

**OILFIELD PROCESSING OF PETROLEUM
VOLUME ONE: NATURAL GAS**

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Preface

Oilfield Processing of Natural Gas is the first book in a three-volume series on the various surface unit operations commonly used in production facilities. Crude oil and oilfield waters will be treated separately in Volumes 2 and 3, respectively.

This book will hopefully serve three needs. First, in the form of typed notes, the current material has been used as a text for a senior-level, petroleum engineering design course on surface production and processing. And, the authors do appreciate the numerous suggestions from the Tulsa University seniors who used these notes.

Second, this book material has been used in short courses for engineers and foremen working in field handling of natural gas. It is hoped that this book will help engineers in other disciplines learn petroleum production concepts.

Thirdly, this book should serve as a refresher and handbook for all engineers interested in natural gas processing.

The mathematical background required to use this book has been purposely kept to a minimum so as to make it easily readable and immediately useful. Where advantageous, current computer simulation has been identified but computer expertise is not required.

The authors express their gratitude and thanks to the University of Tulsa for providing the opportunity and environment to write this book. The University of Tulsa enjoys many long-standing close relationships with the petroleum industry. In fact, so many petroleum-industry engineers helped so much that it is impossible to document every kindness.

Nevertheless the authors are most pleased to thank the following friends and companies for providing up-to-date information, and reviewing drafts:

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T. H. Russell Company Solar Turbines Phillips Petroleum Company	
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While all these friends were exceedingly helpful some contributions demand individual recognition. Dr. Boyd George and Dr. Russ McGalliard individually reviewed, critiqued, and proofread Chapters 1 through 9. Dr. Bill Manning wrote Chapter 7, and coauthored Chapter 8. Dr. Jim Hunt critiqued Chapter 10, while Robin McGlynn's

Chapter 1

Introduction and Scope

Oil and gas production involve a number of surface unit operations between the wellhead and the point of custody transfer or transport from the production facilities. Collectively these operations are called field handling or oilfield processing. Accordingly, *oilfield processing* is defined as the processing of oil and/or gas for safe and economical storage and/or transport by pipeline, tanker, or truck. Oil-field processing also includes *water treatment*, whether produced waters for disposal and/or reinjection, or additional injection waters used for formation flooding or reservoir-pressure maintenance.

The present Volume 1 describes *oilfield processing of natural gas*. Process descriptions, design methods, operating procedures, and troubleshooting are covered in detail. Crude oil and oilfield waters are treated separately in Volumes 2 and 3, respectively. The wellhead is the starting point, and the ultimate destination is either a sales or reinjection pipeline for the natural gas, and a pipeline or storage tank for the natural-gas liquids (NGL). While NGL production and N₂ rejection are not usually major objectives, they are also reviewed.

In this volume “conditioning,” “processing,” and “handling” are used synonymously to refer to all oil-field operations. “Cleaning,” “treating,” dehydration,” and “HC dew-point control” describe specific operations as follows:

Cleaning:	Removing liquids and solids such as sand, pipeline dirt, reservoir fines, corrosion products and inhibitors, liquid or free water, salt, drilling mud
Treating:	Sweetening or removal of acid gases (H ₂ S and/or CO ₂)
Dehydration:	Drying or removing water vapor or controlling H ₂ O dew point
HC dew-point control	Recovery of ethane and heavier hydrocarbons as condensate.

Oil-field processing generally consists of two distinct categories of operations:

1. Separation of the gas-oil-brine wellstream into its individual phases,
2. Removal of impurities from the separated phases to meet sales/transportation/reinjection specifications and/or environmental regulations.

Phase separation is a very important part of field handling that is discussed in the volume on crude-oil treating, and it is not repeated here. *Instrumentation, controls, pressure relief, and flaring* are also discussed in Volume 2. *Corrosion* is treated with oil-field waters in Volume 3. *Safety and environmental concerns* are addressed throughout all three volumes.

Obviously the selection and operation of field handling equipment depends very strongly on the *volume* and *characteristics* of the stream produced at the wellhead. Accordingly, this volume starts by discussing:

- characterization of natural gas and its products
- phase and thermodynamic behavior of natural gas
- water-natural gas phase behavior.

Then the *individual unit operations* commonly used in field handling of natural gas are described. These include:

- basic field-processing schemes
- prevention of hydrate formation
- sweetening (removing H₂S, CO₂)
- dehydration using TEG, solid desiccants, LTX, and CaCl₂
- condensate recovery and HC dew-point control
- compression
- flow measurement
- heating and cooling
- pipeline transport of natural gas.

Next, design or sizing calculations are presented for two wellstreams—a large-volume offshore and a limited-volume onshore. These *case histories* are used to illustrate how

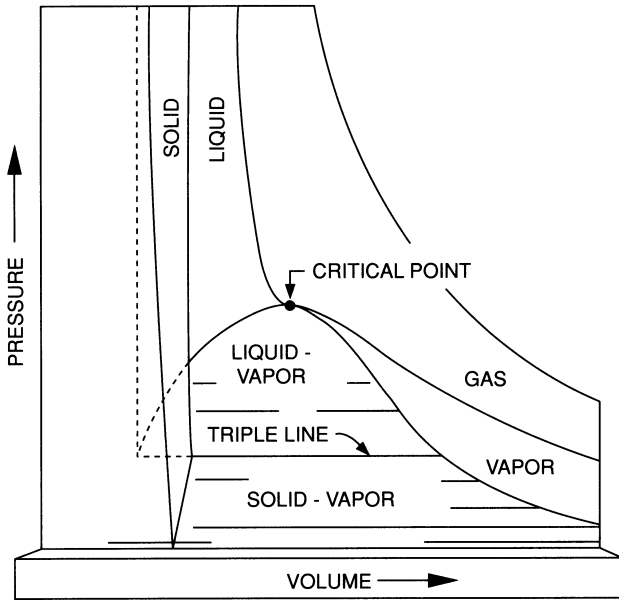


Figure 3-2b. P-V diagram for pure substances that expand on freezing (Lee and Sears, 1963, p. 40).

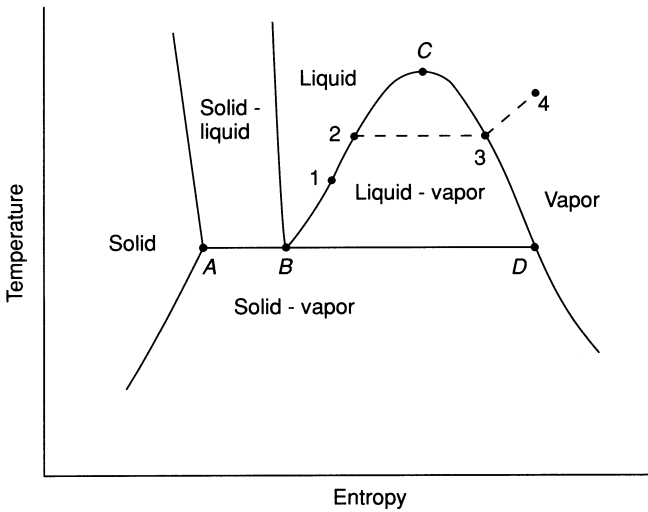


Figure 3-2c. Temperature-entropy (T-s) diagram for a single-component system (Smith and van Ness, 1975, p. 213).

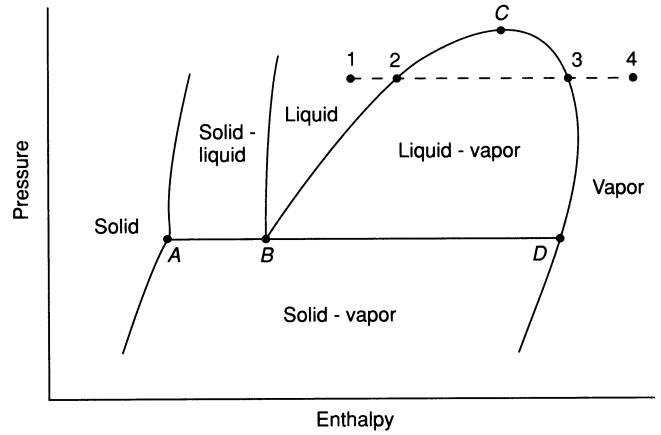


Figure 3-2d. Pressure-enthalpy (1n P-h) diagram for a single-component system (Smith and van Ness, 1973, p. 214).

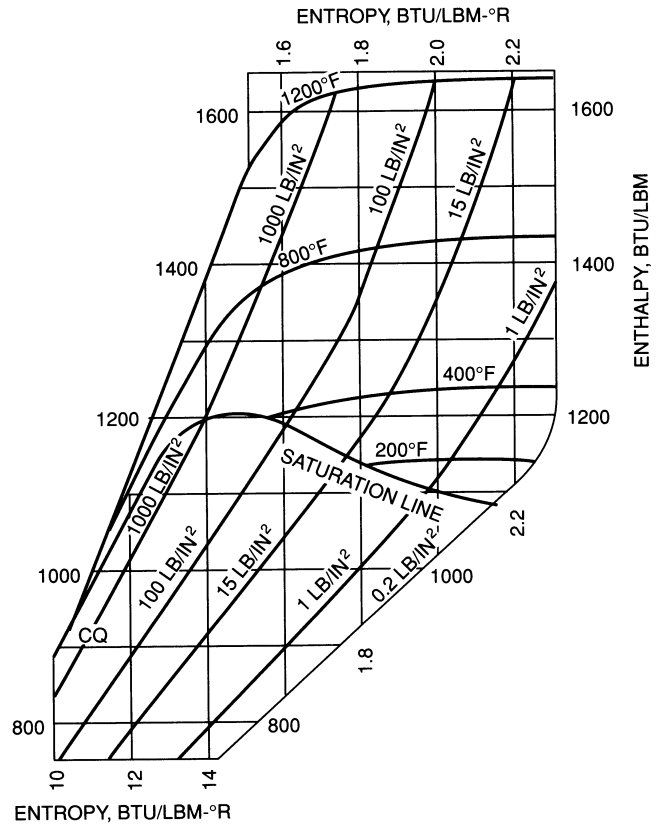


Figure 3-2e. The Mollier (h-s) diagram for water (Lee and Sears, 1963, p. 259).

Figure 3-2. Thermodynamic diagrams for pure substances.

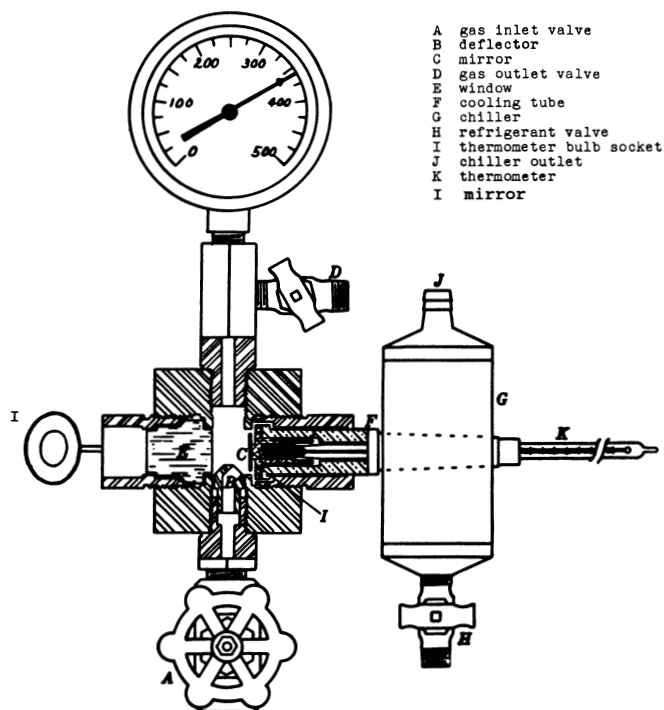


Figure 4-1. Bureau of Mines dew-point tester (Deaton and Frost, 1938; ASTM, 1963).

chamber through outlet valve, D. The mirror, C, is cooled by cooling tube, F, which is attached to the chiller, G. Refrigerant enters the chiller at valve, H, and leaves at J. Any dew on the mirror, C, is observed through the transparent lucite window, E. The temperature at which dew is observed is read using the calibrated thermometer, K. Mirror I permits simultaneous viewing of the mirror C and reading of the thermometer, K.

Dew-point measurement involves cooling the mirror, C, with a suitable refrigerant (C3 or Freon 12 down to -20°F , liquid CO_2 down to -90°F , dry ice/acetone down to -100°F , or liquid N_2 down to -200°F); flowing the sample gas over the polished mirror; and reading the temperature and pressure at which dew first appears and disappears on the mirror surface.

The following precautions will improve accuracy (Chandler Engineering, 1986):

1. Use an illuminated magnifier and/or an LED temperature readout if the lighting makes it difficult to observe condensation.
2. Purge the tester to remove all air.
3. Do not cool the mirror faster than $2^{\circ}\text{F}/\text{min}$ when within 5°F of the dew point.
4. While observing the mirror and thermometer, record the temperature at which dew first forms.

5. Let the mirror warm up and observe the temperature at which the dew disappears.
6. Repeat steps 4 and 5 until the two temperatures agree within 2°F .
7. Take the average of the two temperatures as the dew point.

A water dew-point measurement can be confirmed by measuring the dew point of the same gas sample at several pressures. The observed dew points should change so the resulting water contents remain constant. This implies that uncertainties in the gas-sample pressure and/or any overlooked pressure drops will cause corresponding errors in the reported water content.

Liquid hydrocarbons, alcohols, or glycols also can condense on the mirror before the water dew point is reached. The following characteristics distinguish water dew points (Gibson, 1980; Chandler Engineering, 1986):

1. Water dew forms a distinct, opaque, grey circular spot in the center of the mirror (coldest spot). Water should not “wet” the mirror and should resist being blown off the mirror by increasing the gas flow. Ice crystals form an irregular white pattern against the previously-formed, grey water condensate. Barium sulfate and “water-cut” paste can confirm water dew points also.
2. In contrast, liquid-hydrocarbon condensates wet the mirror, expand in rainbow-like rings to cover all the mirror, and can be “blown off” or “streak” the mirror by a sudden increase in the sample gas flowrate.
3. Alcohol dew points appear as white spots with indistinct edges. Advanced alcohol spots are larger, increasingly white, and eventually form liquid drops that do not freeze.
4. Glycol dew points are darker, cover the entire mirror, and do not evaporate.

With the exception of the thermometer and pressure gauge, the Bureau of Mines tester requires no calibration. The method is relatively inexpensive and easy to operate. However, this type of measurement can be time-consuming and cannot be recorded automatically. Accuracy can be very good but varies with operator skill and dedication.

Electrolysis Method

The electrolysis method involves adsorbing and electrolyzing the water vapor in the sample gas. The heart of this instrument is an electrolytic cell consisting of two 5-mil wires spirally wound throughout the inner wall of an insulating tube. A thin film of phosphorus pentoxide (P_2O_5) is applied between these two wires which are spaced 5 mil apart. As shown in Figures 4-2 and 4-3 (Mayeaux,

shown by curve 1-2 in Figure 5-2a. As shown, the pipeline path is one of decreasing pressure with temperature falling rapidly to an almost constant level. This occurs because the flowing gas temperature often approaches ambient temperature in a short distance. Two-phase flow requires a larger pipe diameter than single-phase flow. Furthermore, the condensate must be handled in a slug catcher at the pipeline end.

Condensate removal requires cooling the gas to condense liquids, followed by phase separation in a vapor-liquid separator (Fig. 3-9). The phase diagram of the liquids-depleted gas is shown in Figure 5-2b; transport for the path shown results in no condensation. In this alternative a separate means of condensate transport or disposal is required.

In dense-phase transport the gas is maintained at a pressure

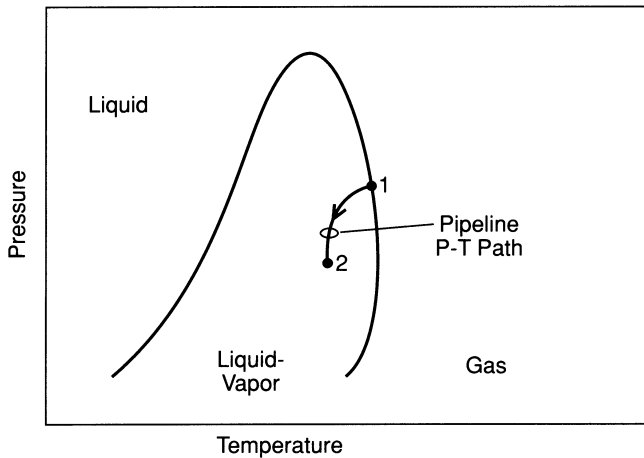


Figure 5-2a. Phase diagram for pipeline gas with condensation.

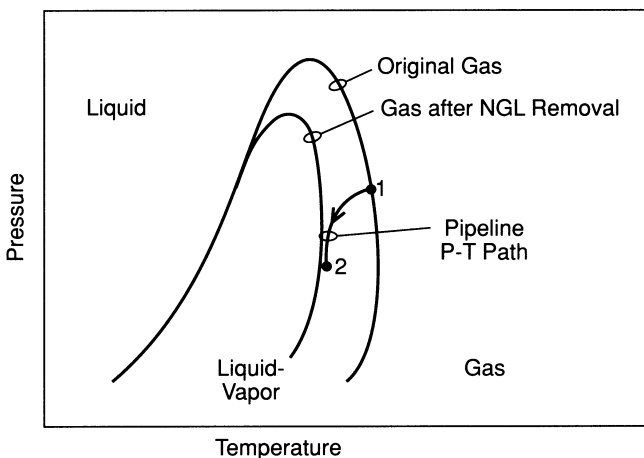


Figure 5-2b. Phase diagram for pipeline gas after NGL removal.

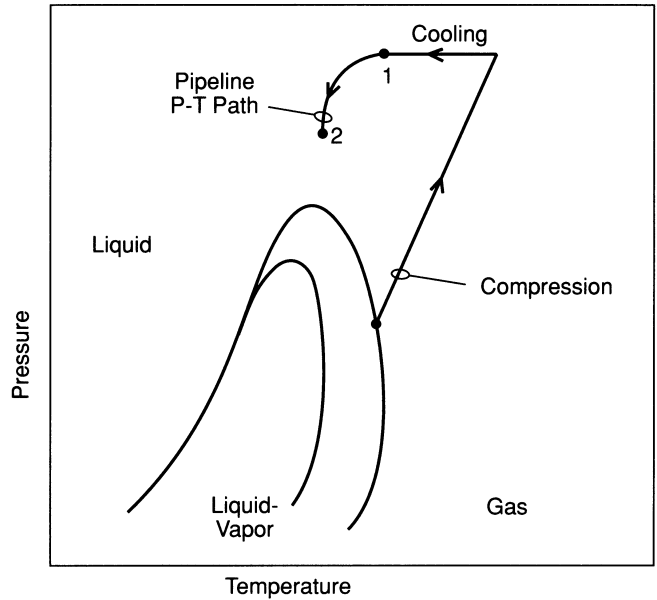


Figure 5-2c. Phase diagram for dense-phase pipeline gas.

higher than the cricondenbar throughout the line, which prevents the formation of two phases at any point (Figure 5-2c). Expensive compression may be required and pipe with high pressure rating and thickness is required, but the diameter will be smaller because of the increased density of the compressed fluid.

In a given case, any one of the above alternatives might be preferable. Comparison of costs and other constraints must be made.

Salable Gas. Production of sales-quality gas requires all processing necessary to meet specifications of the type shown in Table 2-8. Hydrogen sulfide and CO₂ must be removed if present in sufficient amount. Dehydration is required also, generally after compression, since free water is condensed out in the compressor aftercooler. Removing free water in a separator reduces the load on and cost of the downstream TEG dehydration unit.

Recovery of condensate depends on the amount present, the heating value requirement of the sales gas, and the hydrocarbon dew-point specification (if any). If the condensate content is low, there may be little need to remove it. If the gas contains a high percentage of nitrogen, it may be necessary to retain the heavier hydrocarbons in order to meet the heating-value specification. If the HC dew point is regulated, condensate recovery may be required to meet the dew-point specification.

Three basic techniques are used for condensate recovery. From the standpoint of the phase diagram, the task is to move the state of the system to the left of the dew-point line of the gas. In other words, cool the gas below its

i.e., the decomposition of the salts formed during absorption of acid gases—is more difficult. A reclaimer operating at a higher temperature than the reboiler is usually used to augment regeneration.

Diethanolamine, DEA. *DEA* is currently the *most widely used* gas sweetening solvent. Compared with *MEA*, it has lower heats of reaction with H_2S and CO_2 , is less corrosive, and can be used in higher concentrations with greater acid gas loadings. This results in a reduced circulation rate and in lower capital and operating costs. *DEA* also is very resistant to degradation from *RSH* and *COS*. This was very significant in the early commercial successes in Canada (Goar, 1972). Major disadvantages are the inability to slip CO_2 and that some newer processes are more economical for specific situations.

There is an adaptation—*SNPA*, developed and licensed by Société Nationale Elf-Aquitaine—that achieves very high acid gas loadings—as much as 0.7 mol AG/mol *DEA*—without excessive corrosion. However, to achieve this (and the reduction in solvent circulation and regeneration cost) high inlet acid gas partial pressures are needed, e.g., 4 atmospheres (Dailey, 1970). The process is used extensively in Canada.

Diisopropanolamine, DIPA. *DIPA* is the amine used most frequently in the *ADIP* process licensed by Shell—*MDEA* is occasionally used. Klein (1970) reports low steam requirements, low corrosion rates, and suitability for gas streams containing *COS*. However, Bucklin (1982) rates the irreversible degradation from CO_2 and *COS* higher than that for *MEA*, *DEA*, or *DGA*. It is used to remove H_2S and *COS* from *LPG* also (Ouwkerk, 1978).

Diglycolamine, DGA. *DGA* is a primary amine with the same molecular weight as *DEA*. As practiced in the *Econamine* process which is licensed by Fluor, a 50–70% solution can be loaded to 0.4 mol AG (acid gas)/mol *DGA*. This reduces the circulation rate substantially below that for *DEA* (Bucklin, 1982; Moore *et al.*, 1984).

A solution containing 65% *DGA* freezes at -40°F . This makes *DGA* very suitable for cold climates. Note that 20% *MEA* and 30% *DEA* solutions freeze at 15°F and 20°F , respectively. Similarly to *MEA*, it is suitable for treating gas streams with low partial pressures of acid gases, and a reclaimer is needed to complete the regeneration. *DGA* also exhibits a significant affinity for organic sulfur compounds.

Methyldiethanolamine, MDEA. *MDEA* has gained a greater share of the gas treating market in recent years. This success is due in part to the fact that tertiary amines

such as *MDEA* exhibit a selectivity for H_2S over CO_2 when contacting gas streams containing both acid gases. This selective property is useful in upgrading the H_2S content of sulfur plant feed gas (Blanc *et al.*, 1981) and removing H_2S from CO_2 used for flooding projects (Laengrich *et al.*, 1982).

MDEA solutions have the *lowest heat requirements* for regeneration because they can be used at 50% strength and acid gas loadings of 0.4 mol/mol, have the lowest heats of reaction with H_2S and CO_2 , and the lowest specific heat (Pearce, 1978 and Daviet *et al.*, 1984). Solvent losses are very low and the freezing point is about -25°F . Also *MDEA* is used in many of the special solvent formulations.

Special Solvents. Several *new alkanolamine-based solvents* have been developed recently. Some of Dow's *Gas/Spec* and Union Carbide's *Amine Guard Solvents* are *MEA* and *DEA* formulations with corrosion inhibitors. These permit the use of substantially higher concentrations, e.g., 30% for *MEA* and 50% for *DEA*. The results are significant reductions in the amine circulation rate and the heat requirements for regeneration (Kosseim *et al.*, 1984; and Pearce and Wolcott, 1986).

The most significant penetrations into the gas sweetening market—currently there are over 100 units—are Dow Chemical's *Gas/Spec* and Union Carbide's *Ucarsol* solvents. Some of these are *MDEA*-based with other *amines*, *buffers*, *promoters*, *corrosion inhibitors*, and *antifoamants* added. These additives control both the extent and rate of the reactions with H_2S and CO_2 . The proprietary solvents are blended for specific applications; e.g. selective H_2S removal, partial or bulk CO_2 removal with or without high H_2S removal, high acid gas loadings, *COS* removal, etc. (Bacon and Pearce, 1985; Robinson *et al.*, 1988; Thomas, 1988; and Dwyer, 1989)

Both Dow Chemical and Union Carbide have extensive research and development programs, and it is very likely that new formulations with even better performance will be developed. Vickery *et al.* (1988) show that the addition of relatively small amounts of *MEA* or *DEA* to *MDEA* can be used to control the selectivity and acid gas loading.

Exxon's *Flexsorb* solvents use *steric hindrance*—i.e., the presence of a large group next to the nitrogen atom—(Fig. 7-4)—and basicity to control the CO_2 /amine reaction (Sartori and Savage, 1983; and Goldstein *et al.*, 1984). There are *Flexsorb* solvents for selective H_2S removal and bulk CO_2 removal (Clem *et al.*, 1985).

Mixed Solutions. Shell's *Sulfinol* was the first of these processes. The solution uses *sulfolane* as the *physical solvent* and either *DIPA* or *MDEA* as the *amine* (Wansink, 1985). In addition to absorbing organic sulfur compounds,