{rev}}{T} \tag{2.42}$$

The term dQ_{rev} indicates that the heat change occurs through a reversible process.

Sensible heat

Enthalpy is a function of temperature and pressure

$$H = f(T,P)$$

or

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

or

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{2.43a}$$

In the above equation, the second term is zero for the following conditions:

a. When the pressure is constant
b. When enthalpy is independent of the pressure, for example, low-pressure gas

Considering the above conditions, the change in enthalpy can be defined as

$$dH = C_P dT \tag{2.43b}$$

where C_P is the isobaric specific heat.

Thermodynamic properties

The following thermodynamic properties are extremely important in all process engineering calculations. This section will discuss the method to estimate these thermodynamic properties.

- Isobaric specific heat of hydrocarbon ideal gases
- Isobaric specific heat of hydrocarbon real gases
- Isobaric specific heat of hydrocarbon gas mixtures
- Isobaric specific heat of ideal liquids
- Isobaric specific heat of real liquids
- Enthalpy of gases
- Enthalpy of gas mixtures
- Entropy of ideal gases
- Entropy of real gases
- Entropy of hydrocarbon gas mixtures
- Viscosity of ideal liquids
- Viscosity of ideal hydrocarbon vapors
- Liquid viscosity of defined mixtures at low pressure
- Vapor viscosity of defined mixtures at low pressure
- Thermal conductivity of pure hydrocarbon liquids at low pressure
- Thermal conductivity of pure hydrocarbon vapors at low pressure

Isobaric specific heat of hydrocarbon ideal gases

Specific heat at a constant pressure is an important parameter for engineering calculations. This value is largely influenced by the temperature and the actual pressure of the fluid. The specific heat of pure components for an ideal gas is calculated as [1]

$$C_P/R = A + BT + CT^2 + DT^{-2} \tag{2.44}$$

where

C_P = specific heat of ideal gas, kJ/(kmol·K)
R = universal gas constant, kJ/(kmol·K)
T = temperature, K
A,B,C,D = constants

Constants for the calculation of the specific heat of commonly used ideal gases are presented in Table 2.4.

Example 2.4

Estimate the heat required to raise the temperature of 1 kmol methane from 100°C to 400°C.

Table 2.4 Constants for the Calculation of Specific Heat—Ideal Gases

Ideal Gases	MW	$T_{\max}$ (K)	A	$B * 10^3$	$C * 10^6$	$D * 10^{-5}$
Methane	16.043	1500	1.702	9.081	−2.164	
Ethane	30.070	1500	1.131	19.225	−5.561	
Propane	44.097	1500	1.213	28.785	−8.824	
n-Butane	58.123	1500	1.935	36.915	−11.402	
i-Butane	58.123	1500	1.677	37.853	−11.945	
n-Pentane	72.150	1500	2.464	45.351	−14.111	
n-Hexane	86.177	1500	3.025	53.722	−16.791	
n-Heptane	100.204	1500	3.570	62.127	−19.486	
n-Octane	114.231	1500	4.108	70.567	−22.208	
Air	28.851	2000	3.355	0.575		−0.016
Nitrogen	28.014	2000	3.280	0.593		0.040
Oxygen	31.999	2000	3.639	0.506		−0.227
Hydrogen	2.016	3000	3.249	0.422		0.083
Hydrogen sulfide	34.082	2300	3.931	1.49		−0.232
Carbon monoxide	28.010	2500	3.376	0.557		−0.031
Carbon dioxide	44.01	2000	5.457	1.045		−1.157
Water	18.015	2000	3.47	1.45		0.121

Source: Adapted from Smith, J.M., Van Ness, H.C., and Abbott, M.M., *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, New York, 2001.

Note: Values for other components are available in the literature [1,5,7]. $T_{\max}$ is the maximum temperature, K.

SOLUTION

The heat required can be calculated as

$$
\begin{aligned}
Q = dH &= \int_{T_1}^{T_2} C_P dT \\
&= R\int_{1}^{k} \frac{C_P}{R} dT \\
&= R\left[AT_1(k-1) + B\frac{T_1^2}{2}(k^2-1) + C\frac{T_1^3}{3}(k^3-1) \right]
\end{aligned}
$$

where

T_1 = initial temperature = 373.15 K
k = temperature ratio = 673.15/373.15 = 1.804
A,B,C = constants as per Table 2.4

Solving the above equation for methane

$$Q = 8.314\left[1.702 * 373.15 * 0.804 + 9.801 * 10^{-3}\frac{373.15^2}{2} * \right.$$

$$\left. 2.254 - 2.164 * 10^{-6}\frac{373.15^3}{3} * 4.871\right]$$

$$= 15515\,\text{kJ}$$

Isobaric specific heat of hydrocarbon real gases

Isobaric specific heat is an important thermodynamic parameter and is used in several calculations, including sensible heat effect, Joule–Thomson cooling, and so on [4].

Isobaric specific heat is calculated as

$$C_P = C_P^0 - R\left(\frac{C_P^0 - C_P}{R}\right) \tag{2.45}$$

where

C_P = isobaric specific heat of the real gas, kJ/(kmol·K)
C_P^0 = isobaric specific heat of the ideal gas, kJ/(kmol·K)
R = gas constant = 8.314 kJ/(kmol·K)
$(C_P^0 - C_P)/R$ = dimensionless correction factor

The dimensionless correction factor is calculated as

$$\frac{C_P^0 - C_P}{R} = \left(\frac{C_P^0 - C_P}{R}\right)^0 + \frac{\omega}{\omega^h}\left[\left(\frac{C_P^0 - C_P}{R}\right)^h - \left(\frac{C_P^0 - C_P}{R}\right)^0\right] \tag{2.46}$$

where

$((C_P^0 - C_P)/R)^0$ = effect of the pressure for simple fluid (use Equation 2.47 to calculate)
$((C_P^0 - C_P)/R)^h$ = effect of the pressure for the heavy reference fluid (*n*-octane) (use Equation 2.47 to calculate)

The pressure effect is calculated as

$$\left(\frac{C_P^0 - C_P}{R}\right)^i = 1 + \frac{T_r(\partial P_r/\partial T_r)^2_{V_r}}{(\partial P_r/\partial V_r)_{T_r}} + \left(\frac{\Delta C_V}{R}\right)^i \tag{2.47}$$

where

$$\left(\frac{\partial P_r}{\partial T_r}\right)_{V_r} = \frac{1}{V_r}\left\{1 + \frac{b_1 + b_3/T_r^2 + 2b_4/T_r^3}{V_r} + \frac{c_1 - 2c_3/T_r^3}{V_r^2} + \frac{d_1}{V_r^5} - \frac{2c_4}{T_r^3 V_r^2} \times \left[\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)\right]\right\} \tag{2.48}$$

$$\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = -\frac{T_r}{V_r^2}\left\{1 + \frac{2B}{V_r} + \frac{3C}{V_r^2} + \frac{6D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(3\beta + \left\{5 - 2\left(\beta + \frac{\gamma}{V_r^2}\right)\right\}\frac{\gamma}{V_r^2}\right) \times \exp\left(-\frac{\gamma}{V_r^2}\right)\right\} \tag{2.49}$$

$$\left(\frac{\Delta C_V}{R}\right)^i = -\frac{2(b_3 + 3b_4/T_r)}{T_r^2 V_r} + \frac{3c_3}{T_r^3 V_r^2} + 6E \tag{2.50}$$

where
P_r = reduced pressure
T_r = reduced temperature
V_r = reduced volume = ZT_r/P_r
Z = compressibility

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \tag{2.51a}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \tag{2.51b}$$

$$D = d_1 + \frac{d_2}{T_r} \tag{2.51c}$$

$$E = \frac{c_4}{2T_r^3\gamma}\left\{\beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)\right\} \tag{2.51d}$$

Other constants used in the above equations for both simple and heavy reference fluids are tabulated in Table 2.5.

Table 2.5 Values of Constants

Constants	Simple fluid	Heavy reference fluid
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0	0.016901
c_4	0.042724	0.041577
$d_1 * 10^4$	0.155488	0. 48736
$d_2 * 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754

Source: Adapted from *Technical Data Book—Petroleum Refining*, 4th ed., American Petroleum Institute, Washington, D.C., 1982.

Isobaric specific heat of hydrocarbon gas mixtures

The above method can also be used to calculate the isobaric specific heat of real hydrocarbon gas mixtures [4]. However, the pseudocritical properties are to be used for the calculation. Pseudocritical properties are calculated as

$$P_{pc} = \sum_{i=1}^{n} x_i P_{ci} \tag{2.52}$$

$$T_{pc} = \sum_{i=1}^{n} x_i T_{ci} \tag{2.53}$$

$$\omega = \sum_{i=1}^{n} x_i \omega_i \tag{2.54}$$

$$C_P = \sum w_i C_{pi} \tag{2.55}$$

where

P_{pc} = mixture's pseudocritical pressure, kPa
P_{ci} = critical pressure of component i, kPa
T_{pc} = mixture's pseudocritical temperature, K
T_{ci} = critical temperature of component i, K

n = number of components
x_i = mole fraction of component i
ω = mixture's acentric factor
ω_i = acentric factor of component i
C_P = mixture's isobaric specific heat
C_{Pi} = isobaric specific heat of component i
w_i = weight fraction of component i

Example 2.5

Estimate the isobaric specific heat for

i. Methane at 10,000 kPag and 20°C
ii. Ethane at 3000 kPag and 50°C
iii. Nitrogen at 8000 kPag and 30°C
iv. Mixed gas (nitrogen 10 mol%, methane 45 mol%, and ethane 45 mol%, at 3000 kPag and 30°C) (ignore the interaction parameters)

SOLUTION

i. Isobaric specific heat of ideal gas = 34.74 kJ/(kmol·K)
Compressibility = 0.81698

$$\left(\frac{\partial P_r}{\partial T_r}\right)_{Vr} = 2.3698$$

$$\left(\frac{\partial P_r}{\partial V_r}\right)_{Tr} = -3.4043$$

$$\left(\frac{\Delta CV}{R}\right)^i = -0.2418$$

$$\left(\frac{C_P^0 - C_P}{R}\right)^0 = -1.77765$$

$$\left(\frac{C_P^0 - C_P}{R}\right) = -1.7572$$

C_P = 34.74 + 8.314 * 1.7572 = 49.35 kJ/(kmol·K)
(*HYSYS® calculated value is 49.32 kJ/(kmol·K)*)

ii. Isobaric specific heat of ideal gas = 56.226 kJ/(kmol·K)
Compressibility = 0.77283

$$\left(\frac{C_P^0 - C_P}{R}\right) = -1.6363$$

C_P = 69.83 kJ/(kmol·K)
(*HYSYS calculated value is 69.98 kJ/(kmol·K)*)

iii. Isobaric specific heat of ideal gas = 29.13 kJ/(kmol·K)
Compressibility = 0.98869

$$\left(\frac{C_P^0 - C_P}{R}\right) = -0.3971$$

C_P = 32.43 kJ/(kmol·K)
(*HYSYS calculated value is 32.99 kJ/(kmol·K)*)

iv. Pseudocritical pressure = 4625.48 kPa
Pseudocritical temperature = 235.88 K
Acentric factor = 0.05354
Compressibility factor = 0.87746 (Note-1)
Isobaric specific heat of methane at 30°C = 35.38 kJ/(kmol·K)
Isobaric specific heat of ethane at 30°C = 53.61 kJ/(kmol·K)
Isobaric specific heat of nitrogen at 30°C = 29.13 kJ/(kmol·K)
Weight fraction of methane = 0.3064
Weight fraction of ethane = 0.5743
Weight fraction of nitrogen = 0.1193
Isobaric specific heat of ideal mixtures = 45.11 kJ/(kmol·K)

$$\left(\frac{C_P^0 - C_P}{R}\right) = -0.7559$$

C_P = 51.4 kJ/(kmol·K)
(*HYSYS calculated value is 49.64 kJ/(kmol·K), Note-1*)

Note-1: The compressibility factor is calculated without considering the interaction parameters. As a result, both the compressibility factor and the isobaric specific heat of real gas mixtures will be different from the calculated value using the interaction parameters.

Joule–Thomson coefficient

If we consider a case where volume V_1 of a gas at pressure P_1 is allowed to pass to a lower pressure P_2, through a semipermeable membrane slowly and reversibly, the volume at the lower pressure side will increase to V_2 ($V_2 > V_1$) as shown in Figure 2.3. If we assume that the piston is frictionless and the system is thermally insulated and there is no heat change ($dQ = 0$), then the work done can be defined as

Work done by the high-pressure side = P_1V_1
Work done by the low-pressure side = P_2V_2

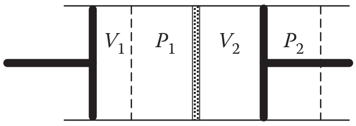


Figure 2.3 Joule–Thomson effect.

Now, from the first law of thermodynamics

$$dU = -dW = P_1V_1 - P_2V_2$$

or

$$U_1 + P_1V_1 = U_2 + P_2V_2$$

or

$$H_1 = H_2$$

or

$$\Delta H = 0$$

This indicates that an adiabatic expansion is also isenthalpic.

However, during this expansion, there will be a change in the temperature, and this variation of temperature is called the Joule–Thomson effect.

The rate of change in temperature with pressure is called the Joule–Thomson coefficient.

$$\mu = \left(\frac{dT}{dP}\right)_H \tag{2.56}$$

Generally, the value of μ is positive, meaning that with a drop in pressure, the temperature will also drop. However, in some cases (hydrogen, helium at room temperature), the value of μ is negative, meaning that there will be an increase in temperature with a decrease in pressure.

Now, $H = f(T,P)$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

or

$$\mu = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \tag{2.57}$$

Again

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = -\frac{RT^2}{P}\left(\frac{\partial Z}{\partial T}\right)_P$$

where

Z = compressibility factor

The general equation of the Joule–Thomson coefficient can be defined as [1]

$$\mu = \frac{RT^2}{C_P P}\left(\frac{\partial Z}{\partial T}\right)_P \tag{2.58}$$

Example 2.6

Estimate the Joule–Thomson cooling temperature if methane at 10,000 kPag and 20°C is expanded to the atmospheric pressure.

SOLUTION

This can be calculated by reducing the pressure in steps and estimating the temperature at the end of each step. The isobaric specific heat of a real gas is calculated using the procedure described in Example 2.5.

The PR EOS is used for this calculation.

Let the number of steps be 50; therefore, the reduction in pressure at the end of each step will be 200 kPa.

Constant parameters

Critical pressure = 4640.68 kPa
Critical temperature = 190.7 K
Acentric factor = 0.0115

Step 1 calculation

Calculated the value of m_i (Equation 2.25i) = 0.3923
Calculated the value of a_{ci} (Equation 2.25g) = 247.67
Calculated the value of b_i (Equation 2.25d) = 0.0266
Compressibility (Z) = 0.81792
Value of $(\partial Z/\partial T)_P = 0.00239$
Isobaric heat capacity of a real gas = 49.35 kJ/(kmol·K)
Joule–Thomson coefficient (Equation 2.58) = 0.00342
Drop in temperature (Equation 2.56) = 0.68°C
Temperature after first step = 19.32°C

The above step is repeated 50 times to calculate the final temperature.

Table 2.6 Joule–Thomson Temperature Calculation for Single Component

	Pressure (kPag)			Final temperature (°C)	
Component	Initial	Final	Initial temperature (°C)	HYSYS	Manual
Methane	10,000	0	20	–32.3	–32.0
Methane	8000	0	–7	–60.5	–61.3
Methane	8000	3000	–10	–39.9	–40.4
Ethane	3000	0	60	29.1	30.1
Propane	2000	0	100	78.6	78.8
i-Butane	1000	0	150	141.6	141.6
Carbon dioxide	5000	0	60	8.1	6.1
Nitrogen	8000	0	–7	–30.3	–30.6
Nitrogen	7000	0	10	–8.2	–8.4
Nitrogen	6000	2000	0	–10.6	–10.7

Calculated final temperature = –32.0°C (Note-1)
(*HYSYS calculated temperature* = *–32.3°C*)

Note-1: This calculation is not valid if the liquid phase is detected at any step.

The results of a few typical calculations along with the HYSYS calculated values are presented in Table 2.6.

Isobaric specific heat of ideal liquids

Similarly, specific heat at a constant pressure for liquids can be calculated as

$$C_P/R = A + BT + CT^2 \tag{2.59}$$

Constants for the calculation of specific heat of commonly used liquids are presented in Table 2.7.

Isobaric specific heat of real liquids

The calculation of the isobaric specific heat for a real liquid is identical to the procedure used for a real gas [4]. The isobaric specific heat of real hydrocarbon liquid mixtures is calculated as [4]

$$C_P = \sum w_i C_{pi} \tag{2.60}$$

where

C_P = isobaric specific heat of mixtures
w_i = weight fraction of component *i*
C_{Pi} = isobaric specific heat of component *i*

Table 2.7 Constants for the Calculation of Specific Heat—Liquids

Liquids	A	$B * 10^3$	$C * 10^6$
Ammonia	22.626	−100.75	192.71
Aniline	15.819	29.03	−15.80
Benzene	−0.747	67.96	−37.78
1,3-Butadiene	22.711	−87.96	205.79
Carbon tetrachloride	21.155	−48.28	101.14
Chlorobenzene	11.278	32.86	−31.90
Chloroform	19.215	−42.89	83.01
Cyclohexane	−9.048	141.38	−161.62
Ethanol	33.866	−172.60	349.17
Ethylene oxide	21.039	−86.41	172.28
Methanol	13.431	−51.28	131.13
n-Propanol	41.653	−210.32	427.20
Sulfur trioxide	−2.930	137.08	−84.73
Toluene	15.133	6.79	16.35
Water	8.712	1.25	−0.18

Source: Adapted from Smith, J.M., Van Ness, H.C., and Abbott, M.M., *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, New York, 2001.

Enthalpy of gases

The enthalpy of a gas is estimated by estimating the enthalpy of an ideal gas. The enthalpy of an ideal gas is calculated using the following equation:

$$H_T^0 = H_{25}^0 + \frac{R}{M}\int_{298.15}^{T} \frac{C_P}{R} dT \tag{2.61}$$

where

H_T^0 = ideal gas enthalpy of formation at temperature T, kJ/kg
H_{25}^0 = ideal gas enthalpy of formation at 25°C, kJ/kg
R = gas constant, kJ/(kmol·K)
M = molecular weight
C_P = isobaric specific heat, kJ/(kg·°C)
T = temperature, K

The ideal gas enthalpy of formation at 25°C is presented in Table 2.8 [4].

The enthalpy of a real gas is estimated by using the following equation [1]:

$$H_T = H_T^0 + H^R \tag{2.62}$$

Table 2.8 Ideal Gas Enthalpy of Formation at 25°C

Component	MW	Heat of formation at 25°C (kJ/kg)
Methane	16.043	−4645.1
Ethane	30.070	−2787.5
Propane	44.097	−2373.9
n-Butane	58.123	−2164.2
i-Butane	58.123	−2308.5
n-Pentane	72.150	−2034.1
n-Hexane	86.177	−1937.2
n-Heptane	100.204	−1872.7
n-Octane	114.321	−1827.4

Source: Adapted from *Technical Data Book—Petroleum Refining*, 4th ed., American Petroleum Institute, Washington, D.C., 1982.

Note: Values for other components are available in the literature [4].

where

H_T = enthalpy of real gas, kJ/kg
H^R = residual enthalpy, kJ/kg

Residual enthalpy is calculated as [1]

$$\frac{H^R}{RT} = \frac{1}{M}\left\{Z - 1 + \left[\frac{d\ln\alpha(T_r)}{d\ln(T_r)} - 1\right]qI\right\} \tag{2.63}$$

Different equations are used for different EOSs to calculate the value of $\alpha(T_r)$ are indicated below [1].

For the PR EOS

$$\alpha(T_r) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2 \tag{2.64a}$$

For the SRK EOS

$$\alpha(T_r) = [1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5})]^2 \tag{2.64b}$$

where

ω = acentric factor

The value of q is calculated using the following equation [1]:

For the PR EOS

$$q = \frac{0.457235\alpha(T_r)}{0.077796T_r} \tag{2.65a}$$

For the SRK EOS

$$q = \frac{0.42747\alpha(T_r)}{0.08664(T_r)} \tag{2.65b}$$

The value of I is calculated using the following equations [1]:

$$I = \ln\left(\frac{Z+\beta}{Z}\right) \tag{2.66}$$

where

Z = compressibility

and for the PR EOS

$$\beta = 0.077796\frac{P_r}{T_r} \tag{2.67a}$$

For the SRK EOS

$$\beta = 0.08664\frac{P_r}{T_r} \tag{2.67b}$$

where

P_r = reduced pressure
T_r = reduced temperature

Enthalpy of gas mixtures

For hydrocarbon gas mixtures, a similar procedure is used to estimate the enthalpy of gas mixtures with some modifications to the pressure and temperature parameters [4].

The critical temperature is replaced by a pseudocritical temperature using the following equation:

$$T_{pc} = \sum_{i=1}^{n} x_i T_{ci} \tag{2.68}$$

The critical pressure is replaced by a pseudocritical pressure using the following equation:

$$P_{pc} = \sum_{i=1}^{n} x_i P_{ci} \tag{2.69}$$

The mixture acentric factor is calculated as

$$\omega = \sum_{i=1}^{n} x_i \omega_i \tag{2.70}$$

The ideal gas enthalpy of the mixture is calculated as

$$H^0 = \sum x_{wi} H_i^0 \tag{2.71}$$

where

T_{pc} = pseudocritical temperature of the mixture, K
T_{ci} = critical temperature of component i, K
x_i = mole fraction of component i
P_{pc} = pseudocritical pressure of the mixture, kPa
P_{ci} = critical pressure of component i, kPa
ω = mixture acentric factor
ω_i = acentric factor of component i
H^0 = ideal gas enthalpy of the mixture, kJ/kg
x_{wi} = weight fraction of component i
H_i^0 = ideal gas enthalpy of component i
n = number of components

Example 2.7

Estimate the enthalpy of methane at 293.15 K and 10,101.3 kPa and *n*-butane at 500 K and 5000 kPa. Use the PR EOS for the calculation.

SOLUTION

Enthalpy of methane

The enthalpy of methane at 25°C is –4645.1 kJ/kg.

The change in enthalpy for a temperature change from 298.15 to 293.15 K is calculated using the following equation:

$$dH = \int_{T_1}^{T_2} C_P dT$$

$$= \frac{R}{M}\left[AT_1(k-1) + B\frac{T_1^2}{2}(k^2-1) + C\frac{T_1^3}{3}(k^3-1)\right]$$

where

R = gas constant, kJ/(kmol·K) = 8.314
T_1 = initial temperature = 298.15
k = temperature ratio = 0.983
A = constant = 1.702
B = constant = $9.081 * 10^{-3}$
C = constant = $-2.164 * 10^{-6}$
M = molecular weight = 16.043
Differential enthalpy = –10.9 kJ/kg
The enthalpy of ideal methane at 20°C is –4656 kJ/kg

Calculation of residual enthalpy

The compressibility of methane at 10,101.3 kPa and 293.5 K is 0.8179. (The calculation of compressibility has been discussed before.)

Acentric factor = 0.011498
Critical pressure = 4640.7 kPa
Critical temperature = 190.7 K
Reduced pressure = 2.177
Reduced temperature = 1.573
Value of $\alpha(T_r) = 0.82065$
Value of $q = 3.1376$
Value of $I = 0.1263$
Residual enthalpy = –120.2 kJ/kg
Enthalpy of real gas = –4776.2 kJ/kg
(*HYSYS calculated enthalpy = –4795 kJ/kg*)

Enthalpy of *n*-butane

The enthalpy of methane at 25°C is –2164.2 kJ/kg.

The change in enthalpy for a temperature change from 298.15 to 500 K is calculated using the following equation:

$$dH = \int_{T_1}^{T_2} C_P dT$$

$$= \frac{R}{M}\left[AT_1(k-1) + B\frac{T_1^2}{2}(k^2-1) + C\frac{T_1^3}{3}(k^3-1)\right]$$

where

R = gas constant, kJ/(kmol·K) = 8.314
T_1 = initial temperature = 298.15
k = temperature ratio = 1.6773
A = constant = 1.935
B = constant = $36.915*10^{-3}$
C = constant = $-11.402*10^{-6}$
M = molecular weight = 58.123

Differential enthalpy = 427.7 kJ/kg
The enthalpy of ideal methane at 500 K = –1736.5 kJ/kg

Calculation of residual enthalpy

The compressibility of methane at 5000 kPa and 500 K is 0.6908. (The calculation of compressibility has been discussed before.)

Acentric factor = 0.201
Critical pressure = 3796.6 kPa
Critical temperature = 425.2 K
Reduced pressure = 1.317
Reduced temperature = 1.176
Value of $\alpha(T_r) = 0.8895$
Value of $q = 4.446$
Value of $I = 0.1188$
Residual enthalpy = –89.1 kJ/kg
Enthalpy of real gas = –1825.6 kJ/kg
(*HYSYS calculated enthalpy = –1827 kJ/kg*)

Entropy of ideal gases

The entropy of an ideal gas at 25°C can be calculated using the following equation [4]:

$$S_{25}^0 = 4.1867 * (6.2854B + 1.0734C + 0.43207D + 0.0206E + 0.001037F + G) \tag{2.72}$$

where

S_{25}^0 = entropy of ideal gas at 25°C, kJ/(kg·K)
B,C,D,E,F,G = constants

The constants used in the above equation are presented in Table 2.9.

The ideal gas entropy at temperature T can be calculated using the following equation [4]:

$$S_T^0 = S_{25}^0 + \int_{298.15}^{T} \frac{C_P^0}{T}\,dT \tag{2.73}$$

or

$$S_T^0 = S_{25}^0 + \frac{R}{M}\left[A\ln T + BT + \frac{CT^2}{2} - \frac{DT^{-2}}{2}\right]_{298.15}^{T} \tag{2.74}$$

Table 2.9 Constants for the Calculation of Entropy—Ideal Gases

Ideal Gases	*B*	*C*	*D*	*E*	*F*	*G*
Methane	0.53829	−0.21141	0.33928	−1.16432	1.38961	−0.50287
Ethane	0.26461	−0.02457	0.29140	−1.28103	1.81348	0.08335
Propane	0.16030	0.12608	0.18143	−0.91891	1.35485	0.26090
n-Butane	0.09969	0.26655	0.05407	−0.42927	0.66958	0.34597
i-Butane	0.09907	0.23874	0.09159	−0.59405	0.90965	0.30764
n-Pentane	0.11183	0.22852	0.08633	−0.54465	0.81845	0.18319
n-Hexane	0.08971	0.26535	0.05778	−0.45221	0.70260	0.21241
n-Heptane	0.08978	0.26092	0.06345	−0.48471	0.75546	0.15776
n-Octane	0.07780	0.27936	0.05203	−0.46312	0.75074	0.17417
Nitrogen	0.25410	−0.01662	0.01530	−0.03100	0.01517	0.04868
Oxygen	0.22172	−0.02052	0.03064	−0.10861	0.13061	0.14841
Hydrogen	3.19962	0.39279	−0.29345	1.09007	−1.38787	−3.93825
Hydrogen sulfide	0.23745	−0.02323	0.03881	−0.11329	0.11484	−0.04064
Carbon monoxide	0.25284	−0.01540	0.01608	−0.03434	0.01757	0.10562
Carbon dioxide	0.15884	−0.03371	0.14811	−0.96620	2.07383	0.15115

Source: Adapted from Smith, J.M., Van Ness, H.C., and Abbott, M.M., *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, New York, 2001.

Note: Values for other components are available in the literature [4].

where

S_T^0 = entropy of ideal gas at temperature T, kJ/(kg·K)
S_{25}^0 = entropy of ideal gas at 25°C, kJ/(kg·K)
C_P^0 = specific heat of ideal gas, kJ/(kg·K)
T = temperature, K
A,B,C,D = constants as per Table 2.4

Entropy of real gases

The entropy of a pure real gas can be calculated using the following equation [4]:

$$S = S_T^0 - \frac{R}{M}\left(\frac{S^0 - S}{R}\right) \tag{2.75}$$

where

S = entropy of real gas, kJ/(kg·K)
S_T^0 = entropy of ideal gas at temperature T, kJ/(kg·K)

R = gas constant, kJ/(kmol·K)
M = gas molecular weight
$((S^0 - S)/R)$ = dimensionless effect of pressure on entropy

The dimensionless effect of pressure on entropy can be calculated as [4]

$$\left(\frac{S^0 - S}{R}\right) = -H^R \frac{M}{RT_c} + \ln\left(\frac{f}{p}\right) + \ln\left(\frac{p}{6.8947}\right) \tag{2.76}$$

where
H^R = residual enthalpy, kJ/kg; calculated using the previous method
f/p = fugacity correction
p = pressure, kPa
T = temperature, K
T_c = critical temperature, K
M = molecular weight

Fugacity correction

Fugacity correction can be calculated using the following equation [4]:

$$\ln\frac{f}{p} = \left(\ln\frac{f}{p}\right)^0 + \frac{\omega}{\omega_h}\left[\left(\ln\frac{f}{p}\right)^h - \left(\ln\frac{f}{p}\right)^0\right] \tag{2.77}$$

where $(\ln(f/p))^i$ can be calculated using the following equation:

$$\left(\ln\frac{f}{p}\right)^i = Z - 1 - \ln Z + \frac{B}{V_r} + \frac{C}{2V_r^2} + \frac{D}{5V_r^5} + E \tag{2.78}$$

where
Z = compressibility

Other parameters are calculated using the method described under specific heat calculation and constants in Table 2.5.

Entropy of hydrocarbon gas mixtures

The entropy of a defined hydrocarbon gas mixture can be calculated using the following equation [4]:

$$S^0 = \sum_{i=1}^{n}\left[x_{wi}S_i^0 - \frac{R}{M}(x_i \ln x_i)\right] \tag{2.79}$$

where

S^0 = entropy of the gas mixture, kJ/(kg·K)
x_{wi} = weight fraction of component i
R = gas constant, kJ/(kmol·K)
M = molecular of the gas mixture = $\sum_i x_i M_i$
x_i = mole fraction of component i
M_i = molecular weight of component i

Example 2.8

Estimate the entropy of the following pure components using the PR EOS.

a. Methane at 10,000 kPag and 20°C
b. Ethane at 4800 kPag and 30°C

SOLUTION

a. Methane at 10,000 kPag and 20°C
Phase = vapor
Entropy at 25°C = 11.629 kJ/(kg·K)
Entropy at 20°C = 11.593 kJ/(kg·K)
Residual enthalpy calculated using the previous method = –120.2 kJ/kg
Entropy pressure correction = 6.27

$$\text{Entropy at 10,000 kPag, } 20°\text{C} = 11.593 - \frac{8.314}{16.04} * 6.27$$
$$= 8.343\,\text{kJ}/(\text{kg·K})$$

(*HYSYS calculated value is 8.733 kJ/(kg·K)*)

b. Ethane at 4800 kPag and 30°C
Phase = liquid
Entropy at 25°C = 7.626 kJ/(kg·K)
Entropy at 30°C = 7.656 kJ/(kg·K)
Residual enthalpy calculated using the previous method = –300.8 kJ/kg
Entropy pressure correction = 9.803

$$\text{Entropy at 4800 kPag, 30°C} = 7.6558 - \frac{8.314}{30.07} * 9.803$$

$$= 4.945\ \text{kJ}/(\text{kg}\cdot\text{K})$$

(*HYSYS calculated value is 4.664 kJ/(kg·K)*)

Viscosities of ideal liquids

The viscosity of pure components depends primarily on the temperature and can be calculated using the following general equation [5]:

$$\mu = \exp\left\{A * \left(\frac{1}{T} - \frac{1}{B}\right)\right\} \tag{2.80}$$

Table 2.10 Constants for the Calculation of Liquid Viscosity—Pure Components at Low Pressure

Ideal Components	*A*	*B*
Methane	114.14	57.60
Ethane	156.60	95.57
Propane	222.67	133.41
n-Butane	265.84	160.20
i-Butane	302.51	170.20
n-Pentane	313.66	182.48
n-Hexane	362.79	207.09
n-Heptane	436.73	232.53
n-Octane	473.70	251.71
Nitrogen	90.3	46.14
Oxygen	85.68	51.50
Hydrogen	13.82	5.39
Hydrogen sulfide	342.79	165.54
Carbon monoxide	94.06	48.90
Carbon dioxide	578.08	185.24
Methanol	555.30	260.64
Ethanol	686.64	300.88
Propanol	951.04	327.83
Benzene	545.64	265.34
Toluene	467.33	255.24
Water	658.25	283.16

Source: Adapted from Coulson, J.M. and Richardson, J.F., *Chemical Engineering*, Volume 6 (SI Unit), Pergamon Press, USA, 1986.

Note: Values for other components are available in the literature [5].

where

μ = viscosity, cP
A,B = constants as per Table 2.10
T = temperature, K

Viscosity of water

The viscosity of water at low pressure can also be calculated using the following equation. The following equation is valid for a temperature range of 0–150°C.

$$\mu = \exp\left\{-3.827 + \frac{609.246}{138.89 + t}\right\} \tag{2.81}$$

where

μ = viscosity, cP
t = temperature, °C

Viscosity of ideal hydrocarbon vapors

The viscosity of ideal vapors can be calculated using the following equation [4]:

$$\mu = \frac{1000\,AT_R^B}{(1 + (C/T_R) + (D/T_R^2))} \tag{2.82}$$

where

μ = viscosity, cP
T_R = temperature, R
A,B,C,D = constants as per Table 2.11

Liquid viscosity of defined mixtures at low pressure

The liquid viscosities of defined mixtures at low temperature can be calculated using the following equation [4]:

$$\mu_m = \left\{\sum_{i=1}^{n} x_i \mu_i^{1/3}\right\}^3 \tag{2.83}$$

where

μ_m = viscosity of the mixture, cP
μ_i = viscosity of component i, cP
n = number of components
x_i = mole fraction of component i

Table 2.11 Constants for the Calculation of Vapor Viscosity—Pure Components at Low Pressure

Ideal Components	*A*	*B*	*C*	*D*
Methane	3.715E–7	5.901E–1	190.3	0
Ethane	1.737E–7	6.799E–1	178.0	0
Propane	1.670E–7	6.861E–1	322.7	–2.67E4
n-Butane	1.528E–7	6.944E–1	409.9	–4.73E4
i-Butane	5.090E–7	5.214E–1	412.2	0
n-Pentane	3.853E–8	8.476E–1	75.10	0
n-Hexane	1.155E–7	7.074E–1	282.8	0
n-Heptane	4.100E–8	8.284E–1	154.4	0
n-Octane	1.806E–8	9.292E–1	99.16	0
Nitrogen	4.588E–7	6.081E–1	98.48	0
Oxygen	7.906E–7	5.634E–1	173.3	0
Hydrogen	1.201E–7	6.850E–1	–1.06	4.536E2
Hydrogen sulfide	3.223E–8	1.017	670.3	–2.08E5
Carbon monoxide	8.133E–7	5.338E–1	170.5	0
Carbon dioxide	1.639E–6	4.600E–1	522.0	0
Water	4.152E–7	6.778E–1	1525.0	–2.4E5

Source: Adapted from *Technical Data Book—Petroleum Refining*, 4th ed., American Petroleum Institute, Washington, D.C., 1982.

Note: Values for other components are available in the literature [4].

Vapor viscosity of defined mixtures at low pressure

The viscosity of defined hydrocarbon mixtures at low pressure can be calculated using the following equation [4,8]:

$$\mu_m = \sum_{i=1}^{n} \frac{\mu_i}{1 + \sum_{\substack{j=1 \\ j \neq i}}^{n} \phi_{ij} \dfrac{x_j}{x_i}} \tag{2.84}$$

$$\phi_{ij} = \frac{[1 + (\mu_i/\mu_j)^{0.5}(M_j/M_i)^{0.25}]^2}{\sqrt{8}\,[1 + (M_i/M_j)]^{0.5}} \tag{2.85}$$

where

μ_m = viscosity of the mixture, cP
μ_i = viscosity of component *i*, cP
ϕ_{ij} = interaction parameter of component *i* with respect to *j*
x_i = mole fraction of component *i*
x_j = mole fraction of component *j*
M_i = molecular weight of component *i*
M_j = molecular weight of component *j*
n = number of components in the mixture

Example 2.9

Estimate the viscosity of a gas mixture at 0 kPag and 30°C.

Component	Mole fraction
Methane	0.9
Ethane	0.02
Carbon monoxide	0.02
Carbon dioxide	0.03
Nitrogen	0.03

SOLUTION

The viscosity of individual components can be calculated as

	Constants				
Component	*A*	*B*	*C*	*D*	Viscosity (cP)
Methane	3.715E−7	0.5901	190.3	0	0.0114
Ethane	1.737E−7	0.6799	178.0	0	0.0095
Carbon monoxide	8.133E−7	0.5338	170.5	0	0.0179
Carbon dioxide	1.639E−6	0.4600	522.0	0	0.0152
Nitrogen	4.588E−7	0.6081	98.48	0	0.0179

The interaction parameters can be calculated as

Interaction	M_i	M_j	ϕ_{ij}	$\phi_{ij}\ (x_j/x_i)$	$\Sigma\phi_{ij}\ (x_j/x_i)$
1-2	16.043	30.070	1.4824	0.03294	
1-3	16.043	28.010	1.0340	0.02298	
1-4	16.043	44.010	1.3500	0.04500	
1-5	16.043	28.014	1.0332	0.03444	0.13536
2-1	30.070	16.043	0.6623	29.80284	
2-3	30.070	28.010	0.7228	0.72275	
2-4	30.070	44.010	0.9526	1.42885	
2-5	30.070	28.014	0.7223	1.08341	33.03785
3-1	28.010	16.043	0.9344	42.04872	
3-2	28.010	30.070	1.4619	1.46190	
3-4	28.010	44.010	1.3561	2.03408	
3-5	28.010	28.014	0.9992	1.49880	47.04350
4-1	44.010	16.043	0.6592	19.77659	
4-2	44.010	30.070	1.0411	0.69409	
4-3	44.010	28.010	0.7328	0.48850	
4-5	44.010	28.014	0.7322	0.73224	21.69142
5-1	28.014	16.043	0.9352	28.05564	
5-2	28.014	30.070	1.4633	0.97552	
5-3	28.014	28.010	1.0008	0.66720	
5-4	28.014	44.010	1.3573	1.35726	31.05562

Calculated viscosity = 0.0119 cP

(*HYSYS calculated value is 0.0117 cP*)

Thermal conductivity of pure hydrocarbon liquids at low pressure

The thermal conductivity of a pure hydrocarbon liquid varies linearly with temperature. With known thermal conductivities at two different temperatures, the value can be calculated at any temperature using linear interpolation.

The thermal conductivity of common hydrocarbon liquids can be presented in Table 2.12.

The thermal conductivity of pure hydrocarbon liquid mixtures can be calculated as

$$k_m = \sum_i \sum_j \phi_i \phi_j k_{ij} \tag{2.86}$$

$$k_{ij} = 2\left[\frac{1}{k_i} + \frac{1}{k_j}\right]^{-1} \tag{2.87}$$

Table 2.12 Thermal Conductivity of Pure Hydrocarbon Liquids at Low Pressure

	Temperature (°C)		Thermal conductivity (W/(m.K))	
Component	Freezing	Normal boiling	At freezing temperature	At normal boiling temperature
Methane	−182.5	−161.5	0.2246	0.1883
Propane	−187.7	−42.0	0.2130	0.1289
n-Butane	−138.3	−0.5	0.1869	0.1176
n-Pentane	−129.7	36.1	0.1782	0.1086
n-Hexane	−95.3	68.7	0.1622	0.1042
n-Heptane	−90.6	98.4	0.1598	0.1025
n-Octane	−56.8	125.7	0.1519	0.0981
Benzene	5.5	80.1	0.1493	0.1265
Toluene	−95.0	110.6	0.1615	0.1116
o-Xylene	−25.2	144.4	0.1430	0.1040
m-Xylene	−47.9	139.1	0.1475	0.1035
p-Xylene	13.3	138.4	0.1326	0.1031

Source: Adapted from *Technical Data Book—Petroleum Refining*, 4th ed., American Petroleum Institute, Washington, D.C., 1982.

Note: Values for other components are available in the literature [4].

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j} \tag{2.88}$$

$$\sum_i \phi_i = 1 \tag{2.89}$$

where

k_m = thermal conductivity of the mixture, W/(m.K)
ϕ_i, ϕ_j = volume fraction of pure components i and j
k_i, k_j = thermal conductivity of pure components i and j, W/(m.K)
V_i, V_j = molar volume of pure components i and j, m^3 per kg·mol
x_i, x_j = mole fraction of pure components i and j

Example 2.10

Calculate the thermal conductivity of the following liquid mixture at 0 kPag and 30°C.

n-Pentane = 40 vol%
n-Hexane = 30 vol%
n-Heptane = 30 vol%

The following data are available for the calculation:

Component	Density (kg/m^3)	MW	Molar volume (m^3/kg·mol)
n-Pentane	615.6	72.15	0.1172
n-Hexane	652.4	86.18	0.1321
n-Heptane	673.8	100.2	0.1487

SOLUTION

Thermal conductivity of *n*-pentane at 30°C = 0.1112 W/(m.K)
Thermal conductivity of *n*-hexane at 30°C = 0.1179 W/(m.K)
Thermal conductivity of *n*-heptane at 30°C = 0.1232 W/(m.K)

$$k_{11} = k_1 = 0.1112$$
$$k_{22} = k_2 = 0.1179$$
$$k_{33} = k_3 = 0.1232$$
$$k_{12} = k_{21} = 0.1145$$
$$k_{13} = k_{31} = 0.1169$$
$$k_{23} = k_{32} = 0.1205$$
$$\phi_1 = 0.4,\quad \phi_2 = 0.3,\quad \phi_3 = 0.3$$

Thermal conductivity of the liquid mixture = 0.1167 W/(m.K)

Table 2.13 Constants for the Calculation of Hydrocarbon Vapor Thermal Conductivity

Ideal components	$A \times 10^3$	$B \times 10^5$	$C \times 10^8$
Methane	16.77	4.358	1.335
Ethane	8.74	4.343	1.364
Propane	7.54	3.362	1.971
n-Butane	6.91	2.809	2.841
n-Pentane	6.76	2.337	2.778
n-Hexane	6.42	2.214	2.180
n-Heptane	4.95	2.444	1.685
n-Octane	3.59	2.710	1.175

Source: Adapted from *Technical Data Book—Petroleum Refining*, 4th ed., American Petroleum Institute, Washington, D.C., 1982.

Note: Values for other components are available in the literature [4].

Thermal conductivity of pure hydrocarbon vapors at low pressure

The thermal conductivity of pure hydrocarbon gas at low pressure can be calculated using the following equation [4]:

$$k = A + BT + CT^2 \tag{2.90}$$

where

k = thermal conductivity, Btu/(h.ft.°F)
A,B,C = constants (refer to Table 2.13)
T = temperature, °F

The thermal conductivity of pure hydrocarbon vapor mixtures can be calculated as [4]

$$k_m = \sum_{i=1}^{n} \frac{k_i}{\dfrac{1}{y_i}\displaystyle\sum_{j=1}^{n} A_{ij} y_j} \tag{2.91}$$

where

k_m = thermal conductivity of the mixture, Btu/(h.ft.°F)
k_i = thermal conductivity of component i, Btu/(h.ft.°F)
n = number of components in the mixture
y_i, y_j = mole fraction of components i and j

$$A_{ij} = \frac{1}{4}\left\{1 + \left[\frac{\mu_i}{\mu_j}\left(\frac{M_j}{M_i}\right)^{0.75} \frac{(1 + (S_i/T))}{(1 + (S_j/T))}\right]^{0.5}\right\}^2 \frac{(1 + (S_{ij}/T))}{1 + (S_i/T)} \tag{2.92}$$

$S_i, S_j = 1.5\ T_b$
$S_{ij} = \sqrt{S_i S_j}$
μ_i, μ_j = viscosities of components *i* and *j*, cP
M_i, M_j = molecular weight of component *i* and *j*
T_b = normal boiling point, R
T = temperature, R

Flash calculation

Flash calculation is probably the most important unit operation to solve process engineering problems. Any mixture at a defined pressure and temperature can exist either in a liquid phase or in a vapor phase, or in two phases. Flash calculation is required to establish the state of the fluid under a specific condition.

Vapor–liquid equilibrium

When a fluid exists in two phases, the mole fraction of any component in the vapor and liquid phases differs depending on the vapor–liquid equilibrium constant. The higher the value of the vapor–liquid equilibrium, the higher will be the ratio of mole fraction between the vapor and liquid phases. Mathematically

$$K_i = \frac{y_i}{x_i} \tag{2.93}$$

where

K_i = vapor–liquid equilibrium constant of component *i*
y_i = mole fraction of component *i* in vapor phase
x_i = mole fraction of component *i* in liquid phase

Once the value of the equilibrium constant is known, it is easy to do a flash calculation and the bubble and dew points can be calculated using the following equations:

Bubble point

$$\sum y_i = \sum K_i x_i = 1.0 \tag{2.94}$$

Dew point

$$\sum x_i = \sum \frac{y_i}{K_i} = 1.0 \tag{2.95}$$

It is clear from the above analysis that a flash calculation can proceed only when an accurate equilibrium constant is available. Any flash calculation is initiated with the preliminary estimated values for equilibrium constants. A large number of correlations and graphs are available in the literature and a preliminary estimate can be made using the following equation [9]:

$$K_i = \frac{P_{ci}}{P} \exp\left\{5.37(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right\} \tag{2.96}$$

where

K_i = vapor–liquid equilibrium constant of component i
P_{ci} = critical pressure of component i
T_{ci} = critical temperature of component i
ω_i = acentric factor of component i
P = operating pressure
T = operating temperature

The mole fraction of component i in the liquid and vapor phases can be estimated as [9]

$$x_i = \frac{z_i}{1+V(K_i-1)} \tag{2.97}$$

$$y_i = x_i K_i \tag{2.98}$$

An overall material balance can result:

$$\sum_{i=1}^{N} \frac{z_i(K_i-1)}{1+V(K_i-1)} = 0 \tag{2.99}$$

where

z_i = overall mole fraction of component i
V = vapor phase mole fraction

Other terms are as defined before.

Using the above equations, the compositions in the vapor and liquid phases can be calculated using a set of equilibrium constants. The adequacy of the calculation needs to be checked through the calculation of the fugacity of each component. For the correct equilibrium condition, the fugacity of each component in both the vapor and liquid phases will be the same. If the fugacity is different, the equilibrium constants are to be modified and recalculated. For the PR EOS, the fugacity of each component in both the liquid and vapor phases is calculated using the following equation [2]:

$$\ln \frac{f_k}{x_k P} = \frac{b_k}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum_i x_i a_{ik}}{a} - \frac{b_k}{b}\right) \times \ln\left(\frac{Z+2.414B}{Z-0.414B}\right) \tag{2.100}$$

where

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{2.101}$$

$$b = \sum x_i b_i \tag{2.102}$$

$$a_{ij} = (1-\delta_{ij}) a_i^{0.5} a_j^{0.5} \tag{2.103}$$

δ_{ij} = interaction parameter, generally determined experimentally
f_k = fugacity of component k

Other parameters are as defined in Table 2.1.

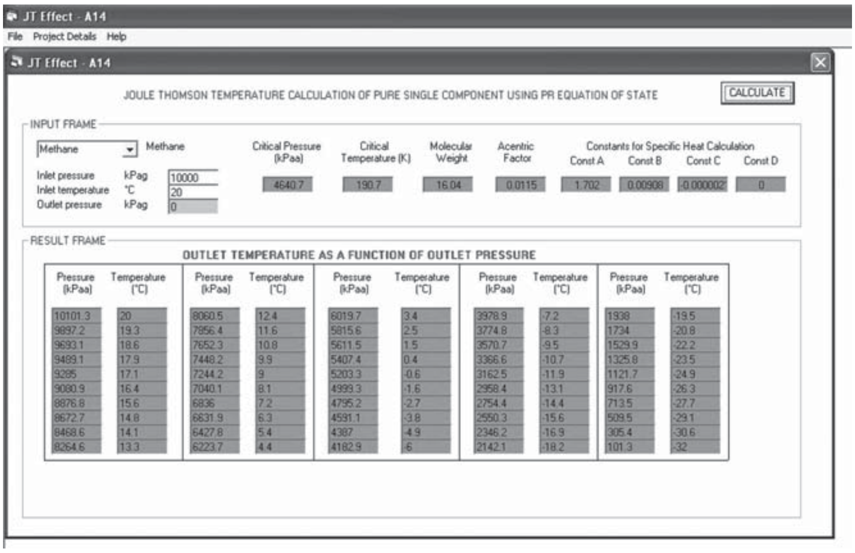
Equation 2.100 is solved for both the liquid and vapor phase parameters to calculate the fugacity in both phases.

Programming

Calculation of JT effect due to drop in pressure

This program has been developed to estimate the impact of the Joule–Thomson effect when a gas is expanded through a pressure reduction unit. The following basis has been used in this estimation:

- The calculation is based on the PR EOS.
- It is assumed that the expansion is adiabatic and not isentropic. Generally, the temperature drop is larger in isentropic expansion in comparison to adiabatic expansion.
- This calculation assumes only the vapor phase expansion and does not perform any enthalpy balance due to a change in phase.



JOULE THOMSON TEMPERATURE CALCULATION OF PURE SINGLE COMPONENT USING PR EQUATION OF STATE

Methane Methane

Inlet pressure kPag 10000
Inlet temperature °C 20
Outlet pressure kPag 0

Critical Pressure (kPaa)	Critical Temperature (K)	Molecular Weight	Acentric Factor	Constants for Specific Heat Calculation Const A	Const B	Const C	Const D
4640.7	190.7	16.04	0.0115	1.702	0.00908	-0.000002	0

OUTLET TEMPERATURE AS A FUNCTION OF OUTLET PRESSURE

Pressure (kPaa)	Temperature (°C)	Pressure (kPaa)	Temperature (°C)	Pressure (kPaa)	Temperature (°C)	Pressure (kPaa)	Temperature (°C)	Pressure (kPaa)	Temperature (°C)
10101.3	20	8060.5	12.4	6019.7	3.4	3978.9	-7.2	1938	-19.5
9897.2	19.3	7856.4	11.6	5815.6	2.5	3774.8	-8.3	1734	-20.8
9693.1	18.6	7652.3	10.8	5611.5	1.5	3570.7	-9.5	1529.9	-22.2
9489.1	17.9	7448.2	9.9	5407.4	0.4	3366.6	-10.7	1325.8	-23.5
9285	17.1	7244.2	9	5203.3	-0.6	3162.5	-11.9	1121.7	-24.9
9080.9	16.4	7040.1	8.1	4999.3	-1.6	2958.4	-13.1	917.6	-26.3
8876.8	15.6	6836	7.2	4795.2	-2.7	2754.4	-14.4	713.5	-27.7
8672.7	14.8	6631.9	6.3	4591.1	-3.8	2550.3	-15.6	509.5	-29.1
8468.6	14.1	6427.8	5.4	4387	-4.9	2346.2	-16.9	305.4	-30.6
8264.6	13.3	6223.7	4.4	4182.9	-6	2142.1	-18.2	101.3	-32

Figure 2.4 Solution of Example 2.6.

- If the liquid phase is detected at any step in the calculation, the program generates a note "Note-1: Liquid phase detected. Results may not be accurate."
- This calculation is performed using 50 steps and a downstream pressure–temperature relationship can be developed from the results.

Checking Example 2.6
The Visual Basic® solution of Example 2.6 is presented in Figure 2.4.

Nomenclature

a	acceleration, m/s^2
C_P	heat capacity at constant pressure, kJ/(kg·°C)
C_V	heat capacity at constant volume, kJ/(kg·°C)
E_K	kinetic energy
E_P	potential energy
F	force, N
g_c	acceleration due to gravity, m/s^2
H	enthalpy, kJ
l	displacement, m
K	vapor–liquid equilibrium constant
m	mass, kg
MW	molecular weight

P	pressure, kPa
Q	heat, kJ
R	universal gas constant, kJ/(kmol·K)
S	entropy, kJ/(kmol·K)
T	temperature, K
U	internal energy, kJ
v	velocity, m/s
V	volume, m^3
W	work, kNm
z	elevation, m
Z	compressibility

Greek characters

γ	ratio of specific heats
η	efficiency
ω	acentric factor
μ	Joule–Thomson coefficient

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