GPSA ENGINEERING DATABOOK ERRATA
(2004 SI Edition)

PAGE	DESCRIPTION
3–11	Correct typo
7–15	Change references in Ex. 7-3
13–9	Change Eq. 13-16a and units
14–13	Change Fig. 14-26 reference
20–19	Change wording for Eq. 20-8
20–21	Change wording in Ex. 20-10
20–45	Make "Solid Desiccant Dehydration" a major heading
20–46	Change Fig. 20-87 reference
23–11	Change Fig. 23-3 reference
23–34	Change Eq. 23-22

FIG. 3-10

Orifice Meter Installation Requirements without a Flow Conditioner

Minimum straight unobstructed meter tube length from the upstream and downstream side of the orifice plate (in multiples of published internal pipe diameter, D_I)

Diameter ratio β	**a. Single 90° elbow.** **b. Two 90° elbows in the same plane with SEP > 30D_i.** **c. Two 90° elbows in perpendicular planes with SEP > 15D_i.**	**Two 90° elbows in the same plane "SEP" configuration spacer SEP ≤ 10D_i.**	**Two 90° elbows in the same plane "SEP" configuration 10 D_i < SEP ≤ 30D_i.**	***Two 90° elbows in perpendicular planes, SEP < 5D_i.***	**Two 90° elbows in perpendicular planes, 5D_i ≤ SEP ≤ 15D_i.**	**Single 90° Tee used as an elbow but not as a header element**	**a. Single 45° elbow.** **b. Two 45° elbows in the same "SEP" configuration SEP ≥ 22D_i.**	**Gate valve at least 50% open**	**Concentric reducer**	**Any other configuration (catch all category)***	**Downstream meter tube length**
	UL	**UL**	**UL**	**UL**	**UL**	**UL**	**UL**	**UL**	**UL**	**UL**	**DL**
	6	10	10	50	19	9	30	17	6	70	2.8
0.30	11	10	12	50	32	9	30	19	6	108	3.0
0.40	16	10	13	50	44	9	30	21	6	145	3.2
0.50	30	30	18	95	44	19	30	25	7	145	3.5
0.60	44	44	30	95	44	29	30	30	9	145	3.9
0.67	44	44	44	95	44	36	44	35	11	145	4.2
0.75	44	44	44	95	44	44	44	44	13	145	4.5
Recommended length for maximum range β ≤ 0.75	44	44	44	95	44	44	44	44	13	145	4.5

UL – Minimum meter tube length upstream of the orifice plate in internal pipe diameter, D_i (See Figure 3-9).Straight length shall be measured from the downstream end of the curved portion of the nearest (or only) elbow or of the tee or the downstream end of the conical portion of reducer or expander.

DL – Minimum downstream meter tube length in internal pipe diameters, D_i (See Figure 3-9).

SEP – Separation distance between piping elements in internal pipe diameter, D_i, measured from the downstream end of the curved portion of the upstream elbow to the upstream end of the curved portion of the downstream elbow.

Note : The tolerance on specified lengths for UL and DL is ± 0.25D_i.

* – This installation exhibits strong effect of Reynolds number and pipe roughness on the recommended length due to rate of decay of swirl. The present recommendations have been developed for high Reynolds numbers and smooth pipes to capture the worst case.

Used by the permission of the copyright holder, American Gas Association. Reproduced courtesy of the American Petroleum Institute.

where the two immiscible liquid phases separate within the vessel by the differences in density of the liquids. Sufficient retention time must be provided in the separator to allow for the gravity separation to take place. The second category is defined as "coalescing separation." This is where small particles of one liquid phase must be separated or removed from a large quantity of another liquid phase. Different types of internal construction of separators much be provided for each type of liquid-liquid separators. The following principles of design for liquid-liquid separation apply equally for horizontal or vertical separators. Horizontal vessels have some advantage over verticals for liquid-liquid separation, due to the larger interface area available in the horizontal style, and the shorter distance particles must travel to coalesce.

There are two factors that may prevent two liquid phases from separating due to differences in specific gravity:

- If droplet particles are so small that they may be suspended by Brownian movement. This is defined as a random motion that is greater than directed movement due to gravity for particles less than 0.1 µm in diameter.
- The droplets may carry electric charges due to dissolved ions. These charges can cause the droplets to repel each other rather than coalesce into larger particles and settle by gravity.

Effects due to Brownian movement are usually small and proper chemical treatment will usually neutralize any electric charges. Then settling becomes a function of gravity and viscosity in accordance with Stoke's Law. The settling velocity of spheres through a fluid is directly proportional to the difference in densities of the sphere and the fluid, and inversely proportional to the viscosity of the fluid and the square of the diameter of the sphere (droplet), as noted in Eq 7-3. The liquid-liquid separation capacity of separators may be determined from Equations 7-13 and 7-14, which were derived from Equation 7-3[9]. Values of C* are found in Fig. 7-23.

Vertical vessels:

$$W_{cl} = C^*\left(\frac{S_{hl} - S_{ll}}{\mu}\right)(0.785)\, D_v^2 \qquad \textbf{Eq 7-13}$$

Horizontal vessel:

$$W_{cl} = C^*\left(\frac{S_{hl} - S_{ll}}{\mu}\right) L_l\, H_l \qquad \textbf{Eq 7-14}$$

Since the droplet size of one liquid phase dispersed in another is usually unknown, it is simpler to size liquid-liquid separation based on retention time of the liquid within the separator vessel. For gravity separation of two liquid phases, a large retention or quiet settling section is required in the vessel. Good separation requires sufficient time to obtain an equilibrium condition between the two liquid phases at the temperature and pressure of separation. The liquid capacity of a separator or the settling volume required can be determined from Eq 7-12 using the retention time given in Fig. 7-22.

The following example shows how to size a liquid-liquid separator.

Example 7-3 — Determine the size of a vertical separator to handle 100 m^3/day of 0.76 relative density condensate and 10 m^3/day of produced water. Assume the water particle size is 200 µm. Other operating conditions are as follows:

Operating temperature = 25°C
Operating pressure = 6900 kPa(ga)
Water relative density = 1.01
Condensate viscosity = 0.55 mPa • s @ 25°C
Condensate relative density = 0.76

From Eq 7-13

$$W_{cl} = C^*\left(\frac{S_{hl} - S_{ll}}{\mu}\right)(0.785)\,(D_v)^2$$

From Fig. 7-23 for free liquids with water particle diameter = 200 microns, C* = 1880.

FIG. 7-23

Values of C* Used in Equations 7-13 and 7-14

Emulsion Characteristic	Droplet Diameter, µm	Constant,[10] C*
Free Liquids	200	1880
Loose Emulsion	150	1060
Moderate Emulsion	100	470
Tight Emulsion	60	170

$$100\text{m}^3/\text{day} = 1880\,\frac{1.01 - 0.76}{(0.55)}\,(0.785)\,(D_v)^2(10^{-6})$$

$$(D_v)^2 = (1.43)\,(10^5)$$

$$D_v = 390 \text{ mm}$$

Using the alternate method of design based on retention time as shown in Eq 7-12 would give:

$$U = \frac{W\,(t)}{1440}$$

From Fig. 7-22, use 3 minutes retention time.

$$U = \frac{(110)\,(3)}{1440} = 0.23 \text{ m}^3$$

A 390 mm diameter vessel will hold about 0.12 m^3 per 1000 mm of height. The small volume held in the bottom head can be discounted in this size vessel. The shell height required for the retention volume required would be:

$$\text{Shell height} = \frac{0.23}{0.12} = 1.9 \text{ m} = 1900 \text{ mm}$$

Another parameter that should be checked when separating amine or glycol from liquid hydrocarbons is the interface area between the two liquid layers. This area should be sized so the glycol or amine flow across the interface does not exceed approximately 100 m^3 per day per m^2.

The above example indicates that a relatively small separator would be required for liquid-liquid separation. It should be remembered that the separator must also be designed for the vapor capacity to be handled. In most cases of high vapor-liquid loadings that are encountered in gas processing equipment design, the vapor capacity required will dictate a much larger vessel than would be required for the liquid load only. The properly designed vessel has to be able to handle both the vapor and liquid loads. Therefore, one or the other will control the size of the vessel used.

lation. The closest k value column may be safely used without a second interpolation.

Volumetric efficiencies for “high speed” separable compressors in the past have tended to be slightly lower than estimated from Eq 13-14. Recent information suggests that this modification is not necessary for all models of high speed compressors.

In evaluating efficiency, horsepower, volumetric efficiency, etc., the user should consider past experience with different speeds and models. Larger valve area for a given swept volume will generally lead to higher compression efficiencies.

Equivalent Capacity

The net capacity for a compressor, in cubic meters per hour @ 100 kPa (abs) and suction temperature, may be calculated by Eq. 13-16a which is shown in dimensioned form:

$$\mathrm{m^3/h} = \frac{\mathrm{PD\ \ m^3/h} \bullet \dfrac{\mathrm{VE\%}}{100} \bullet \mathrm{P_s\ kPa\ (abs)} \bullet \mathrm{Z_{100}}}{\mathrm{100\ kPa\ (abs)} \bullet \mathrm{Z_s}} \qquad \textbf{Eq 13-16a}$$

which can be simplified to Eq. 13-16b when Z_{100} is assumed to equal 1.0.

$$\mathrm{m^3/h} = \frac{\mathrm{PD} \bullet \mathrm{VE} \bullet \mathrm{P_s}}{\mathrm{Z_s} \bullet 100} \qquad \textbf{Eq 13-16b}$$

For example, a compressor with 425 m^3/h piston displacement, a volumetric efficiency of 80%, a suction pressure of 517 kPa (abs), and suction compressibility of 0.9 would have a capacity of 1953 m^3/h. If compressibility is not used as a divisor in calculating m^3/h, then the statement “not corrected for compressibility” should be added.

In many instances the gas sales contract or regulation will specify some other measurement standard for gas volume. To convert volumes calculated using Equation 13-16 (i.e. at 100 kPa (abs) and suction temperature) to a P_L and T_L basis, Eq 13-17 would be used:

$$\mathrm{m^3/h\ \ at\ P_L,\ T_L} = (\mathrm{m^3/h\ from\ Eq\ 13–16})\left(\frac{100}{\mathrm{P_L}}\right)\left(\frac{\mathrm{T_L}}{\mathrm{T_s}}\right)\left(\frac{\mathrm{Z_L}}{\mathrm{Z_s}}\right) \qquad \textbf{Eq 13-17}$$

Discharge Temperature

The temperature of the gas discharged from the cylinder can be estimated from Eq 13-18, which is commonly used but not recommended. (Note: the temperatures are in absolute units, °R or K.) Eqs 13-31 and 13-32 give better results.

$$\mathrm{T_d} = \mathrm{T_s}\,(\mathrm{r}^{(k-1)/k}) \qquad \textbf{Eq 13-18}$$

The discharge temperature determined from Eq 13-18 is the theoretical value. While it neglects heat from friction, irreversibility effects, etc., and may be somewhat low, the values obtained from this equation will be reasonable field estimates.

Rod Loading

Each compressor frame has definite limitations as to maximum speed and load-carrying capacity. The load-carrying capacity of a compressor frame involves two primary considerations: horsepower and rod loading.

The horsepower rating of a compressor frame is the measure of the ability of the supporting structure and crankshaft to withstand torque (turning force) and the ability of the bearings to dissipate frictional heat. Rod loads are established to limit the static and inertial loads on the crankshaft, connecting rod, frame, piston rod, bolting, and projected bearing surfaces.

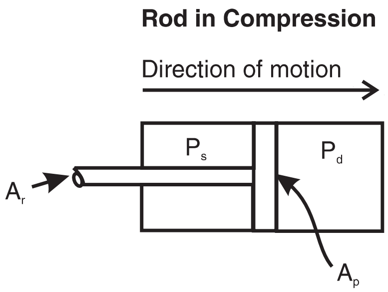
Good design dictates a reversal of rod loading during each stroke. Non-reversal of the loading results in failure to allow bearing surfaces to part and permit entrance of sufficient lubricant. The result will be premature bearing wear or failure.

Rod loadings may be calculated by the use of Eqs 13-19 and 13-20.

$$\text{Load in compression} = \mathrm{P_d\,A_p - P_s\,(A_p - A_r)}$$

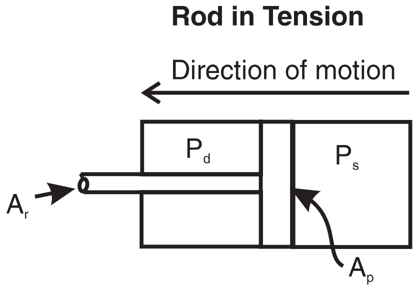
$$= \mathrm{(P_d - P_s)\,A_p + P_s\,A_r} \qquad \textbf{Eq 13-19}$$

$$\text{Load in tension} = \mathrm{P_d\,(A_p - A_r) - P_s\,A_p}$$


Rod in Compression

$$= \mathrm{(P_d - P_s)\,A_p - P_d\,A_r} \qquad \textbf{Eq 13-20}$$

Using Eqs. 13-19 and 13-20, a plus value for the load in both compression and tension indicates a reversal of loads based on gas pressure only. Inertial effects will tend to increase the degree of reversal.


Rod in Tension

The true rod loads would be those calculated using internal cylinder pressures after allowance for valve losses. Normally, the operator will know only line pressures, and because of this, manufacturers generally rate their compressors based on line-pressure calculations.

A further refinement in the rod-loading calculation would be to include inertial forces. While the manufacturer will consider inertial forces when rating compressors, useful data on this point is seldom available in the field. Except in special cases, inertial forces are ignored.

A tail-rod cylinder would require consideration of rod cross-section area on both sides of the piston instead of on only one side of the piston, as in Eqs 13-19 and 13-20.

that is not subcooled. Thus the use of the heat exchanger effectively shifts vapor from the low stage of compression to the high stage, thus saving power. The resultant process impact is very similar to the flash economization previously discussed.

Design and Operating Considerations

The following are some of the important parameters that should be considered while designing any refrigeration system to provide a safe, reliable, and economical operation.

Oil Removal — Oil removal requirements from evaporators are related to the type of the refrigerant, lubricant, evaporator, and compressor used in the refrigeration cycle. Fig. 14-27 illustrates the application of an oil reclaimer in a propane refrigerant cycle. In order to remove oil from the refrigerant, a slip stream of refrigerant from the bottom of the chiller is drained into the reclaimer where hot propane refrigerant from the compressor discharge is used to evaporate the refrigerant into the compressor suction. The oil is removed from the bottom of the reclaimer. Similar arrangements can be utilized for other hydrocarbon and ammonia refrigerants. Operation may be designed for either manual or automatic.

Where halocarbon refrigerants and/or synthetic lubricants are employed, it is imperative that the oil reclaimer system be approved by the compressor manufacturer.

Liquid Surge and Storage — All refrigeration systems should have a liquid surge and storage vessel, commonly called a receiver. A surge vessel is required on all systems where the operating charge in the evaporator(s) and the condenser(s) varies due to variable load conditions. In addition to accommodating a varying refrigerant charge, the receiver drains the condenser(s) of liquid so that the effective condensing surface is not reduced by liquid backing up. The refrigerant charge in a receiver may vary over a wide range, from a minimum at full load to a maximum at no load.

Systems with inadequate surge vessels often cause problems as they lose the liquid seal due to load variations that always occur. Surge vessels or receivers are relatively inexpensive and when sizing them, consideration should be given to: (1) a volume equal to 100% of the system inventory at 80% full level, and (2) the availability and quantity of refrigerant makeup.

Vacuum Systems — Refrigeration systems can operate with a suction pressure below atmospheric pressure. These vacuum systems require special considerations:

- Where hydrocarbons are used with reciprocating compressors (which employ rod "packing"), air can enter the compressor and possibly form a hazardous mixture. Extreme care should be taken where such systems are used. These systems must have a manual or automatic purge system. Double acting packing should be employed.
- Where halocarbons such as R-11, R-114, R-113, and other low pressure, high volume refrigerants are employed with centrifugal compressors, the deep vacuums may "draw" air and moisture through flanges, seals, etc. This water-oxygen combination in the presence of halocarbons forms acid and causes "crevice corrosion" of the tubes along with some other problems. A positive purge system must be employed and frequent monitoring of the moisture content in the refrigerant is suggested.
- High pressure halocarbons R-12, R-22, and others are employed in vacuum systems with reciprocating, centrifugal, and screw compressors. These systems will suffer from the same corrosion problems as defined above, but to a lesser extent. However, since they are generally used at lower temperatures, water in the system can freeze the control valve and in the evaporator. Refrigerant dryers are required in these systems. A good purge system is also required.
- Ammonia has been employed with reciprocating, centrifugal, and screw compressors in vacuum service for many years. Since water will not freeze in the presence of ammonia and the aqua-ammonia formed is only

FIG. 14-18

Heat Exchanger Economizing

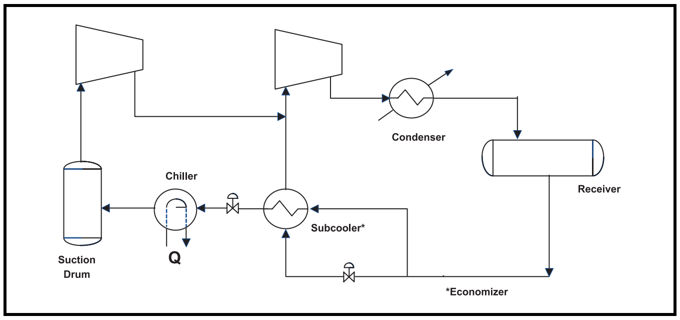
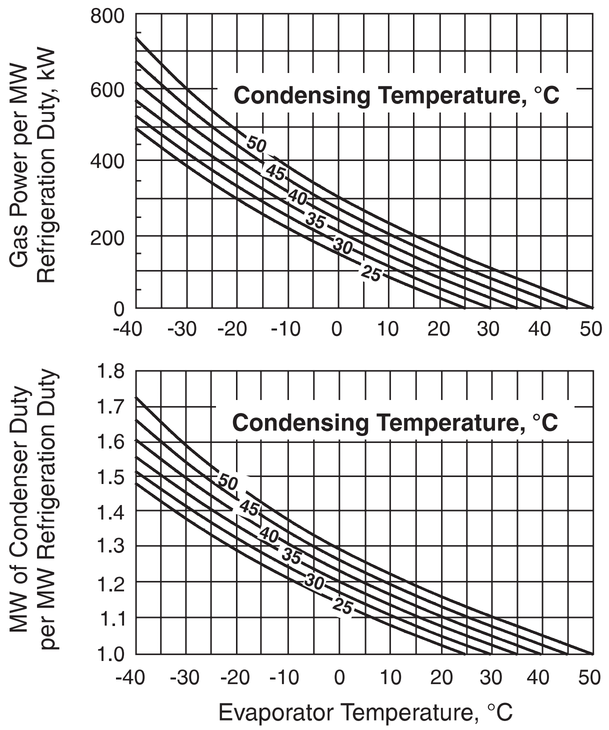


FIG. 14-19

Gas Power and Condenser Duty for Two Stage R-22 Refrigeration



economic advantage versus methanol recovered by distillation. At cryogenic conditions (below −40°C) methanol usually is preferred because glycol's viscosity makes effective separation difficult.

Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) glycols have been used for hydrate inhibition. The most popular has been ethylene glycol because of its lower cost, lower viscosity, and lower solubility in liquid hydrocarbons.

Physical properties of methanol and methanol-water mixtures are given in Fig. 20-34 through Fig. 20-37. Physical properties of the most common glycols and glycol-water mixtures are given in Fig. 20-38 through Fig. 20-49. Tabular information for the pure glycols and methanol is provided in Fig. 20-56.

To be effective, the inhibitor must be present at the very point where the wet gas is cooled to its hydrate temperature. For example, in refrigeration plants glycol inhibitors are typically sprayed on the tube-sheet faces of the gas exchangers so that it can flow with the gas through the tubes. As water condenses, the inhibitor is present to mix with the water and prevent hydrates. Injection must be in a manner to allow good distribution to every tube or plate pass in chillers and heat exchangers operating below the gas hydrate temperature.

The viscosities of ethylene glycol and its aqueous solutions increase significantly as temperature decreases, and this must be allowed for in the rating of refrigeration-plant exchangers and chillers.

The inhibitor and condensed water mixture is separated from the gas stream along with a separate liquid hydrocarbon stream. At this point, the water dewpoint of the gas stream is essentially equal to the separation temperature. Glycol-water solutions and liquid hydrocarbons can emulsify when agitated or when expanded from a high pressure to a lower pressure, e.g., JT expansion valve. Careful separator design will allow nearly complete recovery of the diluted glycol for regeneration and reinjection. Fig. 20-57 shows a flow diagram for a typical EG injection system in a refrigeration plant.

The regenerator in a glycol injection system should be operated to produce a regenerated glycol solution that will have a freezing point below the minimum temperature encountered in the system. This is typically 75-80 wt%. Fig. 20-58 shows the freezing point of various concentrations of glycol water solutions.

The minimum inhibitor concentration in the free water phase may be approximated by Hammerschmidt's equation.[25]

$$d = \frac{K_H X_I}{MW_I (1 - X_I)} \qquad \textbf{Eq 20-5}$$

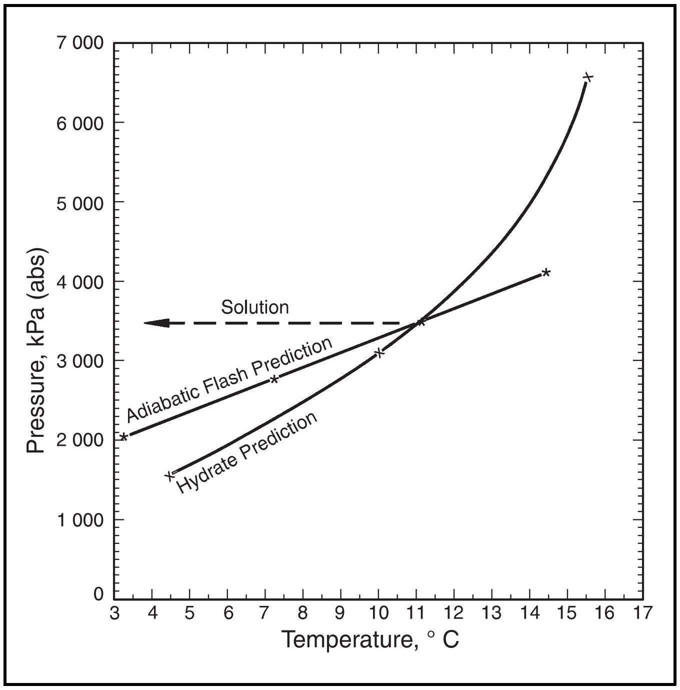
$$X_I = \frac{dMW_I}{K_H + dMW_I} \qquad \textbf{Eq 20-6}$$

Where K_H (glycols) = 1297 to 2222 and
K_H (methanol) = 1297

The K_H range of 1297 to 2222 for glycols reflects the uncertainty in the value of this parameter. At equilibrium, such as for a laboratory test, 1297 is applicable as illustrated on Fig. 20-60. In some field operations, however, hydrate formation has been prevented with glycol concentrations corresponding with K_H values as high as 2222. This is because hydrate suppression with glycols depends on the system's physical and flow characteristics (i.e., the system dynamics, configuration, location and method of glycol injection, amount of free water, etc.) as well as the properties of the gas and the glycol. Therefore, in the absence of reliable field-test data, a system should be designed for a K_H of 1297. Once the system is operating, the glycol concentration can be reduced to tolerable levels.

FIG. 20-30

Solution Sketch for Example 20-8



Eq 20-5 and Eq 20-6 should not be used beyond 20-25 wt% for methanol and 60-70 wt% for the glycols. For methanol concentrations up to about 50%, the Nielsen-Bucklin equation[26] provides better accuracy:

$$d = -72.0 \ln(x_{H_2O}) \qquad \textbf{Eq 20-7}$$

Note that "x_{H_2O}" in Eq 20-7 is a mole fraction, not a mass fraction. Expressing mole fraction in terms of mass fraction, dewpoint depression is plotted against the weight percent methanol in Fig. 20-59.

Maddox *et al.*[27] presents a method of estimating the required inhibitor concentration for both methanol and EG. The method is iterative but converges easily after a few iterations.

Figs. 20-60 thru 20-64 provide a comparison of various inhibitor correlations with experimental data.[28,29,30] Experimental data at very high inhibitor concentrations is limited.

Once the required inhibitor concentration has been calculated, the mass of inhibitor solution required in the water phase may be calculated from Eq 20-8

$$m_I = \frac{X_R \bullet m_{H_2O}}{X_L - X_R} \qquad \textbf{Eq 20-8}$$

The amount of inhibitor to be injected not only must be sufficient to prevent freezing of the inhibitor water phase, but also must be sufficient to provide for the equilibrium vapor phase content of the inhibitor and the solubility of the inhibitor in any liquid hydrocarbon. The vapor pressure of methanol is high enough that significant quantities will vaporize. Methanol vaporization losses may be estimated from Fig. 20-65[31] Fig. 20-65 is extrapolated above 4800 kPa (abs). Recent studies indicate Fig. 20-65 may underestimate vapor phase methanol losses at higher pressures. Glycol vaporization losses are generally very small and are typically ignored in calculations.

Inhibitor losses to the hydrocarbon liquid phase are more difficult to predict. Solubility is a strong function of both the water phase and hydrocarbon phase compositions. Fig. 20-66 presents experimental data[32,33,34] showing solubility of methanol in a paraffinic hydrocarbon liquid as a function of temperature and methanol concentration. Methanol solubility in naphthenic hydrocarbons is slightly less than paraffinic, but solubility in aromatic hydrocarbons may be four to six times higher than in parafins.

Solubility of EG in the liquid hydrocarbon phase is extremely small.[29] A solubility of 40 g/m^3 of NGL is often used for design purposes. However, entrainment and other physical losses may result in total losses significantly higher than this.

Example 20-10—2.83 (10^6) Sm^3/day of natural gas leaves an offshore platform at 38°C and 8300 kPa (abs). The gas comes onshore at 4°C and 6200 kPa (abs). The hydrate temperature of the gas is 18°C. Associated condensate production is 56 m^3/Standard m^3 (10^6). The condensate has a density of 778 kg/m^3 and a molecular mass of 140. Calculate the amount of methanol and 80 mass% EG inhibitor required to prevent hydrate formation in the pipeline.

Solution Steps:

Methanol

1. Calculate the amount of water condensed per day

   from Fig. 20-4,
   $$W_{in} = 850\ mg/Sm^3$$
   $$W_{in} = \underline{152\ mg/Sm^3}$$
   $$\Delta W = 698\ mg/Sm^3$$

   Water condensed = $(2.83 \times 10^6)(698)$ = 1975 (10^6) mg/day = 1975 kg/day

2. Calculate required methanol inhibitor concentration from Eq 20-5 and 20-7 (with Fig. 20-59).

   $d = 14°C \qquad M = 32$

   Solving for X_I,

   $X_I = 0.255$, Eq 20-5

   $X_I = 0.275$, Eq 20-7 (use this value in subsequent calculations)

3. Calculate mass rate of inhibitor solution in water phase from Eq. 20-8 (assume 100% methanol is injected)
   $$m_I = \frac{X_R \bullet m_{H_2O}}{X_L - X_R} = \frac{(0.275)\,(1975)}{(1 - 0.275)} = 749\ kg/day$$

4. Estimate vaporization losses from Fig. 20-65.

   @ 4°C and 6200 kPa (abs),
   $$\text{losses} = 16.8\ (10^{-6})\ \frac{kg/m^3}{wt\%\ MeOH}$$
   daily losses = $(1.68 \times 10^{-6})(2.83 \times 10^6)(27.5)$ = 1310 kg/day

5. Estimate losses to hydrocarbon liquid phase from Fig. 20-66.

   @ 4°C and 27.5 wt% MeOH, $x_{MeOH} \approx 0.2$ mol%

   lb • mols of condensate per day –
   $$\left(\frac{2.83 \times 10^6\ Sm^3}{day}\right)\left(\frac{56m^3}{10^6\ Sm^3}\right)\left(\frac{778kg}{m^3}\right)\left(\frac{1\ kg \bullet mol}{140\ kg}\right)$$
   = 881 kg • mol/day

   kg • mol methanol = (881)(0.002) = 1.76 kg • mols/day

   kg methanol = (1.76)(32) = 56 kg/day

   Total methanol injection rate = 749 + 1310 + 56

   = 2115 kg/day

Methanol left in the gas phase can be recovered by condensation with the remaining water in downstream chilling processes. Likewise, the methanol in the condensate phase can be recovered by downstream water washing.

80 wt% EG

1. Calculate required inhibitor concentration from Eq 20-6.

   $d = 14°C \qquad M = 62$

   Solving for X_I, $X_I = 0.28$

2. Calculate mass rate of inhibitor in water phase from Eq. 20-8.
   $$m_I = \frac{(0.28)(1975)}{(0.8 - 0.28)} = 1063\ kg/day$$

Vaporization and liquid hydrocarbon losses are negligible.

Inhibitor losses represent a significant operating cost and can cause problems in downstream process units. Efficient inhibitor separation should be provided.

Low Dosage Hydrate Inhibitors (LDHIs) — LDHIs can provide significant benefits compared to thermodynamic inhibitors including:

- Significantly lower inhibitor concentrations and therefore dosage rates. Concentrations rante from 0.1 to 1.0 mass percent polymer in the free water phase, whereas alcohols can be as high as 50%
- Lower inhibitor loss caused by evaporation, particularly compared to methanol
- Reduced capital expenses through decreased chemial storage and injection rate requirements; and no need for regeneration because the chemicals are not currently recovered. These are especially appropriate for offshore where weight and space are critical to costs
- Reduced operating expenses in many cases through decreased chemical consumption and delivery frequency
- Increased production rates, where inhibitor injection capacity or flowline capacity is limited
- Lower toxicity

Kinetic Hydrate Inhibitors — KHIs were designed to inhibit hydrate formation in flowlines, pipelines, and downhole equipment operating within hydrate-forming conditions such as subsea and cold-weather environments. Their unique chemical structure significantly reduces the rate of nucleation and hydrate growth during conditions thermodynamically favorable for hydrate formation, without altering the thermodynamic hydrate formation conditions (i.e., temperature and pressure). This mechanism differs from methanol or glycol, which depress the thermodynamic hydrate formation temperature so that a flowline operates outside hydrate-forming conditions.

KHIs Compared to Methanol or Glycols— KHIs inhibit hydrate formation at a concentration range of 0.1–1.0 mass percent polymer in the free water phase. At the maximum recommended dosage, the current inhibition capabilities are –2°C of subcooling in a gas system and –7°C in an oil system with efforts continuing to expand the region of effectiveness. For relative comparison, methanol or glycol typically

Calcium Chloride

Calcium chloride ($CaCl_2$) can be used as a consumable desiccant to dehydrate natural gas. Solid anhydrous $CaCl_2$ combines with water to form various $CaCl_2$ hydrates ($CaCl_2 \bullet XH_2O$). As water absorption continues, $CaCl_2$ is converted to successively higher states of hydration – eventually forming a $CaCl_2$ brine solution.

10 to 20 mm $CaCl_2$ pellets are installed in a fixed bed much like a dry desiccant tower. Gas flow is upflow. The more efficient designs utilize 3-4 trays below the solid bed to pre-contact the gas with the brine solution. This removes a portion of the water from the gas before contact with the solid $CaCl_2$ and increases unit capacity. One such unit is shown in Fig. 20-89.

The solid $CaCl_2$ near the bottom of the fixed bed will typically be $CaCl_2 \bullet 4H_2O$ or $CaCl_2 \bullet 6H_2O$ and the $CaCl_2$ at the top of the fixed bed will be anhydrous $CaCl_2$ or $CaCl_2 \bullet H_20$. In this way the gas contacts successively drier $CaCl_2$ as it flows upwards and in theory leaves the fixed bed in equilibrium with the $CaCl_2$ at the top of the bed.

Outlet water contents of 16 mg/Sm^3 have been achieved with $CaCl_2$ dehydrators. Typical $CaCl_2$ capacity is 0.3 kg $CaCl_2$ per kg H_20. Superficial bed velocities are 6–9m and length to diameter ratio for the bed should be at least 3 to 4:1.

$CaCl_2$ dehydrators may offer a viable alternative to glycol units on low rate, remote dry gas wells. The $CaCl_2$ must be changed out periodically. In low capacity – high rate units this may be as often as every 2-3 weeks. Brine disposal raises environmental issues. In addition, under certain conditions the $CaCl_2$ pellets can bond together to form a solid bridge in the fixed bed portion of the tower. This results in gas channeling and poor unit performance.

Dehydration by Refrigeration

The dehydration of natural gas can also be achieved by refrigeration and/or cryogenic processing down to –100°C in the presence of methanol hydrate and freeze protection. The condensed water and methanol streams decanted in the cold process can be regenerated by conventional distillation or by a patented process called IFPEX-1®.

In the latter process illustrated in schematic form in Figure 20-90[48] a slip stream of water saturated feed gas strips essentially all the methanol in the cold decanted methanol water stream originating in the cold process at feed gas conditions to recirculate the methanol to the cold process. The water stream leaving the stripper contains generally less than 100 ppm wt of methanol. No heat is required for the process and no atmospheric venting takes place.

Dehydration By Membrane Permeation

Membranes can be used to separate gas stream components in natural gas such as water, CO_2 and hydrocarbons according to their permeabilities. Each gas component entering the separator has a characteristic permeation rate that is a function of its ability to dissolve in and diffuse through the membrane.

The driving force for separation of a gas component in a mixture is the difference between its partial pressure across the membrane. As pressurized feed gas flows into the metal shell of the separator, the fast gas component, such as water and CO_2, permeate through the membrane. This permeate is collected at a reduced pressure, while the non-permeate stream, i.e., the dry natural gas, leaves the separator at a slightly lower pressure than the feed.

The amount of methane and other natural gas components in the permeate stream is dependent on pressure drop and the surface area of the membranes. However, 5–10% of the feed stream is a realistic figure. Dehydration by membrane permeation is therefore normally only considered for plants that can make use of low pressure natural gas fuel.

LIQUID DEHYDRATION

Many liquid streams must be dehydrated to allow further processing or meet requirements of a handling chain to a direct consumer. Commercial propane must be dry before entering the fuel market to prevent freezing problems as the liquid vaporizes at temperatures below the hydrate point, or even below the freezing point of any free water that may be present.

The amount of water that can be in solution with light hydrocarbon liquid is very small, even at the saturation point. Effective drying to very low levels of moisture is usually required. The solubility of water in liquid hydrocarbons is presented in Fig. 20-2. The desired maximum moisture level for commercial propane is approximately 10 ppmw. However, liquids exposed to cryogenic temperatures require virtually all the moisture be removed.

The water content in light hydrocarbon liquids can be determined by using recommended methods in GPA Publication 2140 (Cobalt Bromide or Freeze Valve methods), or electronic instruments designed to indicate the moisture content directly.

Gas Stripping

One simple method of dehydrating liquid hydrocarbons is counter current stripping with a dry gas. This method is currently used to dry condensate produced offshore prior to export from the production platform. The contactor is usually trayed. Stripping gas rates depend on the condensate rate, the amount of entrained water in the condensate, stripper temperature and pressure.

Advantages of this process are simplicity and low capital cost. Disadvantages include the requirement for a dry natural gas stream, and the coincidental stripping of some of the volatile hydrocarbons from the condensate. The stripping gas may be recycled to the gas dehydration unit or it can be used as fuel gas.

SOLID DESICCANT DEHYDRATION

Several solid desiccant processes are available to dry liquid hydrocarbons.

Liquid velocity is usually 1–1.5m/minute through solid desiccant beds with a minimum travel of at least 5 feet to ensure good distribution. Direction of flow can be upflow or downflow in the adsorption cycle.

Special care must be taken in designing the bed supports in the liquid dehydrator vessels to prevent desiccant loss, desiccant damage, and to ensure proper distribution. Layers of ceramic balls are installed in decreasing size from the support screen. The support ball sizes may vary with the type and size of solid desiccant used but the layers of support balls should never be graduated in size more than twice the diameter of the balls being supported.

The regeneration of solid desiccant beds is very similar to gas dehydrators with the following exceptions:

- Liquid draining and filling time must be allowed.
- Pressuring and depressuring must be done carefully to avoid bed movement.
- Adequate bed cooling is required before liquid re-entry to minimize flashing.

It is important to prevent movement of the bed particles to prevent attrition that would require premature replacement. Also, desiccant dust particles can cause downstream plugging, equipment damage, and excessive filter maintenance. Liquid and vapor velocities must be controlled carefully and flashing of liquids or accelerated blow-down rates that would "lift" or "float" all or portions of the bed should be avoided.

Desiccant bed life can be extended by doing several or all of the following activities:

- Prevent the desiccant particles from moving.
- Keep contaminants out of the dehydrating portion of the bed by upstream conditioning or by providing a sacrificial layer of less expensive desiccant to act as a catcher of any compounds such as amine, glycol or oil.
- Prevent overheating the bed to reduce the formation of carbon during the regeneration cycle.
- Analyze the heating/cooling regeneration temperature cycles to minimize the time the bed is at elevated temperatures. This will also minimize energy requirements.

A typical heating/cooling regeneration temperature cycle plot is shown in Fig. 20-86, with a description of the stage activities. There are typically four (4) distinct stages in a normal cycle:

Stage 1—First bed-heating stage

Stage 2—Desorption stage

Stage 3—Second bed-heating stage

Stage 4—Bed-cooling stage

For a period of time after the heat source is introduced into a desiccant bed being dehydrated, the bed must be heated to a temperature where the water will start to be desorbed (Stage 1). As the water is desorbed (Stage 2), the bed temperature will usually rise only a few degrees because the regeneration gas heat is utilized to provide the heat of vaporization of the water being removed. The completion of the water desorption stage is characterized by a rapid increase in bed temperature measured as the outlet temperature. At this point the heating may be discontinued while bed heating will continue from residual heat in the heating cycle (Stage 3). As the unheated regeneration gas stream continues to pass through the bed, the bed will be cooled (Stage 4).

At near ambient pressures, regeneration of silica gel and alumina can be accomplished at 150°C. Molecular sieve requires 260–290°C to maintain the low dewpoint potential, and the higher temperatures may increase desiccant life by providing more complete removal of adsorbed hydrocarbons.

Capacity and performance data for new solid desiccants are usually presented based on a static test. Under operating conditions (dynamic) the performance data may be significantly different. Typically the effective capacity at operating conditions is about one-half of the capacity at equilibrium (static) conditions for most solid desiccants. This operating characteristic must be considered when designing a dehydration system and can be influenced by careful design and good control of operating parameters such as temperatures, contaminant levels, regeneration cycles, and desiccant selection. Solid desiccant manufacturers should be consulted for the most current product information and design criteria.

Molecular Sieve

Molecular sieve is not normally used for liquid dehydration because the required level of water removal is usually moderate and the cost of molecular sieve is considerably more than other types of suitable desiccants, such as activated alumina. However, in extreme cases where the moisture content of the liquid must be kept at an unusually low concentration, molecular sieve should be considered.

Molecular sieve may be used for removing other undesirable compounds, such as H_2S, COS, mercaptans, etc., from liquid streams. Dehydration may be a secondary benefit of using this type of treating method.

Refer to the discussion of molecular sieve for gas dehydration elsewhere in this Section for more information.

Activated Alumina

There are several types of alumina available for use as a solid desiccant. Alumina is widely used for drying liquid product streams following gas processing, treating, or fractionation. Most alumina desiccants will produce a dewpoint below –70°C if applied properly. Alumina tends to adsorb heavy hydrocarbons which are difficult to remove during regeneration. Alumina is alkaline and is subject to reaction with mineral acids which are found in some well treating fluids.

The design of a solid desiccant liquid dehydration system is similar to a gas dehydration system. An effective desiccant capacity of 4-5% is typically used in liquid dehydrator design.

Calcium Chloride

Calcium chloride is used as a consumable desiccant. Solid calcium chloride combines with water to form a brine solution. From one to two pounds of water can be absorbed by a pound of calcium chloride. Large liquid $CaCl_2$ dehydrators are usually operated in a series that can be reversed with a moisture monitor located between the beds. In that way when the lead sacrificial bed is exhausted, no wet product is produced. The exhausted $CaCl_2$ bed is then recharged and the vessels reversed in service.

The bed size can be estimated using a superficial velocity of 1 to 1.5m/min and an L/D of 2.5 to 4:1.

Calcium chloride dehydration has become less popular because of the environmental problem of disposing of the produced brine.

Distillation

Wet NGLs can be dehydrated by distillation in specially designed fractionation columns. It will generally suffice to withdraw a sidestream liquid distillate three to four fractionation trays below the top of the distillation column to assure a dry product. Water in the NGL feed is passed overhead and is decanted in the overhead reflux drum while reflux is returned to the top of the column. Some extra costs will be required for the sidestream liquid withdrawal and cooling, but this can still be the most cost-effective manner to achieve the dehydration of propane and/or butane LPG products to adequate dryness specifications. The bottoms product of the distillation should be bone dry.

Example 23-1 — Pure component properties

Using Fig. 24-27, the P- H diagram for propane, calculate the density of propane vapor at 110°C and 2000 kPa (abs).

Solution

On the P-H diagram at the intersection of the T = 110°C, P = 2000 kPa (abs) lines read v = 0.03 m^3/kg. Then:

$$\rho = 1/0.03 = 33.33 \text{ kg/m}^3$$

Using the EZ*THERMO[90] version of the SRK[91] equation of state, ρ is calculated to be 32.83 kg/m^3, from which v = (1/32.83) = 0.03 m^3/kg.

For propane at 110°C and 2000 kPa (abs) using data from Fig. 24-27:

$$Z = \frac{MW \bullet P}{R \bullet T \bullet \rho} = \frac{(44.10)(2000)}{(8.3145)(273 + 110)(33.33)} = 0.831$$

The SRK calculation gives ρ = 32.93 kg/m^3, and Z = 0.842.

Gas Mixtures

GPA Standard 2172, "Calculation of Gross H Value, Relative Density and Compressibility Factor for N Gas Mixtures from Compositional Analysis" contains additional information regarding the calculation of Z-factors for mixtures at pressures below 1000 kPa (abs).

Minor Amounts of Non-hydrocarbons — Fig 23-4[1] shows Z-factors for typical sweet natural gases. Using Z-factors from Fig. 23-4 should yield mixture volumes (densities) within 2% to 3% of the true values for reduced temperatures from slightly greater than 1.0 to the limits of the chart for both temperature and pressure. The chart has been prepared from data for binary mixtures of methane with ethane, propane and butane and data for natural gas mixtures. All mixtures have average molecular masses less than 40, and all gases contain less than 10% nitrogen and less than 2% combined hydrogen sulfide and carbon dioxide. Fig. 23-4 applies for temperatures –7°C or more above saturation up to pressures of 70 000 kPa (abs).

Appreciable Amount of Non-Hydrocarbons — Figure 23-4 does not apply for gases or vapors with more than 2% H_2S and/or CO_2 or more than 20% nitrogen. Use other methods for vapors that have compositions atypical of natural gases mixtures or for mixtures containing significant amounts of water and/or acid gases, and for all mixtures as saturated fluids, other methods should be employed.

Figure 23-4 provides reasonably accurate gas Z-factors for natural gases with high nitrogen content, up to 50% (or even higher) when using the molar average pseudo-criticals from Eqs 23-3a and 23-4a. The same approach applies to gas condensate fluids containing appreciable amounts of heptanes and heavier components. Critical temperatures and pressures for heptane and heavier fractions can be estimated from molecular weight and relative density, or average boiling point and relative density, using correlations presented in this section.

Figs. 23-5, 23-6 and 23-7 provide Z-factors for low molecular mass natural gases. These figures cover a wide range of molecular masses (15.95 to 26.10), temperatures (-70 to 500°C) and pressures [up to 35 000 kPa (abs)]. For gases with molecular weights between those shown in Figs. 23-5 through 23-7, linear interpolation between adjacent charts is sufficient to compute the Z-factors.

In general, Z-factors for gases with less than 5% noncondensable non-hydrocarbons, such as nitrogen, carbon dioxide, and hydrogen sulfide, result with less than 5% error. When the molecular weight is above 20 and the Z-factor is below 0.6, errors as large as 10% may occur.

Effect of Acid Gas Content — Natural gases containing H_2S and/or CO_2 exhibit different Z-factor behavior than do sweet gases. Wichert and Aziz[3] present a calculation procedure to account for these differences. Their method uses the standard gas Z-factor chart (Fig. 23-4) and provides accurate sour gas Z-factors that contain as much as 85% total acid gas. Wichert and Aziz define a "critical temperature adjustment factor," ε, that is a function of the concentrations of CO_2 and H_2S in the sour gas. This correction factor adjusts the pseudo-critical temperature and pressure of the sour gas according to the equations:

$$T_c' = T_c - \varepsilon \qquad \textbf{Eq 23-6}$$

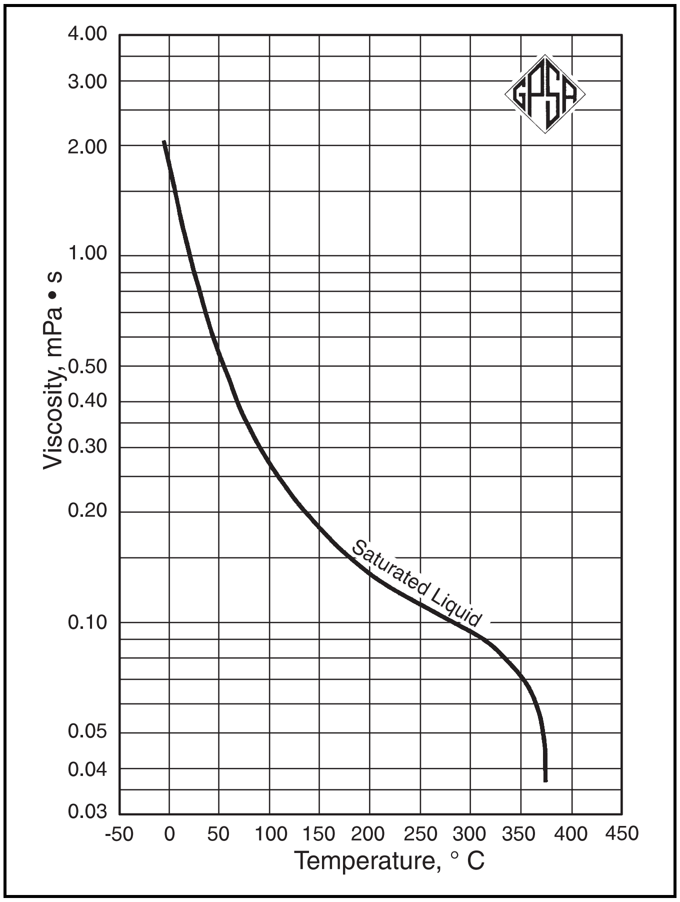
FIG. 23-3

Calculation of Pseudo-critical Temperature and Pressure for a Natural Gas Mixture

Component	Mole Fraction, y_i	Component Critical Temperature, T_{ci}, K	Component Critical Pressure, Pci, kPa	Component Molecular Mass, MWi	Pseudocritical Temperature $y_i \cdot T_{ci}$, K	Pseudocritical pressure $y_i \cdot p_{ci}$, Kpa	Mixture Molecular Mass $y_i \cdot MW_i$
Methane	0.8319	190.6	4599	16.043	158.560	3825.908	13.346
Ethane	0.0848	305.4	4880	30.070	25.898	413.824	2.550
Propane	0.0437	369.8	4240	44.097	16.160	185.288	1.927
i-Butane	0.0076	407.8	3640	58.123	3.099	27.664	0.442
n-Butane	0.0168	425.1	3784	58.123	7.142	63.571	0.976
i-Pentane	0.0057	460.4	3381	72.150	2.624	19.272	0.411
n-Pentane	0.0032	469.6	3365	72.150	1.503	10.768	0.231
n-Hexane	0.0063	507.5	3012	86.177	3.197	19.976	0.543
	1.0000				218.184 = T_c	4565.271 = P_c	20.426 = M_W
G = 20.246/28.9625 = 0.705							

FIG. 23-27

Water Viscosity at Saturated Conditions



$$\mu = (1.21)\,(0.0105) = 0.0127 \text{ mPa} \bullet \text{s}$$

The method of Dean and Stiel[41] is best for calculating the viscosity of a gaseous mixture with large amounts of non-hydrocarbons. This method is particularly useful for handling natural gas with high CO_2 content. Compared to 30 CO_2-N_2 mixtures, this method has an average deviation of 1.21% at pressures up to 3525 psia. The method uses a factor, ξ, defined as:

$$\xi = 5.4402\left[\frac{T_{cm}^{1/6}}{P_{cm}^{2/3}\left(\sum_i y_i MW_i\right)^{1/2}}\right] \qquad \textbf{Eq 23-20}$$

If $T_r > 1.5$, then
$\xi\mu_A = 166.8(10^{-5})(0.1338\ T_r - 0.0932)^{5/9}$ **Eq 23-21**

If $T_r \leq 1.5$, $\xi\mu_A = 34.0(10^{-5})\ (T_r^{8/9})$ **Eq 23-22**

In either case, μ_A is $\xi\mu_A$ divided by ξ.

Equations 23-20 through 23-22 predict the viscosity of pure gases as well as mixtures. To apply the Dean and Stiel[41] method to mixtures, calculate the pseudo-critical volumes, Z-factors, and temperatures using the Prausnitz and Gunn[42] mixing rules:

$$V_{cm} = \sum_i y_i V_{ci} \qquad \textbf{Eq 23-23}$$

$$Z_{cm} = \sum_i y_i Z_{ci} \qquad \textbf{Eq 23-24}$$

$$T_{cm} = \sum_i y_i T_{ci} \qquad \textbf{Eq 23-25}$$

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_{cm}} \qquad \textbf{Eq 23-26}$$

Example 23-9 — For a temperature of 10°C and a pressure of 2000 kPa (abs), estimate the viscosity of a mixture of 80 mole percent methane, 15 mole percent nitrogen, and 5 mole percent carbon dioxide. See Fig. 23-30:

$$P_{cm} = \frac{Z_{cm}\ R\ T_{cm}}{V_{cm}}$$

$$= \frac{(0.2871)\ (8.31)\ (186.6)}{0.0973} = 4581.8 \text{ kPa (abs)}$$

Substituting from the calculation table in Fig. 23-30 into Eq 23-20:

$$\xi = \frac{(21.74)\ (186.6)^{1/6}}{(19.237)^{1/2}\ (4581.8)^{2/3}} = 0.043$$

$$T_r = \frac{T}{T_{cm}} = \frac{283}{186.6} = 1.52$$

Because $T_r > 1.5$, the expression for $\xi\mu_A$ is Eq 23-21.

$$\xi\ \mu_A = \left[166.8\ (10^{-5})\right]\left[(0.1338\ T_r - 0.0932)^{5/9}\right]$$

$$= \left[166.8\ (10^{-5})\right]\left[(0.1338 \bullet 1.52 - 0.0932)^{5/9}\right]$$

$$\xi\ \mu_A = 48.98\left(10^{-5}\right)$$

$$\mu_A = 0.01147 \text{ mPa} \bullet \text{s}$$

Using Fig. 23-22 and correcting for the nitrogen and carbon dioxide content of this mixture gives a μ_A of 0.0116 cp. This is a good check. Had a 20% N_2 content been chosen for this example, the N_2 range of Fig. 23-22 would have been exceeded and use of the Dean and Stiel method would have been required. When the conditions at hand fall within the limits of Fig. 23-22, use this figure and not the Dean and Stiel correlation.

Viscosity of Petroleum Fractions

Mid-Boiling Point Method — The viscosity of a crude oil or crude oil fraction can be estimated using the equations given below if the mid-boiling point and gravity are known:

Mid-boiling point is defined as the boiling point at 50% volume distilled.

$$\eta = A \bullet e^{B/T} \qquad \textbf{Eq 23-27}$$

$$A = \left(91.83\ T_b^{-0.175} - 29.263\right)\frac{K_w}{B} \qquad \textbf{Eq 23-28}$$

$$\ln(B) = 4.717 + 0.00526\ T_b \qquad \textbf{Eq 23-29}$$

Example 23-10 — At 40°C and 100°C find the viscosity of a heavy condensate having a mid-boiling point of 163°C and a relative density of 0.7688.

Solution Steps