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Development of Alaskan Gas Hydrate Resources

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G.D. Sharma
V.A. Kamath
S.P. Godbole
S.L. Patil
S.G. Paranjpe
P.N. Mutalik
N. Nadem

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For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Petroleum Development Laboratory
437 Duckering, University of Alaska
Fairbanks, Alaska 99775-1260

MASTER

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1.0 TECHNICAL PERSPECTIVE

Solid, ice-like mixtures of natural gas and water in the form of natural gas hydrates have been found immobilized in the rocks beneath the permafrost in Arctic basins, and in muds under the deep waters along the American continental margins in the North Sea and several other locations around the world. The Arctic areas of the United States may contain as much as 500 trillion SCF of natural gas in the form of gas hydrates (Lewin and Associates, 1983).

While the U.S. Arctic gas hydrate resources may have enormous potential and represent the long term future source of natural gas, the recovery of this resource from reservoir completely "frozen" with gas hydrates has not been commercialized yet. Continuing study and research is essential to develop technologies which will enable a detailed characterization and assessment of this alternative natural gas resource; development of cost effective extraction technology.

2.0 OVERALL PROJECT GOALS

The overall project objectives are outlined as follows:

1. **To Gather Data and Information Relevant to Gas Hydrates in the Arctic**

   The specific aspects include:

   - Geology of Alaska's North Slope Region
   - Geothermal Gradient Data for Alaska's North Slope (ANS)
   - Tar Sand Deposits of Alaska's North Slope
   - Land-Sat and Other Related Remote Sensing Surveys of ANS
   - Depths, Thicknesses and the Areal Extent of Permafrost on the ANS
   - Seismic Data of ANS
   - Electromagnetic Surveys and Profiles of ANS
   - Ground Water Availability of ANS
   - Subsea Permafrost of the Beaufort Sea
   - Data and Maps of the ANS Oil and Gas Well Locations

2. **To Review Gas Hydrate Literature, Current Research, State-of-the-Art Technology**

   The specific aspects include:

   - Compilation and Review of Gas Hydrate Phase Equilibrium Data and Predictive Models
   - Review of Gas Hydrate Recovery Models
   - Review of Gas Hydrate Properties and Compilation of Available Literature Data
   - Review of Geologic Occurrence of Gas Hydrates
   - Review of Methods for Detection of Gas Hydrates
   - Review of Potential of Gas Hydrates as an Energy Resource
   - Review of Other Gas Hydrate Literature and Current Hydrate Research

3. **To Develop Contacts**

To develop contacts within the petroleum industry and other agencies within the State of Alaska to obtain access to well logs, core samples, water samples and for in-situ measurement of potential gas hydrate zones and to provide DOE with all of the public information.

4. **To Study Implications of Dissociation of In-Situ Gas Hydrate Deposits**

   The following aspects are addressed:

   - Implications Related to Drilling and Production from Hydrates
   - Development of Thermal Model to Predict, the Degree of Dissociation of Gas Hydrates During Drilling
   - Development of Guidelines for Drilling in Presence of Hydrates
   - Effect of Dissociation of Gas Hydrates on Subsidence
   - Mechanical Properties of In-Situ Gas Hydrates

5. **To Conduct Experimental and Theoretical Modelling Work for the Development of Techniques for Recovery of Natural Gas from Gas Hydrates**

   A. The experimental work on study of hydrate cores address the following:

   - Formation of Gas Hydrates Within the Porous, Unconsolidated Cores and Measurement of Hydrate Formation Rates and Study of Kinetics
   - Measurement of Permeability of Cores During Hydrate Formation, as a function of hydrate saturation.
   - Dissociation of Hydrates Under Various Conditions (such as, depressurization, hot brine and steam injection and measurment of gas production rates)
   - Study Hydrate Dissociation Mechanism, Heat Transfer Mechanism and Convection Effects Under Above Conditions

   B. The hydrate recovery modelling efforts include:

   - Development of a fundamental hydrate dissociation model which considers unsteady state heat transfer to hydrates in r-z directions. This will be a finite difference simulator and will include both heat conduction and convection effects.

- Application of the model to brine, hot water, steam injection and depressurization methods. Experimental data will serve as the basis of our theoretical model.

6. **To Conduct Economic Analysis of Gas Hydrate Production**

The analysis will consider various hydrate recovery methods and compare relative costs. The results of our hydrate recovery models will serve as the basic data for the economic analysis. Also, the various options of natural gas utilization will be evaluated.

7. **To Conduct Experimental Study of Hydrate Formation in the Presence of Heavy Oil**

In reservoirs where gas hydrates coexist with heavy oil or tar sands it is possible that gas hydrates might have affected the properties of these heavy oils and also may affect the performance of thermal recovery methods. To develop better understanding of hydrate-heavy oil relationship the research is devoted to the following:

- Study hydrate formation from light hydrocarbon gases and West Sak and Prudhoe Bay crudes
- Measure equilibrium hydrate forming conditions
- Study effect of hydrate formation on the oil properties (such as, bubble point pressure, density and viscosity)

3.0 WORK PERFORMED DURING FIRST YEAR

Section I: Alaskan Arctic North Slope Data Gathering

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SECTION I

ALASKAN ARCTIC NORTH SLOPE DATA GATHERING

Prepared by

G.D. Sharma
Petroleum Development Laboratory
437 Duckering
University of Alaska
Fairbanks, Alaska 99775-1260

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1. Alaskan Arctic North Slope Data Gathering

During the past year, we have conducted a thorough literature search to gather available information on geology of ANS; geothermal gradient data for ANS; Land-Sat and other related remote sensing surveys; depths, thicknesses and the areal extent of permafrost on the ANS, seismic data, electromagnetic surveys and profiles of ANS; ground water availability, maps and data of ANS oil and gas well locations. A complete bibliography of all the published information has been prepared. Review reports for some of these areas are given in this section. We will submit review reports for other areas later. A set of documents have been delivered in the past to DOE-METC.

In addition to the published information, we have also focussed our attention on acquiring digitized well log data for wells located on the ANS and offshore Prudhoe Bay areas. We have received digitized well log data on magnetic tapes from Alaska Oil and Gas Conservation Commission. The well log data will include wells from the following areas of ANS:

1. West Sak Sands in the Kuparuk River Unit (25 wells)
2. Ugnu Sands in the Kuparuk River Unit (10 wells)
3. Kuparuk Formation in the Kuparuk River Unit (250 wells)
4. Prudhoe Bay Unit (200 wells)
5. Offshore Prudhoe Bay Unit (not yet received)

For well log analysis, we have received software packages LOGCALC and LOGCALCII from Scientific Software Intercomp. These software packages have been installed and tested. Histograms, crossplots, three-dimensional plots can be generated using these interactive software packages to aid quick well log analysis.

2. Geology of Alaska's North Slope Region

Alaskan North Slope region is subdivided tectonically into three major east-west trending elements. These elements are the Barrow Arch, Colville Trough, and Brooks

Orogen. The Barrow Arch is a subsurface broad regional structure. The axis of this arch follows the Beaufort Coast from the foothills of the Brooks Range to Point Barrow and continues onto the Chuckchi Sea. The arch developed during Late Jurassic or Early Cretaceous time on the northern providence of the Arctic platform. Consequently, southward-sloping platform south of the arch and a northward-sloping continental margin north of the arch evolved Cretaceous and Tertiary sedimentation north of the arch prograded the Beaufort continental terrace north from the arch across the presently formed continental margin.

The earliest known tectonic feature on the North Slope region is the east-west oriented Colville Geosyncline. Between Cambrian and Devonian times, the geosyncline was filled with miogeosyncline of rocks, both ev- and miogeosyncline facies, which are metamorphosed. Sometimes during the Devonian time the region was uplifted and a broad stable Arctic platform extended along Northern Alaska. Marine sedimentation continued for late Devonian or Early Mississippian through Early Cretaceous times and created the second sequence of rocks. Clastic and carbonate sediments derived from a nothern source area were deposited on the platform. Near Prudhoe Bay these rocks contain giant oil and gas accumulations. At the close of the Jurassic or the beginning of Cretaceous time, intense tectionic activity compressed the southern part of the platform and thrusted Paleozonic to Cretaceous rocks northward onto the central part of the platform. The compression resulted in the uplifting of the Brooks Range - Herald Arch, which subsequently supplied sediments detritus for the third sequence. Cretaceous sedimentary rocks of the Colville Geosyncline underlie most of the Nothern Chuckchi Shelf and North Slope.

The major filling of the Colville Geosyncline occurred during the Cretaceous. The continued uplift in the Brooks Range intermittantly supplied detritus northward during the Tertiary. The area was exposed and submerged under the sea repeatedly. From the Middle Eocense until Middle Pliocene time the region was above sea level. The area may have submerged briefly as a result of deposition of the fourth sequence. During the Tertiary a stream-sculptured topography similar to that observed today probably developed on the North Slope region.

At the beginning of the Pleistocene epoch crustal warping resulted in marine transgression and the final sequence of sediments was deposited on the North Slope region. The sediment deposited during the Pleistocene have covered the Tertiary topography and formed a monotonously flat platform.

The Pleistocene epoch also connotes a repeated ice cover during glacial stages and the wanning of glaciers during interglacial stages. Each glacial cycle was followed by changes of sea level in Northern Alaska. The brightest sea level attained during the interglacial stage is estimated at about 30M higher than present sea level. During intense glacial marine intervals the sea level fell about 100M below the present strandline.

On the North Slope the unconsolidated Quaternary sediments overlie Tertiary or Cretaceous sediments. The Quarternay sediments are mostly fine-grained sand and silt and occasionally clay and gravel, which are product of frosting and aeolian deposition. The entire regions is underlain by permafrost, which acts as a cement for these sediments. However, annual freezing and thawing in the upper layer forms loose sediments, which are modified by alluvial, Lacustrine, and aeolian reworking and tundra soil development.

The Brooks Range Orogen is dominated by thrust faults, and the subsurface geology in the area is not well known. Northern parts of the Brooks Range, the Foothill Fold Belt, consists of shallow folds with complex axial shale cores while southern zone comprising similar complex folds and thrust faults. Several structures in the northern part of the Foothills Fold Belt are hydrocarbon bearing and may have contributed to formation of gas hydrates.

The potential reservoir beds in the North Slope region of pre-Tertiary age in ascending order are:

1. Mississippian-Pennsylvanian clastic facies of the Lisburne Group;
2. Mississippian "Dolomite Unit" of the Alaph Limestone;
3. Pennsylvanian-Perian Wahoo Limestone;
4. Permian Ikiakpaurak member of the Echooka Formation;
5. Triassic "Ivishak Sandstone";
6. Triassic Sag River Sandstone;
7. Early Jurassic "Barrow Standstone";
8. Late Jurassic "Simpson Sandstone";
9. Jurassic-Neocaomian Kuigak Formation includes potential reservoirs "Peard Sandstone", Neocomian "Kealok Anomaly"; and
10. Cretaceous rocks include "Pebble Shale" sandstone, "Walakpa Sandstone", Basal Torok", and marine and nonmarine sandstones of the Nanushuk Group.

3. Groundwater Availability of ANS

Most of the North Slope region is underlain by as much as 550m thick layer of perenial frozen material called permafrost. Between the ground surface and the upper permafrost is a shallow layer of soil that thaws to a maximum depth of 0.5m during the brief summer and refreezes during late fall. This soil accumulates water from rain, snow and ice melt but deeper infiltertion of water is prevented by the permafrost. The presence of permafrost in the North Slope region provides unlimited supply of surface water during summer, the lack of subsurface drainage severely limits the availability during other seasons.

North Slope region is covered by numerous large and small lakes and marshes and drained by numerous rivers and streams. Arctic lakes can be divided into two categories: 1) glacial lakes and, 2) thaw lakes. Glacial lakes are formed in the foothills and upper reaches of the Brooks Range close to the source of the glacier. These are few in numbers and are mostly located in the southern regions.

Thaw lakes, quite common and numerous are formed by the pooling of melted snow and ice in shallow depressions, augmented during summer by the thaw from underlying permafrost. Summer thaw over long period widens and deepens the lake.

During winter water supply can be drawn from unfrozen alluvium located beneath deeper lakes and deep meander pools along the channels of the major rivers, commonly known as thaw-bulb. Near the coast thaw-bulb may contain brackish and saline water, inland the water quality is generally good. The year round availability of potable water from thaw-bulb have been evaluated, however, overall quantity and reliability of the fresh water supply in the North Slope region has not been fully explored. Black (1955) reported large quanitites of ground water on the Arctic Slope in deep lakes, major perennial streams, and in hot spring areas. He noted that permafrost surface is significantly lower or even absent under major rivers which flow throughout winter and have flood plains extending over hundreds of meters. The thickness of alluvium containing sandy gravel of varying thickness, generally between few meters and 10's meters.

The alluvium aquifers underlying river generally have better quality water and greater storage potential than those underlying lakes because rivers recharge their acquifers during flow period. Lakes on the otherhand at surface freeze to a depth of 2-3 meter and thus transfer inpurities to the underlying unfrozen bottom water.

The winter storage capacity of some thaw-bulb can be increased by pumping freshwater during thaw period. The storage will depend on the extent of the reservoir, rock type and flow characteristic including porosity, permeability and geothermal gradient.

4. Geothermal Gradient Data for Alaska's North Slope (ANS)

The northern part of the North Slope is mostly covered by thaw lakes and ponds.

The area is also drained by numerous rivers and their tributaries. The remainder of the areas have a thin cover of unconsolidated thin veneer of sediments with or without vegetation cover typical of Arctic tundra. Beneath these surface geomorphic features is a thick layer of permafrost. The nature of the permafrost is dependent on the lithology and the texture of the rock.

At shallow depths the geothermal gradient in the Arctic is influenced primarily by the following:

1. Actual temperature of the ground surface
2. Presence of surface water, i.e. thawed lakes, ponds and river beds
3. Presence of tundra and their vegetation cover
4. Texture and lithology of the substrate

The thickness of the underlying permafrost is to some extent dependent on the geothermal gradient, therefore, the depth of the permafrost in the Arctic varies according to the prevailing surface conditions.

During World War II the increased construction of roads and buildings in the Arctic necessitated a need for the study of characteristics and behavior of perennial frozen soil and ground. Thus, a great interest was evolved in measurements of the geothermal gradients in the Arctic. Later activities prior to and subsequent to the development of the vast fossil energy and mineral resources further intensified the investigation and measurement of the geothermal gradients throughout Alaska.

The early investigations and measurements of the geothermal gradients in the Arctic were conducted by MacCarthy (1952). Measurements near Barrow indicated that the seasonal surface variations in temperature could lower the subsurface temperatures to a maximum of $-10^{o}C$. He further noticed that the $0^{o}C$ isotherm varied between the depths 670 and 1,300 feet. In general, increasing in depth with increasing distance from the nearest large body of water. The depth of $0^{0}C$ isotherm also defines the depth of the permafrost in this region.

Brewer (1958) published thermal data collected over a period of six years. Most importantly he identified the problems related to the temperature and distribution of permafrost in the Arctic. He confirmed earlier observations by MacCarthy that the lowest subsurface temperature reached to -10.6°C and effect of seasonal variations was limited to depth varying between 70 and 100 feet. The variations in shallow thermal gradients due to seasonal variations depended on the surface temperature, snow cover, soil moisture content and other physical properties.

The investigations of Brewer (1958) also revealed the Arctic lakes with diameter of approximately one-half mile or more and with depth of seven feet or more remained unfrozen at the bottom during winters.

5. North Slope Bibliography

Topic: Permafrost

Chamberlain, Edwin J., Sellmann, P.V., Hopkins, D.M., and Lewellen, R.I., 1978, "Engineering Properties of Subsea Permafrost in the Prudhoe Bay Region of the Beaufort Sea", Third International Conference on Permafrost, Edmonton, Alberta, Canada, 10-13 July 1978, pp 629-635, CRREL, U.S. Army Corps of Engineers, Hanover, New Hampshire

Ferrians, Oscar J. Jr., Kachadorian, Reuben, and Grene, W. Gordon, 1969, "Permafrost and Related Engineering Problems in Alaska", Geological Survey Professional Paper 678, pp 1-37, U.S. Dept. of the Interior, Reston, Virginia

Philainen, J.A. and Johnston, G.H., 1963, "Guide to a Field Description of Permafrost for Engineering Purposes", National Research Council, Ottawa, Canada, Associate Committee on Soil and Snow Mechanics, Technical Memorandum 79

Pewe, L. Troy, 1966, "Permafrost and Its Effects on Life in North" p 40, Orego State University Press, Corvallis, Oregon

Black, F. Robert, 1957, "Some Problems in Engineering Geology Caused by Permafrost in the Arctic Coastal Plain, Northern Alaska", Arctic Vol. No. 7, pp 230-240, Study Sponsored by U.S. Geological Survey

Stewart, J.M. and Weaver, J.S., 1983, "Permafrost and Hydrates Under the Beaufort Sea", Society of Professional Well Loggers Association, 24th Annual Logging Symposium, pp 1-18, June 27-30, 1983.

Topic: Ground Water Availability

Anderson, Dwayne, M., 1970, "Phase Boundary Water in Frozen Soil", pp 1-17, CRREL Res. Rept 274

Barnes, P., Reimntz, D.D., and Toimil, L., 1977, "Miscellaneous Hydrologic and Geologic Observations on the Interior Beaufort Sea Shelf, Alaska", Open File Report 77-477, pp A1-A19, U.S. Dept. of the Interior Geological Survey, Rouston, Va.

Hopkins, David M., Karlstorm, N.V., and others, 1955, "Permafrost and Ground Water in Alaska", pp 113-146, Geological Survey Professional Paper 264 - Fus Dept. of the Interior, Reston, Virginia

Ward, Dennis L., and Peterson, L.A., 1970, "A Summary of Water Use Problems Related to North Slope Petroleum Development", Proceedings of the 27th Alaskan Conference, pp 53-57, University of Alaska, Fairbanks, Alaska

Williams, John R., 1965, "Ground Water in Permafrost Regions - An Annotated Bibliography", pp 1-37, Geological Survey Water Supply Paper - 1792, U.S. Department of Interior, Reston, Va.

Williams, John R., 1970, "Ground Water in Permafrost Regions of Alaska", Geological Survey Professional Paper 696, pp 1-83, U.S. Dept. of Interior, Reston, Va.

Water Resources Division, Alaska District, 1969, Open File Report, "Water Resources of Arctic Slope Region, Alaska", U.S. Dept. of the Interior Geological Survey, Reston, Va.

Williams, John R., "A Review of Water Resources of the Umiat Area, Northern Alaska", Geological Survey Circular 636, U.S. Dept. of the Interior, Reston, Va.

Topic: Geology

Ahlbrandt, T.S., 1979, "Introduction to Geological Studies of the Nanushuk Group, North Alaska", U.S. Geological Survey Circular 794, pp 1-4

Barnes, P., Reimnitdz, E., Maurer, D., and McDowell, David, 1979, "Core Description and Preliminary Observation of Vibracores From the Alaskan Beaufort Sea Shelf", U.S. Geological Survey, Reston, Va.

Bird, K.J., and Andrews, J., 1979, "Subsurface Studies of the Nanushuk Group, North Slope, Alaska", U.S. Geological Survey Circular 794, pp 32-41, Tetra Tech Inc., Houston, Texas

Black, R.F., 1969, "Geology Especially Geomorphology of Northern Alaska", Dept. of Geology, pp 283-299, University of Wisconsin, Madison

Carman, J.G., and Hardwick, P., 1983, "Geology and Regional Setting of Kuparuk Oil Field, Alaska", AAPG Bulletin, pp 1014-1031

Collins, F.R., 1961, "Core Tests and Test Wells, Barrow Area, Alaska", Geological Survey Professional Paper 305-k, pp 596-640, U.S. Dept. of Interior, Reston, Va.

Davidson, D.T., Roy, C.J., and Associates, 1959, "The Geology and Engineering Characteristics of Some Alaskan Soils", The Iowa State University Bulletin, Vol. LVIII, No. 29, pp 131-149

Grantz, A. and Dinter, D.A., 1980, "Constraints of the Geologic Processes on Western Beaufort Sea Oil Development", Oil and Gas Journal, May 1980, pp 304-318

Grantz, A., Barnes, P.W., Dinter, D.A., Lynch, M.B., Reimnitz, E., and Scott, E.W., 1980, "Geologic Framework, Hydrocarbon Potential, Environmental Conditions and Anticipated Technology for Exploration and Development of the Beaufort Shelf, North of Alaska", U.S. Dept. of Interior, Possible Oil and Gas Lease Sale No. 71, Open File Report 80-94, Menlopark, California

Fox, James E., 1979, "A Summary of Reservoir Characteristics of the Nanushuk Group, Umiat Test Well No. 11, National Petroleum Reserve in Alaska", U.S. Geological Survey Circular 794, pp 42-52.

Kunze, J.F. and Lofgren, B.E., 1983, "Pilgrim Springs, Alaska Geothermal Resource Exploration, Drilling and Testing", Geothermal Resources Council Trans., Vol. 7, pp 301-304

Plafker, G. and Jones, D.L., 1982, "Geology and Tectonic Evolution of Alaska", Prospective in Regional Geological Synthesis, Edited by A.R. Palmer, pp 77-80

Reed, J.C. Sr., "U.S. Geological Resource Symposium - Abstracts with Program", National Science Foundation, Division of Polar Program, Washington, D.C.

Walker, J.H., 1974, "The Colville River and the Beaufort Sea: Some Interactions", Proceedings of a Symposium on Beaufort Sea Coast and Shelf Research, Edited and Published by Reed, J.C. and Sater, J.E., 1974, in "The Coast and Shelf of the Beaufort Sea", pp 513-539.

Robinson, F.M., 1958, "Test Well Gubik Area, Alaska", Geological Survey, Professional Paper 305-C, pp 207-261, U.S. Dept. of the Interior, Reston, Va.

Robinson, F.M. and Bergquist, H.R., 1956, "Core Tests and Test Wells Oumalik Area, Alaska", pp 1-7, Geological Survey Professional Paper 305-A, U.S. Dept. of the Interior, Reston, Va.

Robinson, F.M., 1958, "Test Well Grandstand Area, Alaska", Geological Survey Professional Paper 305-E, pp 317-338, U.S. Dept. of Interior, Reston, Va.

Satare, J.E., 1963, "The Arctic Basin", Tidewater Publishing Corp., Centerville, Md.

Wescott, E.M., Turner, D.L., and Backy, P., 1982, "A Geophysical Study of Hot Springs Bay Valley, Akutan Island, Alaska", Geothermal Resources Council, Trans., Vol. 6, pp 158-188

Topic: Electromagnetic Survey

Sellman, P.V., Hoekstra, P., and Delandy, A., 1974, "Electrical Resistivity Measurements at Alaska Pipeline Pump Stations 1 Through 5", Internal Report, pp 1-30

Stokes, W.P., 1971, "North Slope Construction Criteria for Roads and Facilities", JPT, pp 1209-1214

Topic: Geothermal Gradient

Brewer, M.C., 1958, "Some Results of Geothermal Investigations of Permafrost in Northern Alaska", Trans. American Geothermal Union, Vol. 39, No. 1, pp 19-26

Brown, W.G., 1982, "Simple Graphical Methods for Estimating the Location of Permafrost Under Shallow Lakes and Rivers", Proceedings of Canadian Conference on Permafrost, pp 226-231.

Isselhard, C.F., Motyka, R., Matlick, J.S., Parmentier, P.P., and Hutter, C.W., 1983, "Geothermal Resource Model for the Makushin Geothermal Area", Trans. Vol. 7, pp 99-102

MacCarthy, G.R., 1953, "Geothermal Investigations on the Arctic Slope of Alaska", Trans. American Geophysical Union, Vol. 33, No. 4, pp 500-505

Wescott, E.M. and Truner, D.L., 1983, "Geothermal Resource Exploration of the Eastern Copper River Basin, Alaska", Geothermal Resources Council, Trans. Vol. 7, pp 211-213

Topics: Remote Sensing

Baggeroer, A.B., and Duckworth, G.L., 1982, "Seismic Structure Modeling in the Arctic Ocean", IEEE, pp 178-186

Gaydos, L. and Witmer, R.E., "Mapping of Arctic Land Cover Utilizing Ladstat Digital Data", U.S. Geological Survey, Ames Research Center, California, pp 343-346

Metz, P.A., Egan, A., and Johansen, N., "Landsat Linear Features M Model for the Origin of Base Metal and Petroleum Resources of Northern Alaska", Mineral Research Laboratory, UAF, Fairbanks, Alaska, pp 102-112

Pearson, C., Murphy, J., Halleck, P., Herms, R., and Matthews, M., "Sonic and Resistivity Measurements on Berea Sandstone Containing Tetrahydrofuran Hydrates - A Possible Analog to Natural Gas Hydrate Deposits", Earth and Science Division, Los Alamos Laboratory, New Mexico, pp 972-978

Taranik, J.V., 1978, "Principles of Computer Processing of Landsat Data for Geological Applications", U.S. Department of Geological Survey Open File Report 78-117, pp 1-50

Zall, L. and Michael, R., 1980, "Space Remote Sensing Systems and Their Applications to Engineering Geology", Bulletin of the Association of Engineering Geologists, Vol. XII, No. 3, pp 101-152

Topics: Miscellaneous

Gedney, L., Biswas, N., Huang, P., and Pearson, C., 1977, "Seismicity of Northeast Alaska", Geophysical Research Letters (A.G.P.), pp 175-177

Greenwood, J.K. and Murphy, R.S., 1972, "Factors Affecting Water Management on the North Slope of Alaska", Institute of Water Resources, Report No. IWR19, University of Alaska, Fairbanks, Alaska

Lantz, R.J., 1981, "Barrow Gas Fields - North Slope, Alaska", Oil and Gas Journal, March 1981, pp 197-200

McCart, P.J., 1974, "Fisheries Research Associated with Proposed Gas Pipeline Route in Alaska, Yukon, and Northwest Territories", Biological Report Series, Vol. 15, Aquatic Environments Limited, pp 1-35

Mellore, M., 1978, "Undersea Pipelines and Cable in Polar Waters", CRREL, Report 78-22, pp 1-27, U.S. Army Corps Eng., Hanover, New Hampshire

Neel, T.H., 1977, "Both Onshore and Offshore Alaska Holds Vast Exploration Potential", Oil and Gas Journal, June 1977, pp 198-200

SECTION II

REVIEW OF GAS HYDRATE LITERATURE, CURRENT RESEARCH AND STATE-OF-THE-ART TECHNOLOGY

Prepared By

S.P. Godbole
V.A. Kamath

Petroleum Development Laboratory
437 Duckering
University of Alaska Fairbanks
Fairbanks, Alaska 99775-1260

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ABSTRACT

Natural gas hydrates occurring beneath permafrost regions of the world, are gaining increasing importance in view of their enormous potential as a source of natural gas. The review evaluates the present state-of-the-art in gas hydrate literature. Various aspects of hydrate-related studies including occurrence, detection, kinetics, thermodynamics, and phase equilibrium are discussed. Finally, an attempt has been made to point out the inadequacies in areas of practical importance and recommendations for future work are outlined.

SCOPE

Solid ice-like mixtures of natural gas and water in the form of natural gas hydrates have been found immobilized in the rocks beneath the permafrost in Arctic basins and in muds under the deep water along the American continental margins, in the North Sea and several other locations around the world. It is estimated that the arctic areas of the United States may contain as much as 500 trillion SCF of natural gas in the form of gas hydrates (Lewin and Associates, 1983). While the U.S. Arctic gas hydrate resources may have enormous potential and represent long term future source of natural gas, the recovery of this resource from reservoir "frozen" with gas hydrates has not been commercialized yet. Continuing study and research is essential to develop technologies which will enable a detailed characterization and assessment of this alternative natural gas resource, so that development of cost effective extraction technology. This study presents a state-of-the-art review of the various aspects related to gas hydrates. Reviews on gas hydrates have been published earlier by Byk and Fomina (1968) and Makogen (1981). Since then, many articles have been published on different aspects of gas hydrates. An attempt has been made in this review to provide a more complete and up-to-date information of gas hydrate literature.

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1. *INTRODUCTION*

In regions, such as northern Alaska, where low temperatures persist far below the earth's surface, natural gases combine with water to form solids known as natural gas hydrates. Hydrate deposits are also found (Kvenvolden and McMenamin, 1980) in other regions of the world where conditions are thermodynamically favorable for their existence. Gas hydrates are nonstoichiometric, crystalline, ice-like solids formed due to encagement of gas molecules in the interstices of hydrogen bonded water lattices and have a composition of approximately 85 mole % water and 15 mole % of natural gas. They contain approximately 170-180 SCF of natural gas per cubic foot of hydrate and hence represent an attractive source of gas, provided that the gas can be economically recovered. Because of the relatively immobile and impermeable nature of the gas hydrates, they have to be dissociated to gas and water in order to produce natural gas from hydrate reservoirs.

Gas hydrates represent a concentrated form of natural gas and thus an attractive potential energy resource for the future. Enormous quantities of natural gas is estimated to occur in the world in the form of gas hydrates, though the estimated values vary widely ($1.4 \times 10^{13} m^3$ to $7.6 \times 10^{18} m^3$). (Meyer, 1979, Dobrynin, et al, 1979, McIver, 1979). Because of this potential resource, the production of natural gas from these naturally occurring hydrate zones and the problems associated with the production are becoming increasingly important. The possibility of production of natural gas from the hydrate zones has been proposed and preliminary work on modelling the production techniques has been done. There, however, remains a vast amount of information regarding the in situ nature of hydrates, their physical, kinetic and transport properties, that is unknown.

2. NATURE OF GAS HYDRATES:

Gas hydrates are crystalline, ice-like solids wherein the gas molecules are encaged in the interstices of the hydrogen bonded water lattices. The first published study of hydrates of gases goes back to 1810, when the English chemist, Sir Humphrey Davy, formed chlorine hydrates in his laboratory (Faraday, 1823). These studies indicated that hydrates are non stoichiometric compounds and the number of gas molecules per water molecule in the hydrate phase depend upon the conditions under which they were formed. Much of the early work in the late nineteenth century and the start of the twentieth century, on hydrates of methane, ethane, carbon-di-oxide by Faraday, Villard, deForcrand and others has been reviewed by Schroeder (1927).

The study of gas hydrates at the beginning of the twentieth century did not have any direct industrial application until the beginning of the 1930's when Hammerschmidt (1934) first reported that the plugging of natural gas pipelines was caused by hydrates. With the rapid development of gas-producing industries, subsequently, efforts were made to study hydrate forming conditions of different gases and to develop methods of preventing their formation and accumulation in gas pipelines and in wells drilled for gas production.

During the last half century, numerous experimental and theoretical studies have been carried out on measurement of pressure, temperature, and composition conditions for hydrate formation. Interest in gas hydrate research has been renewed, primarily due to the recent discovery of in situ natural gas hydrates in cold regions, such as Alaska, Canada's Northwest Territory, and in deep ocean sediments. (Stoll et al, 1971; Hand et al, 1974; Holder et al, 1976; Holder et al, 1980; Godbole et al, 1986).

3. STRUCTURE OF HYDRATES

Gas hydrates are nonstoichiometric crystalline compounds wherein the gas molecules are encaged in the interstices of the hydrogen bonded water lattices. They belong to a class of inclusion compounds called clathrates (Brown, 1962) which are nothing but chemical compounds wherein one component fits into a cavity in another component without any chemical bonding between them. In case of gas hydrates, the interaction between gas and water molecules is purely physical in nature and as such, the gas molecules are not part of the lattice framework. The gas provides stability to the hydrate phase, since, in absence of gas, no water lattice is formed.

The first attempt to investigate the structure of hydrates was made by Nikitin (1936) who suggested that gas hydrates are nonstoichiometric inclusion compounds, called "clathrates," made up of a metastable "host" crystal lattice of water molecules within which the "guest" gas molecules are held by van der waal forces. Claussen (1951), Pauling and Marshal (1952), and von Stackelberg and Muller (1954) employed x-ray diffraction techniques to study the structure of hydrates and showed that gas hydrates crystallise in either of the two structures called I and II. The water molecules forming the crystal lattice interact among each other through hydrogen bonds whereas they interact with the "guest" gas molecules through weak van der waal forces. The crystalline structure formed by water lattice is composed of cavities of different sizes, and for producing a stable hydrate, only one-third of the cavity has to be occupied by gas molecules.

Structure I unit cell is made up of 46 water molecules, with 2 small and 6 large cavities of 5.1°A and 5.8°A average free diameter respectively whereas structure II consists of 136 water molecules, with 16 small and 8 large cavities of 5°A and 6.7°A average free diameter respectively. The small cavities of structure I are regular pentagonal tetrahedra whereas the tetrakaidecahedral large cavities consists of twelve pentagonal sides and two opposite hexagonal sides and are surrounded by twenty four water molecules. The cavity sizes are more equal in structure II, which is formed only when the "guest" gas molecules are too large to fit in cavities of structure I. Thus, e.g., propane, which has an average free diameter greater than 5.8°A, does not form structure I hydrate and can only form structure II hydrate. The smaller cavities of structure II are pentagonal dodecahedra and are slightly deformed with a mean free diameter of 5°A. On the other hand, the larger cavities of structure II are nearly spherical and are hexadecahedral. Table 1 gives the hydrate latice properties of both the structures. Figures 1 and 2 give molecular arrangement of structures I and II.

Whether structure I or structure II hydrate is formed depends upon gas composition, molecular size and temperature of the system. In general, biogenic gases form structure I, due to smaller molecules, whereas thermogenic gases usually form structure II, with molecules larger than ethane. A hydrate is formed when the lattice has been occupied by sufficient number of molecules to result in a stable structure. The hydrate number is defined as the ratio of number of water molecules to number of gas molecules in the hydrate phase. Different values of n are possible due to the presence of unoccupied cavities at thermodynamic equilibrium. The minimum value of n for structure I is 5.75 when all the cavities are occupied and 7.66 when only the large cavities are occupied. The corresponding values for structure II are 5.67 and 17 respectively. Thus, isobutane, which can only fit into the larger cavities of structure II, should have hydrate number greater than or equal to 17. Table 2 gives the hydrate numbers for different gases.

As pointed above, the hydrate crystals can be stabilized even if the gas molecules partially occupy the available cavities in structure I or II. However, small molecules like methane cannot stablize structure II and even structure I cannot be formed by pure hydrogen. This is because the energy of stabilization results from van der Waal type forces, which are a function of the polarazeability of molecules, and hence small molecules interact weakly with the lattice. Also, as these forces are proportional to $(1/\gamma 6)$, where γ is the average separation between the guest and lattice walls, the empty water lattice cannot be sufficiently stabilized by small molecules in large cavities of structure I and II. However, Barrer and Ruzicka (1962) showed that in presence of other hydrate formers capable of stabilizing the structures, it is possible for methane and even hydrogen molecules to occupy the smaller cavities of structure II.

In addition, Barrer and Edge (1967) and Ceccotti (1966) suggested that, apart from structures I and II, hydrates can also form other structures. Allen (1963) has substantiated this claim by showing that bromine hydrate can have a different structure with 172 water molecules and containing 20 cavities per hydrate crystal.

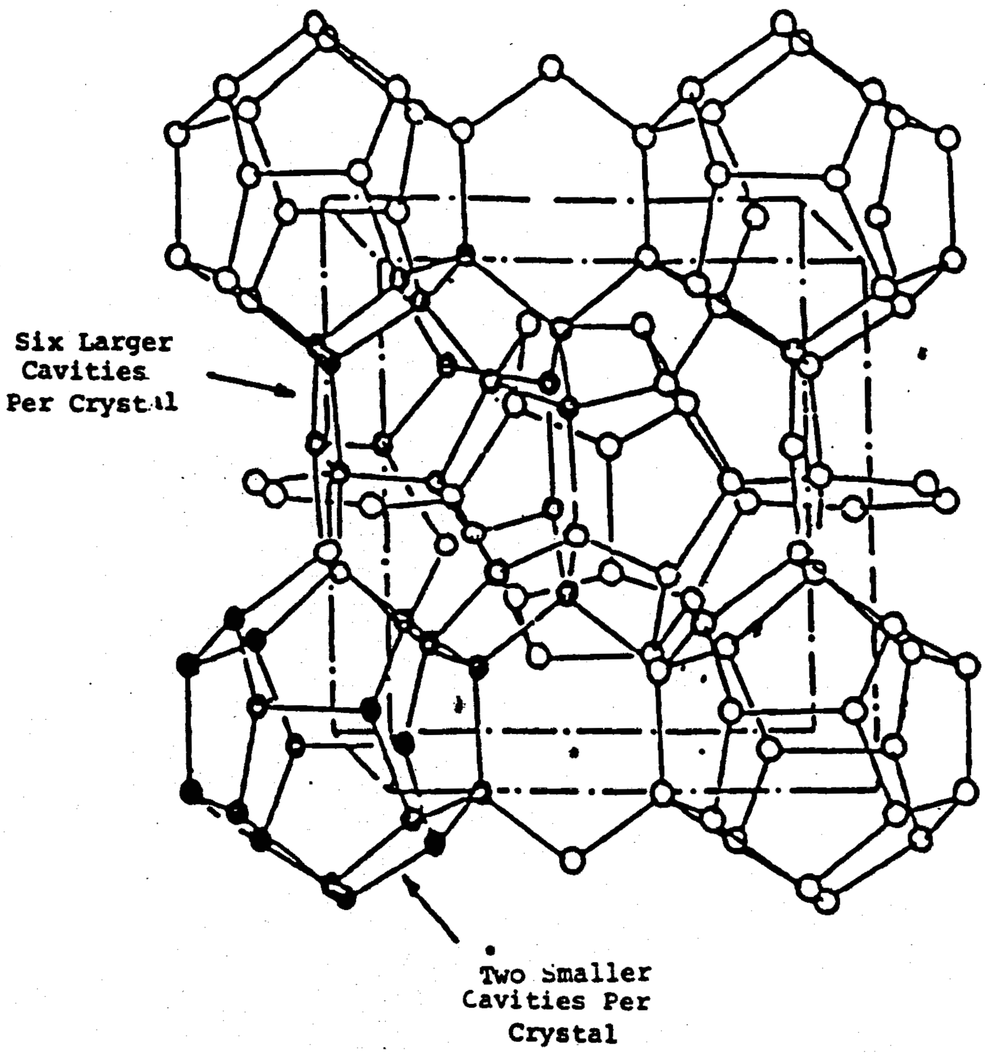


FIGURE 1: STRUCTURE I HYDRATE REPRESENTATION

(AFTER KAMATH, (1982)

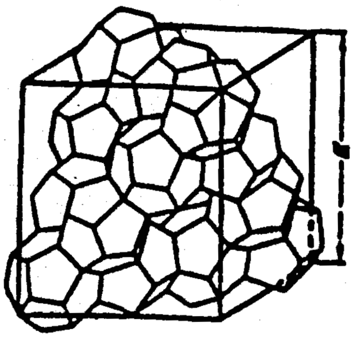


FIGURE 2: STRUCTURE II HYDRATE REPRESENTATION

(AFTER MAKOGEN)

TABLE 1: PROPERTIES OF HYDRATE LATTICE

(After Kamath (1984))

	Small Cavities	Large Cavities	Small Cavities	Large Cavities
Cavities per Unit Cell	2	6	16	8
Cavity Radius, °A	3.95	4.30	3.91	4.73
Co-ordination Number	20	24	20	28
Cavities Per Molecule	1/23	3/23	2/17	1/17

	Structure I	**Structure II**
1) Number of Water Molecules per Unit Cell	46	136
2) Typical Examples	CH_4, C_2H_6, Ar, Kr	C_3H_8, C_3H_6, i-butane, cyclo-propane

TABLE 2: HYDRATE NUMBERS FOR DIFFERENT GASES

Gas	Hydrate No. Experimental	Hydrate No. Theoritical	Reference
1) Methane	6.0		de Forcrand (1902)
	6.0		Hammerschmidt (1934)
	7.0	5.75	Roberts et al (1940)
	5.8-6.3		Kobayashi et al (1976)
	6.15		Kamath (1984)
2) Ethane	7.0		de Forcrand (1902)
	6.0		Hammerschmidt (1934)
	7.0		Roberts et al (1940)
	8.3	7.66	Deaton and Frost (1946)
	7.9-8.5		Kobayashi et al (1976)
	8.0		Kamath (1984)
3) Propane	7.0		Hammerschmidt (1934)
	18.0		Deaton and Frost (1946)
	6.0	17	Miller and Strong (1969)
	19.6-19.8		Ceccotti (1966)
	18.0		Kamath (1984)
4) i-butane	18		Schneider and Farar (1968)
	17.5	17	Rouher and Barduhn (1969)
	15-17		Godbole (1981)
5) Carbon Dioxide	6.0		Villard (1888)
	6.0	7.66	de Forcrand (1902)
	7.0		Deaton and Frost (1946)
	7.2		Kamath (1984)

4. OCCURRENCE OF HYDRATES

The widespread existence of in-situ gas hydrates in nature and their potential as an alternate resource of energy and an attractive resource of natural gas in the future has rekindled interest in gas hydrates in the petroleum industry and among researchers.

One of the earliest discoveries of in situ gas hydrates was in the mid-1960's when huge deposits of natural gas hydrates were found to occur in sediments below permafrost in Siberia in USSR. (Cherski and Makogen, 1970). Subsequently, significant quantities of naturally occurring hydrates on land have been discovered primarily in permafrost regions of the earth where low temperatures are favorable for hydrate production. Some of the regions of best potential where in-situ natural gas hydrates have been detected include the North Slope of Alaska, the McKenzie Delta of Canada, and the Western Siberian Basins of U.S.S.R., including Messoyakha Field. Figure 3 shows the potential regions of hydrate existence on the U.S. land and waters.

Onshore Hydrate Occurences:

Gas Hydrates in the Arctic

As mentioned before, the presence of naturally occurring gas hydrates has been established in the Arctic areas of Alaska, Canada, and USSR in the subsurface permafrost zones of hydrate stability. More than 23% of the earth's land mass is covered by permafrost (permanently frozen ground) and is mainly confined to Alaska (75% of the total area), Canada (63%), USSR (47%), polar regions of Scandinavia, Greenland and Antartica (Handbook of Gas Hydrates, 1983).

Katz (1972) suggested that natural gas dissolved in crude oil could form hydrates with water phase in absence of gas phase. The sandstone reservoir of the Messoyokha field in the Soviet Union is the largest known onshore field where gas

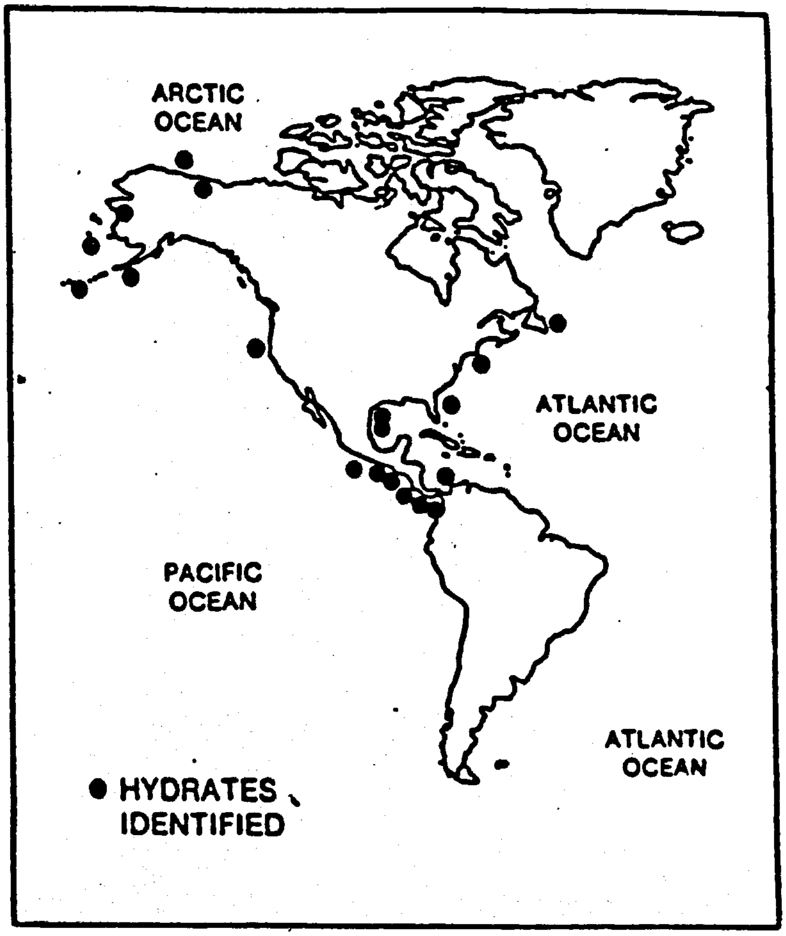


FIGURE 3: POTENTIAL REGIONS OF HYDRATE OCCURRENCE IN U.S. LAND AND WATERS

hydrates occur at a depth of 800 ft. and the reserves are estimated to be 1 billion cubic metres. In Prudhoe Bay, Alaska, hydrates can exist to depths even beyond 1200m, since the depth of permafrost itself is 700m. (Katz 1971, 1972). In fact, a crude oil was found at 1200m denuded of its lighter paraffinic components which might be explained by formation of hydrates.

Natural Gas Hydrates in the Alaskan Arctic

The interest in gas hydrates in the Alaskan Arctic was first stimulated by the discovery of huge oil and natural gas resources on the North Slope of Alaska. Katz (1971) indicated that gas hydrates can be stable up to depths of 1,200 meters on the North Slope of Alaska. On March 15, 1972, ARCO and EXXON provided the first confirmed evidence of the presence of gas hydrates in Alaska when they recovered gas hydrate core samples in pressurized core samples at several depths between 577 and 776 meters from the Northwest Eileen #2 well in the Prudhoe Bay field (Kvenvolden et al, 1980). Collett (1983) and Collett and Economides (1983) examined one hundred and twenty-five wells in the North Slope of Alaska and identified one hundred and two definite hydrate occurrences in thirty-two different wells. Godbole and Economides (1985) examined thirty-four wells in Alaska and indicated that in fourteen wells there is a possibility of hydrate occurrence. Kamath et al (1986) examined forty-six wells and showed that in ten wells gas hydrate deposits may be found.

According to Collett et al (1984), the estimated amount of natural gas trapped within gas hydrates in the Kupurak field is about 5.3 x 10^{10} ft^3 per square mile (579 x 10^6 m3 per square kilometer). They used the Pickett cross plotting technique along with corrected neutron porosity and sonic porosity values to determine depth, thickness, porosity and saturation of in-situ gas hydrates. Recently, Mathews (1986) described the logging characteristics of gas hydrates in the Northwest Eileen Well

#2 and estimated the amount of natural gas trapped within hydrates to be about 1.75×10^{10} - 3.77×10^{10} ft^3 per square mile (192×10^6 - 412×10^6 per square kilometer).

Offshore Hydrate Occurences :

As far as offshore areas are concerned, hydrates have been found to occur naturally mainly in the margins of the outer continental shelf, and have been defected by drilling and seismic profiling of depths of more than 450m. Stoll et al (1971) suggested that gases coming out from ocean sediments cores must be due to hydrate dissociation to gas at atmostpheric pressure. Some of the offshore areas where hydrates have been found include the Beaufort Sea shelf, the Blake Bahama outer ridge on the east coast of United States, the Mid-American Trench, the west coast of Gautemala, the Gulf of Mexico, and Pacific Ocean off West U.S. coast (Halleck et al, 1982).

The presence of hydrates in the Blake Bahama outer ridge was further confirmed when the Glomar Challenger encountered marine sediments of high gas content, which showed high seismic velocities (Mollister et al, 1972) and anomaloussonic reflectors. Such a reflector, called the Bottom Simulating Reflector, was first noted Blake Bahama Outer ridge of the North Atlantic (Marks et al, 1970, Ewing and Hollister, 1972) and were subsequently also found in the North Pacific (Scholl and Creager, 1973). Table 3 gives a summary of the occurrence of gas hydrates in the world.

Estimated Reserves of Hydrates

It has been estimated that the in situ hydrate resources of U.S. may vary from 1 to 25,000 TCF for onshore deposits and from 2700 to 6,700,000 TCF for offshore deposits (McIver 1974, Meyer 1976).

Table 4 gives the estimated reserves of gas in the form of hydrates, both U.S. and worldwide. These figures for estimation of reserves of gas vary widely due to lack of sufficient data.

TABLE 3: SUMMARY OF GAS HYDRATE OCCURRENCES IN THE WORLD

Region	Reference
1) a) North Slope, Alaska b) Norton Sound, Alaska	Jamison et al (1980) Godbole et al (1987) Kvenvolden et al (1980)
2) Messoyakha Gas Field, USSR	Sapir et al (1973) Makogen (1965)
3) Beaufort Sea	Stewart et al (1983) Weaver et al (1982)
4) McKenzie Delta	Bily and Dick (1976)
5) Arctic Islands	Stuart-Smith et al (1976) Franklin (1981) Trofmuk (1977)
6) Middle American Trench	Brooks et al (1983) Hesse et al
7) Bering Sea	Cooper (1979)
8) Northern Canada	Davidson (1978)
9) Northern California Continental Margin	Field and Kvenvolden (1985)
10)Offshore Region of Gautemala	Geotimes (1982)
11)Southeast U.S.	Dillon (1980)
12)Cormorant South Subsea Oil Well	deBoer (1983)
13)a) Volcanic occurences b) Marine sediments	Gaffney (1981) Kaplan (1974) Milton (1976)

TABLE 4: ESTIMATED RESERVES OF GAS IN HYDRATE FORM

	World On-shore	World Off-shore	U.S. On-shore	U.S. Off-shore
Dobyrynin (1979)	$2.8 \times 10^{16} m^3$	7.6×10^{18}	$7.1 \times 10^{16} m^3$	$1.9 \times 10^{17} m^3$
Meyer (1979)	$1.4 \times 10^{13} m^3$	---	$3.1 \times 10^{11} m^3$	---
McIver (1979)	---	$3.1 \times 10^{15} m^3$	---	7.6×10^{13}
Trofimuk (1977)				

5. *KINETICS OF HYDRATE FORMATION*

Although several studies have been made, since the beginning of the present century to measure temperature and pressure conditions at which formation of gas hydrates begins, there has been little effort on the part of investigators to study kinetics and mechanism of hydrate formation. Thus, since the gas-water or gas-ice interfacial surface area could not be characterized satisfactorily, the specific hydrate formation rate could not be measured. Also the heat evolved due to the exothermic nature of hydrate formation at the interface, imposed additional limitations.

Thus the kinetic studies of gas hydrates can be classified into two main categories:

a. Hydrate Formation from Water; and

b. Hydrate Formation from Ice Crystals.

a. *Hydrate Formation from Water*

The first attempt to study the steady state kinetics of gas hydrate formation from water was done by Knox et al (1961), who investigated the kinetcis of propane hydrate formation in a bench scale water desalination unit. They combined liquefied propane (which forms structure II) with artificial water in a 10 gallon CSTR operating at 47 psig and 35°F. Their study indicated that with increase in stirrer speed and thermal driving force, the rate of nucleation and hydrate growth increases, resulting in higher yield but produces smaller crystals. Hence, while separating the hydrate crystals from the brine solution, it is difficult to completely remove the entrapped water molecules within the solid hydrate mass.

In 1965, Pinder studied the kinetics of formation of tetrahdrofuran (THF) hydrate (structure II) at -0.5°C in a stirred batch reactor from various THF-water mixtures and employed refractive index measurements to monitor concentration changes in the solution. In this case, since THF is water soluable, the question of a gas-liquid or liquid-liquid interface did not arise. It was found that the rate is directly proportional to concentration driving force and increases with stirrer speed. It was proposed that diffusion of reactant species between hydrogen-bonded, THF-water association complexes might be a plausible explanation of the mechanism of hydrate formation.

The majority of the studies on hydrate formation have employed dynamic conditions, where the gas-water contact surface is created by techniques like mixing, bubbling of gas through water, mechanical agitation, etc. and which results in the formation of an amorphous mass. In contrast to this, Makagon et al (1981) have studied the nucleation and growth kinetics of hydrates of natural gas under isothermal quiescent conditions. It was found that the first step in the hydrate formation process is nucleation of hydrate crystals and it invariably occurred on an interface (e.g., gas-liquid, liquid-liquid, or solid-liquid). Thus the metal walls of the experimental setup can adsorb gas molecules either from the gas phase or in solution, providing good nucleation sites. Usually hydrate nuclei are formed on the gas-water interface. In presence of crystallization nuclei, initially the crystals grow at high rates till they cover the entire surface of gas-water contact (surface-film hydrate). Subsequently, the growth of hydrate crystals takes place within gas, water or ice phases by volume diffusion mechanism, and is limited by the rate at which the hydrate forming species (probably water) diffuses to the hydrate crystal growth surface. However, the exact mechanism of hydrate formation is not yet clearly understood.

The most important factors that affect the rate of hydrate formation are the composition of parent gas, the thermodynamic conditions, and the type of crystallization. The first step in hydrate formation is the formation of crystallization nuclei on the free water surface, and is followed by the diffusion of gas from the gas stream either to the hydrate formation surface or through the hydrate formed on the surface of gas-water contact. The size of hydrate film formed in time T depends upon the rate of formation of nuclei I and the radial growth rate of the surface film hydrate V_T

$$F = \Pi V_T^2 I \tau \qquad \text{.................... (1)}$$

The water diffusion rate M_W through the hydrate film of uniform thickness h and with surface F is given by

$$M_W = D_W \frac{P \Delta f \rho_w}{h} \qquad \text{.................... (2)}$$

where

D_W = diffusivity of water through the hydrate film.

ρ_W = water density in the hydrate phase.

Δ_f = difference in volatality of water between water (ice) and hydrate phases.

The increase in hydrate film thickness with conversion of water or ice hydrate is given by

$$h = \left(\frac{2 D_W \Delta f}{h}\right)^{0.5} \tau \qquad \text{.................... (3)}$$

where

n = hydrate number.

τ = hydrate growth time.

For experimentally obtained diffusivities of 5×10^{-6} to 5×10^{-8} cm^2/sec for methane and 1×10^{-6} cm^2/sec for natural gas, this model gave good agreement for *volume* *diffusion* growth of natural gas hydrate films on a water surface. For experimentally obtained diffusivities of 5 x 10^{-6} to 5 x 10^{-8} cm^2/sec for methane and 1 x 10^{-6} cm^2/sec for natural gas, this model gave good agreement for *volume diffusion* growth of natural gas hydrate films on a water surface.

Maini and Bishnoi (1981) tried to simulate the fate of natural gas bubbles in case of a deep, offshore oil well blow-out by studying formation of hydrates in natural gas bubbles held stationary by downward water flow in a specially designed vertical tunnel. It was observed that hydrates form at the bubble interface at high pressures. However, the rate of conversion was not measured.

Recently, Vysniquskas and Bishnoi (1983, 1985) have studied the kinetics of methane and ethane formation after the start of nucleation in a semibatch stirred tank reactor under isothermal and isobaric conditions. To enable the agitation of the reaction interface by vigorous stirring of water, water was contacted with the gas at temperatures above the freezing point. It was found that though the induction delay time for formation of nuclei depended initially on the history of water sample, it did not affect the overall hydrate formation kinetics, once the nucleation commenced. After an initial induction delay, data was collected only until 5% of the available water was converted, since beyond 5% conversion, the gas-liquid interfacial characteristics were greatly affected by the thickening of water-hydrate slurry. It was found that Arrechenius Law could not be used to describe hydrate growth rate at a function of temperature since it gave a negative value of apparent activation energy, whereas for the activation complex to be unstable, the activation energy should be positive. The growth rate was proportional to the gas-liquid interfacial area and which increased with stirrer speed due to vortex formation.

To describe the gas consumption rate at STP, (r) as a function of gas-liquid interfacial area (a_g), pressure (p), temperature (T) and degree of subcooling (ΔT), they proposed a semi-empirical model and is given by

$$r = A\, a_s\, exp. \left(- \frac{\Delta E_a}{RT} \right) exp. \left(- \frac{a}{\Delta T^b} \right) p^{\gamma} \qquad \text{..................} \quad (4)$$

where

A = lumped pre-exponential factor.

ΔE_a = apparent energy of activation

R = gas constant

a,b = arbitrary constants

r = overall order w.r.t. pressure

Table 5 gives the best fit values obtained by Vysniquskas and Bishnoi (1983, 1985) of the rate expression parameters for methane and ethane.

b. *Hydrate Formation from Ice Crystals*

The first attempt to study hydrate formation from ice crystals was made by Barrer et al (1958, 1962, 1967) when they measured the hydrate formation rate of rare gases A_r, X_e, K_r with ice crystals and ice and chloroform-mixed crystals at low temperatures. They formed fine crystallites by vacuum distilling water and water -chloroform mixtures into the reaction bulb, which was kept immersed in liquid nitrogen. However, the results could not be generalized since surface area was not measured. The hydrate growth was found to increase with temperatures at constant pressure, which might be due to that certain low temperature ice phases exhibit unoccupied hydrate structure.

Fallabella (1975) used an analogous procedure to study the hydrate formation kinetics of natural gases (methane, ethane, ethene, acetylene and carbon dioxide) at low temperatures. Similar to krypton, an induction delay was observed for

TABLE 5: RATE EXPRESSION PARAMETERS FOR METHANE AND ETHANE

	Methane	Ethane
A (cm^3/cm^2/min/bar)	6.55×10^{-26}	2.4×10^{-29}
ΔE_a (kj/gmol)	-106.204	-133.015
r	2.986	2.804
a	0.0778	0.0778
b	2.411	2.411

structure I methane hydrate, whereas, addition of 10% ethane to it, showed no induction delay indicating that ethane has a seeding effect on hydrate nucleation. It was observed that an increase in gas pressure results in a decrease in the induction delay and increase in growth rate. The fractional ice conversion rate was found to be second order w.r.t. unconverted ice and first order w.r.t. the pressure driving force.

$$\therefore -\frac{d(1-x)}{dt} = k\left(1-x\right)^2\left(P-P_{eq.}\right) \qquad \text{.................. (5)}$$

This expression on integration for the case of isothermal, isobaric conditions gives

$$time\,t = \left(-\frac{1}{k}\right)\frac{x}{(1-x)} \bullet \frac{1}{P-P_{eq.}} \qquad \text{.................. (6)}$$

where

P = gas pressure.

$P_{eq.}$ = hydrate equilibrium pressure

k = rate constant

x = fractional conversion of ice.

Fallabella suggested that hydrate growth was primarily due to high surface mobility of ice at low temperature, since the ice sublimation rate was too slow to account for the growth rate of hydrates. Also, the rate constant vs. temperature relationship indicated a maxima at 183°K and so the Arrhenius type equation was invalid.

In 1970, Miller and Smythe formed hydrates from carbon dioxide gas and finely divided ice (prepared by grinding ice and condensing water from air, both at liquid nitrogen temperature of 78°K) under conditions similar to those existing at Martian ice caps (148°K, 6-5 mb CO_2 partial pressure). Under isothermal conditions, the reaction was found to be first order w.r.t. pressure, as given by:

$$t = \frac{1}{k} \bullet ln\left(\frac{P_o - P_\infty}{P - P_\infty}\right) \qquad \text{.................... (7)}$$

where

k = rate constant

P_o = initial CO_2 pressure

$P\infty$ = Final (equilibrium) CO_2 pressure

P = CO_2 pressure at any time t

Using Arγhenius type temperature dependence, the apparent activation energy for CO_2 hydrate formation was found to be 5.9 kcal/gmol which is in reasonable agreement with that observed for the low temperature phase transformation from hexagonal to cubic ice.

Kamath (1984) studied the kinetics of methane hydrate formation from compacted ice crystals formed by condensing water from air at about -20°C and compacting to about 50% porosity inside a vessel. The crystals were initially pressurized to methane pressures of about 7,000 kPa and the temperature raised to just above the melting point of 274°K. The drop in pressure with time was monitored to measure the rate of ice conversion and the experimental results obtained were correlated by two semi-empirical kinetic models. In the first *surface area* model, the rate of hydrate growth was assumed to be proportional to the surface area of ice and the methane concentration driving force.

$$\frac{dx}{dt} = \frac{k S_o V_R M_w n}{M_o} (1 - x)^{\frac{2}{3}} \left(\frac{P_o}{Zo RT} - \frac{P_e}{ZeRT} - \frac{M_o x}{V_R M_w n} \right) \qquad \text{.................. (8)}$$

where

S_o = initial surface area of ice crystals

x = fractional ice conversion

t = time

k = rate constant

M_w = molecular weight of water

T = temperature

R = gas constant

M_o = initial mass of ice

n = hydrate number

V_R = volume of pressure vessel

P_o,P_e = initial and equilibrium pressure

Z_o,Z_e = initial and equilibrium compressibility factor

Numerical integration of the expression using the value of the temperature dependent lumped parameter kS_o between 0.0125 hr^{-1} and 0.038 hr^{-1} gave good agreement with the experimental conversion data.

In the volume model, it is assumed that the rate is considered proportional to the amount of unconverted ice rather than the surface area of ice. In this case,

$$\frac{dx}{dt} = k_2 n\,(1 - x)\left(\frac{P_o}{ZoRT} - \frac{P_o}{Z_e RT} - \frac{M_o x}{V_R M_w n}\right) \qquad \cdots\cdots\cdots\cdots\cdots\cdots \quad (9)$$

The expression was integrated and an analytical solution was obtained. For k2 = 2.439 cc/gmol water/hr, the model give a good agreement with the experimental results with average error of ± 8.8 percent. For methane hydrate formation in unconsolidated sediments, the value of k2 was found to be a function of the percentage of sand in the unconsolidated core.

The first attempt to quantify the surface area of the ice crystals used for hydrate formation was by Nair and Adamson (1970) who used the BET method to measure the surface area. The ice crystals were formed by condensing superheated steam at liquid nitrogen temperatures. The measurement of adsorption isotherms for nitrogen, argon and carbon dioxide gave surface areas are valid only at low temperatures and they can be significantly decreased by using different methods of forming ice crystals or by annealing at high temperatures.

Wright (1986) developed a new experimental technique to measure the rate of hydrate formation of non-condensable gases like methane from melting ice as a function of pressure and surface. He found that the methane hydrate growth rate was gas diffusion limited and applied this technique to determine the effective diffusivity of methane within the structure I methane hydrate film. It was assumed that molar rate of methane hydrate growth per unit of active ice surface area (rH) is equal to the molar rate of diffusion of methane molecules from the gas phase, through the hydrate crystal film to nucleation sites on the ice surface and can be expressed i.t.o. the molar ice conversion rate per unit surface area by

$$V_H = -\frac{1}{n_H s}\frac{dni}{dt} = \left(\frac{D}{RT}\right)\left(-\frac{dP}{dz}\right) \qquad \text{.................. (10)}$$

where *D* is the effective diffusivity based on a nonporous hydrate film and *dP/dz* is the methane gas pressure gradient within the hydrate film.

6. STUDIES ON HYDRATE FORMATION, MODELLING AND PHYSICAL CHRACTERIZATION

A. Introduction

In the early years, hydrates were primarily studied to determine operating conditions to prevent their formation in natural gas pipelines. Thus, efforts were concentrated on defining the vapor-water hydrate equilibrium conditions for binary mixtures of pure gas and water, and also for a few tertiary mixtures. In the 50's, Katz (1959), Scauzillo (1956) and later Koledezni (1970) found that the addition of a non-hydrate forming compound like NaCl or ethanol to the water phase, at a given pressure lowers the hydrate forming temperature. Similar "anti-freeze" effect was observed when the non-hydrate forming compound was added to the gas phase. This early work has been reviewed in detail by Katz et al (1959), Byk & Fomina (1968) and API Technical Data Book (1970).

B. Studies on Hydrate Formation

Extensive literature is available regarding techniques of hydrate formation. In most instances, the experiments and apparatus were designed with the aim of determining:

a) Pressure-temperature equilibrium data as a function of gas composition.

b) The composition of the hydrate phase.

c) The rate of hydrate formation.

Also, it is seen that most of the hydrate data was obtained under such conditions of pressure and temperature that the hydrate formers are in the vapor phase. These have been very well reviewed by Katz et al (1959) and others (Byk and Fomina, 1968; Van der Waal and Platteau, 1959; API Technical Data Book, 1970). Kobayashi et al (1949, 1955) obtained three phase VL_1H equilibrium data for pure methane at pressures up to 60,000 psi, whereas Wilcox et al (1941), Reamer et al

(1952), and Teodorovich (1957) studied paraffinic and olefinic hydrates. Table 6 provides hydrate forming conditions for pure gases. Gaseous mixtures of methane and propane have been studied by Campbell and McLeod (1961) and also Carson and Katz (1966) who reported four phase VL_1L_2H equilibrium point data for methane-propane mixtures.

As far as the formation of hydrates from liquid hydrate formers is concerned, the only studies reported are those for pure liquids like propane by (Wilcox et al, 1941) and ethane, propylene, propane (by Reamer et al, 1952), refrigerants freon (Katz et al, 1959, 1975, 1973) and methyl chloride (Chinworth et al, 1967), an exception being study of propane-propylene liquid mixtures (Wilcox et al, 1952). The remaining studies of hydrate formation from liquid mixtures deal either with the determination of quadraple point VL_1L_2H lows or the effect of non-hydrate formers on it, e.g.: CH_4-C_3H_6 CH_3Cl - $CHCl_3$ and binary mixtures of C_2H_5Cl with $CHCl_3$, CH_3CHCl_2, $(CH_2Cl)_2$, CCl_4, CS_2, and C_6H_6. Tables 7, 8, and 9 give a brief summary of studies on binary, ternary, and quarternary systems of hydrates. From these studies it is possible to say in general that,

a) For pure hydrate forming gases which have critical temperatures below 32°F, hydrates can be formed under two or three phase conditions, only.

b) For pure hydrate formers having critical temperatures greater than 32°F, there exists a four phase VL,L_2H equilibrium temperature above which hydrates cannot be formed, i.e. the three-phase L_1L_2H equilibrium hydrate curves are nearly vertical on a P-T diagram, e.g. propane.

c Similarly, the three-phase L_1L_2H equilibrium hydrates curves on a P-T diagram for a binary liquid mixture of hydrate formers, are nearly vertical if both of them stabilize similar hydrate structures by occupying similar cavities, e.g. propane-propylene mixture (Wilcox et al, 1961).

TABLE 6: HYDRATE FORMING CONDITIONS FOR PURE GASES
(after Kamath (1984))

Gas	a	b	Temp Range (°C)
Methane	16.717	1886.79	-25 to 0
	38.980	8533.80	> 0
Ethane	17.511	3106.56	-25 to 0
	66.273	10626.25	> 0
Propane	17.156	3269.65	-25 to 0
	67.130	16921.86	> 0
Isobutane	18.950	3887.32	-25 to 0
	61.760	15571.63	> 0
Carbon Dioxide	18.596	3161.61	-25 to 0
	66.580	10260.28	0 to 11
Nitrogen	15.129	1506.28	-25 to 0
	37.808	7688.63	0 to 25
Hydrogen Sulphide	16.560	3270.61	-25 to 0
	36.828	8266.10	0 to 25

p = Dissociation Pressure in kPa

T = Temperature, °K

$T = P = \exp\left(a + \frac{b}{T}\right)$

TABLE 7: STUDY OF BINARY SYSTEMS OF HYDRATES (WITH WATER)

SYSTEM	REFERENCES
1) Methane	Villard (1888) Deaton and Frost (1940) Kobayashi and Katz (JPT, AIME - 1949) Campbell and McLeod (1961) Marshall et al (1964) Roberts et al (1941) Kamath (1984)
2) Ethane	Villard (1888) Roberts et al (1941) Deaton and Frost (1940-a) Reamer et al (1952)
3) Acetylene	Calletet (19) Villard (1888-9)
4) Ethylene	Van Cleef and Drepen (1962) Villard (1888) Deaton and Frost (1940) Kobayashi and Katz (1949) Diepen and Scheffer (1950) Reamer et al (1952) Snell et al (1961)
5) Propane	Villard (1888) Deaton and Frost (1940-a, 1941) Reamer et al (1952) Teodorowich (1957) Wilcox et al (1941) Holder and Godbole (1982) Kamath (1984)
6) Cyclopropane	Hafemann (1969)
7) Propylene	Reamer et al (1952) Clarke et al (1964) Byk et al (1955)
8) Isobutane	Wu et al (1976) Holder and Godbole (1982)
9) Normal Butane	Schneider and Ferrar (1968) Uchida and Hayano (1967) McKetta and Katz (1968) Ng and Robinson (1976)
10)Cis and Trans-2-Butane	Holder and Kamath (1984)
11)Dichloroethane	Garg (1979)

TABLE 8: TERNARY SYSTEMS OF HYDRATES (WITH WATER)

SYSTEM	REFERENCES
1) Methane-Ethane	Holder and Grigoriou (1980)
2) Methane-Ethylene	Snell et al (1961)
3) Methane-Propane	Verma (1976)
4) Methane-Isobutane	Wu et al (1976)
5) Methane-Butane	McKetta and Katz (1968) John and Holder (1982) Ng and Robinson (1976)
6) Methane-Hydrogen Sulphide	Noaker and Katz (1956)
7) Methane-Carbon Dioxide	Unruh and Katz (1949)
8) Methane-Ci-2-Butene	Holder and Kamath (1984)
9) Methane-Trans-2-Butene	Holder and Kamath (1984)
10)Methane-Nitrogen	Jhaweri and Robinson (1965)
11)Methane-Ar-Kn	Holder et al (1980)
12)Methane-Hydrogen Sulphide	Noaker and Katz (1956)
13)Methane-Propylene	Otto and Robinson (1960)
14)Methane-Sulpher Hexafloride	Sortland and Robinson (1964)
15)Methane-Carbon Dioxide	Unruh and Katz (1949)
16)Methylene Chloride and Chloroform	Tester and Wiegardt (1969)
17)Propane-Propylene	
18)Propane-Butane	Kamath (1984) Paranjpe et al (1987)
19)Propane-Isobutane	Kamath et al 91982) Patil (1987)
20)Propane-Trans-2-Butane	Kamath et al (1982)
21)Propane-CO_2	Robinson & Mehta (1971)
22)Propane-Hydrogen Sulphide	Platteeuw and Van DerWaals (1959)
23)N-Butane-Isobutane	Rouher and Marsh (1952)

TABLE 8 Continued.

SYSTEM	REFERENCES
12)Carbon Dioxide	Wiebe, R. (1961) Unruh and Katz (1969) Deaton and Frost (1940-a) Bozzo et al (1973)
13)Chlorine	Davy (1810) Marsh (1952)
14)Sulphur Dioxide	Tamman and Kreige (1955)
15)Hydrogen	de Forcrand & Villard (1888)
16)Nitrogen	Van Cleef and Diepen (1960,65)
17)Oxygen	Van Cleef and Diepen (1960,65)
18)Bromine	Dyadin and Aladko (1977)
19)Xenon	Garg (1977)
20)With Brine and Ethanol Solutions	Kobayashi et al (1957)

TABLE 9: FOUR COMPONENT SYSTEMS OF HYDRATES (WITH WATER)

SYSTEM	REFERENCE
1) Methane-Ethane-Propane	Snell et al (1961)
2) Methane, H_2S and CO_2	Robinson and Hutton (1967)
3) Methane, Propane and I-Butane	Patil (1987)
4) Methane, Propane and N-Butane	Paranjpe et al (1987)

d) Due to "antifreeze" effect, non-hydrate forming liquids like benzene lower the quadruple point VL_1L_2H temperature.

One of the most widely used techniques for determining the pressure-temperature data is to contact the gas and water in a high pressure glass window cell through which hydrate crystals can be seen. For pressures up to approximately 70 MPa, the equilibrium point at which the hydrates form, can be determined by visual observation (Holder 1976, Kobayashi, 1955). Beyond these pressures, glass windows are not suitable. Similarly, in measurements below the ice point, the presence of ice makes the visual detection of ice like hydrate very difficult. In such cases, the technique commonly employed is to form large quantities of hydrates at low temperatures. (Marshall et al, 1964). The hydrate formation process is usually accompanied by a decrease in pressure, as the gas molecules enter the denser hydrate phase. An increase in temperature now causes the hydrates to decompose, thereby increasing the corresponding pressure. The equilibrium point is considered as that point at which the pressure-temperature curve breaks indicating the end of hydrate dissociation.

A common technique of determining the composition of pure gas-hydrates is to measure the amount of gas needed to convert a known weight of water into solid hydrate. A drawback of this method is that some water, occluded within the hydrate crystal matrix during crystal growth, is not available for hydrate formation, which can be partially overcome, e.g. by breaking the crystals in a ball mill. Ceccotti (1966) formed hydrates on a silver iodide coated tube, directly from gases saturated with water. However, this method also results in occlusion of water, condensed from the vapor phase or forced stabilization of a new hydrate crystal structure. Barrer et al (1962) determined the composition of hydrates from pure gases by monitoring the concentration change of a tracer or water soluble non-hydrate forming salt in water. In this method, it is necessary to account for the effect of dissolved solids on hydrate equilibrium for greater accuracy. For a gaseous mixture of hydrate formers, the only technique is to melt the hydrate crystals and analyse the gas evolved. However, there might be errors due to water occlusion in hydrate crystal matrix.

For large gas molecules that can only fit in large cavities, the fractional occupancy θ of the gas molecules in the hydrate can be directly obtained from the hydrate composition. This enables the calculations of chemical potential difference for hydrates $\Delta\mu H$ from the van der Waal and Platteauw model, without calculating the Langmuir coefficients.

For temperatures below the ice points, Holder and Godbole (1982) measured VIH dissociation pressures for propane and iso-butane hydrates at temperatures as low as -22°C using a gravimetric technique. The hydrate formation was detected by employing a sensitive electrobalance capable of measuring weights up to 10^{-4}gms.

Kaplan (1976), Evrenos (1971) and Stoll et al (1971), while studying thermal and acoustic properties of gas hydrate sediments, formed hydrates by passing the gas through a column of granular aggregates of water-saturated sand. Subsequently, Stoll and Bryan (1979) employed a pressure vessel with provision for stirring and compacting to form large cores of pure propane hydrates.

Kamath (1984) studied formation and measurement of hydrate dissociation in the core holder, by forming hydrate cores and dissociating these cores by hot water injection method.

C. *Modelling of Dissociation of In-Situ Hydrate*

One of the first attempts to view hydrate dissociation as a moving-boundary process was by Cherski and Pondarev (1972), who, however, failed to provide a complete solution. Kamath et al (1984) conducted interfacial heat transfer studies during dissociation of propane hydrates and developed an experimental technique to measure the rate of heat transfer during dissociation of the solid hydrate phase simultaneously into gas and liquid phases. They showed that the heat transfer rate was a power function of ΔT, the temperature difference between the (warm) bulk heating fluid and the (cold) hydrate surface undergoing phase change. The heat transfer correlation developed was found analogous to that for heat transfer during nudeate boiling of liquids. Later, Kamath and Holder (1987) studied the dissociation heat transfer characteristics of methane hydrates and found that the nucleate boiling analogy could be extended to methane hydrates too. A unified heat transfer correlation for both methane and propane hydrates was developed and, at a fixed ΔT, the heat flux density for propane hydrates was found to be 2 to 2.5 times higher than that for methane hydrates.

Selim and Sloan (1985) modelled the dissociation of a pure hydrate, by assuming that a heat flux is incident on a semi-infinite planer medium with constant physical properties. They considered the hydrate dissociation as a moving boundary ablation process, where it is assumed that the water formed due to dissociation is immediately blown away from the surface by the produced gas.

Ullerich et al (1987) obtained experimental data on rate of dissociation of methane hydrates. The dissociation experiments were conducted using a resistance heater of known heat flux, and the hydrate mass loss measurements were made with an electrobalance. The dissociation process was described by a mathematical model and the agreement between the model and the data was found to be within 10%.

Recently, Selim and Sloan (1987) have modelled hydrate dissociation by thermal stimulation in porous media, wherein the dissociation of hydrate to gas and water is assumed to take place at a moving dissociation boundary. A similanty solution to the conservation equation was obtained and parametric studies were made, which indicated that the hydrate dissociation rate in sediments is strongly influenced by the thermal properties of the system and the porosity of porous medium. For thermal stimulation of hydrates, the average value of the energy efficiency ratio indicated that the heating value of the produced gas was nine times the heat input during dissociation.

D. Physical Characterization of Hydrates

The physical characterization of hydrates is quite important for development of exploration and production techniques. Numerous studies have been done in the past to study various physico-chemical properties of hydrates such as thermal conductivity, dielectric relaxation, acoustic velocity, electrical property measurements, etc. A summary of studies of physico-chemical properties of gas hydrates is presented in Table 10.

Water Content of Gases in Equilibrium with Hydrates

One of the important specifications in the gas processing industry, for the elimination of hydrates from natural gas operations is the water content of gases or fluids, in equilibrium with hydrates. Though the equilibration process to eliminate the metastable liquid water system is difficult and the experiments are time consuming, it has been successfully accomplished. (Aayogi et al, 1979 and Sloan, 1982). In the past, the measurements of water content of gas in equilibrium only with hydrates in two phase region gave less accurate results due to the fact that metastable liquid water could well extend into the gas-hydrate region and also, large amount of gas in equilibrium with hydrates, was required.

One of the first attempts to measure water content of gases was by Laulhere and Briscoe (1939) who employed an adsorption train gravimetric method for determination of water content of natural gas at hydrate conditions. Later, Deaton and Frost (1946), Records and Seely (1951) employed the Bureau of Mines ASTM

TABLE 10: STUDIES ON PHYSICAL & CHEMICAL PROPERTIES OF GAS HYDRATES

PROPERTY	REFERENCE
a) Thermal Conductivity	Cook (1981) Dharmawardana (1983) Russ (1981,1982)
b) Dielectric Relaxation	Gough (1977, 1978) Hawkins and Davidson (1966)
c) Dew Point of Natural Gases in Hydrate Region	Kobayashi and Katz (1955)
d) Acoustic Velocity & Electrical Properties	Lawson (1984) Kieffe ( ) Whiffen (1982)
e) Relative Permeability to Gas	Leas (1986)
f) Sonic and Resistivity Measurements	Pearson (1983)
g) Heat Capacity	Ross (1982)
h) Surface Tension	Sada (1984)
i) Anamalous Wave Velocities	Stoll (1971)
j) Speed of Longitudinal Sound	Whalley (1980)
k) Physical Properties of Sediments	Stoll (1971)

dewpoint tester combined with the vapor pressure of liquid water. Deaton and Frost (1946), McCarthy et al (1950), McKetta and Wehe (1958), and Laughlin (1969) presented water content charts for natural gas in both gas-liquid region and the gas hydrate region. The water content of gas in equilibrium with hydrates was thought to be considerably lower than the water content of natural gas in equilibrium with metastable liquid water.

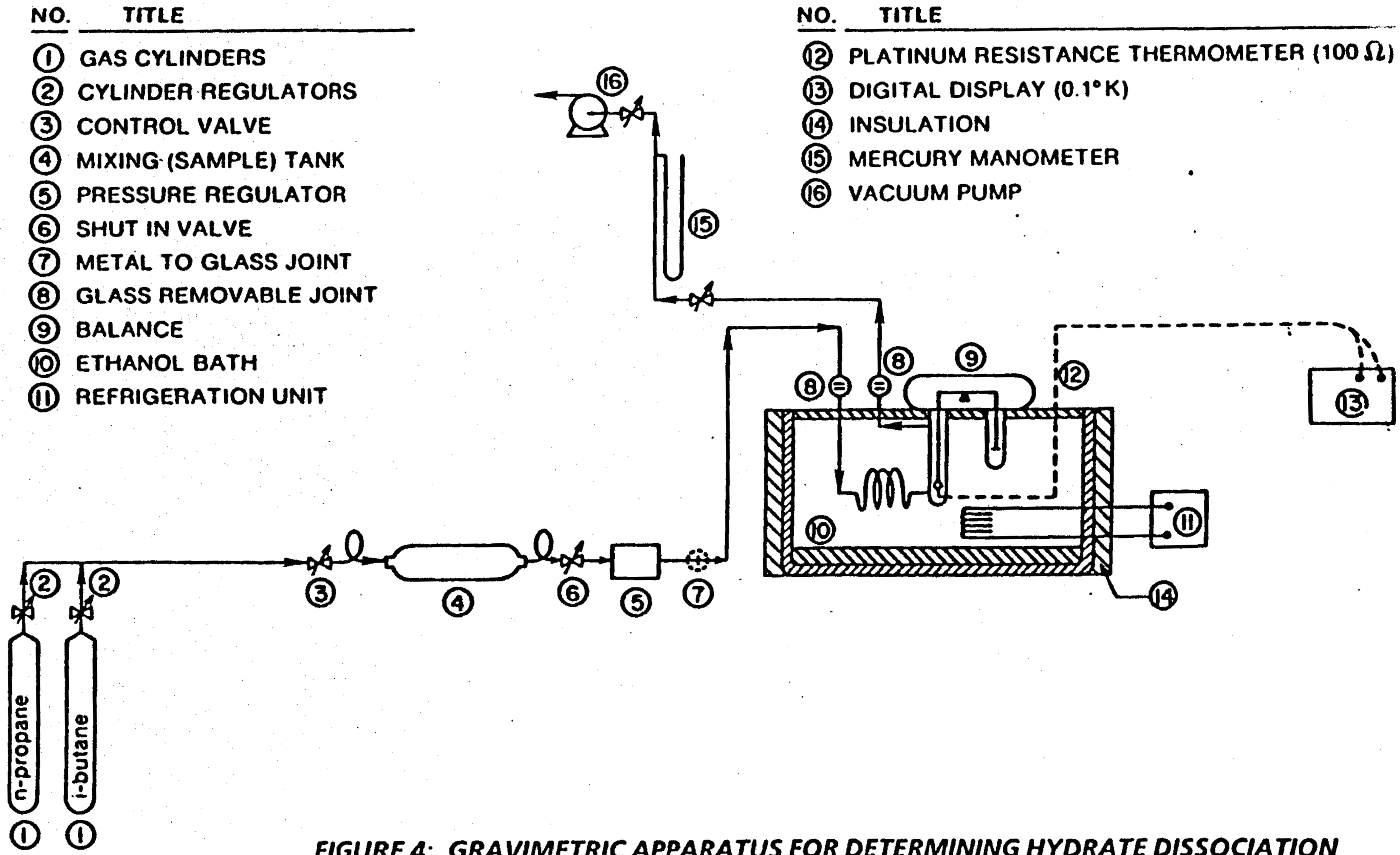
- Sloan et al (1976) successfully eliminated the errors arising due to the unusual metastability of liquid water in the gas-hydrate and developed a chromatographic technique for determining the water content of gas in equilibrium with its hydrate, above 32°F up to 1500 psig. For methane, it was found that in order to prevent hydrate formation the water content of methane should be significantly less than that determined from the water content charts. Sloan et al (1978) also obtained an improved value of the vapor pressure (chemical potential) of the metastable empty hydate, which has been often used in hydrate thermodynamic calculations (Sloan et al, 1976; Aoyagi et al, 1979; Song and Kobayashi, 1981; Holder, 1981; Sloan, 1982).

- Aoyagi et al (1980), while studying water content of methane gas in equilibrium with hydrate, found deviations, from the existing water content charts, of the water content of methane gas at initial hydrate formation condition and which increased with decrease in temperature. Also, the measurements of water content of a simulated lean CO_2 Prudhoe Bay gas and simulated CO_2-rich Prudhoe Bay gas indicated that the water content isobars of the latter converge at lower temperatures, and cross at still lower temperatures.

7. Experimental Techniques of Hydrate Formation

In this section, the various experimental techniques employed for hydrate formation studies have been discussed in detail.

Holder and Godbole (1982) used a gravimetric technique to study VIH data for pure isobutane. As shown in Figure 4, it consists of an electronic balance enclosed in a vacuum head with two inlets to which 42mm diameter hangdown tubes are fitted. The sample can be attached to a suspension wire which is enclosed in the tube and pure gases at any desired pressure (less than 100 kpa) can be admitted through ports. A fine copper wire mesh saturated with distilled water was attached to one suspension wire, whereas an aluminium pan was attached to the other wire to counterbalance the weight of the copper wire mesh and water. The sample weights were displayed on a panel display meter, on a 100 mg scale. The tube enclosing the suspension wire was immersed in an insulated refrigeration bath of volume 10 liters and which could be controlled to ± 0.05°k using a Neslab temperature controller. The actual water sample was about 25 cm below the refrigeration fluid (ethanol) level. Ethanol was extracted from one corner of the bath, pumped through coils in a metal enclosure containing vacuum head and back into the diagonally opposite corner of the bath. Temperature gradients within the system were minimized by cooling the vacuum head, which contained most of the gas. Two platinum resistance thermameters were used for measuring the temperatures, one of which was suspended in the bath, with the sensing element about 10mm from the sample, and the other was inserted into a thermocouple well in the sample tube with its sensing element about 2mm from sample. For pressures above 30 kPa, the temperature readings in the thermowell had to be corrected by 0.1 to 0.3°k. A mercury manometer was used in conjunction with the barometer to measure pressures, which were accurate to 0.2 kPa.



NO.	TITLE
①	GAS CYLINDERS
②	CYLINDER REGULATORS
③	CONTROL VALVE
④	MIXING (SAMPLE) TANK
⑤	PRESSURE REGULATOR
⑥	SHUT IN VALVE
⑦	METAL TO GLASS JOINT
⑧	GLASS REMOVABLE JOINT
⑨	BALANCE
⑩	ETHANOL BATH
⑪	REFRIGERATION UNIT

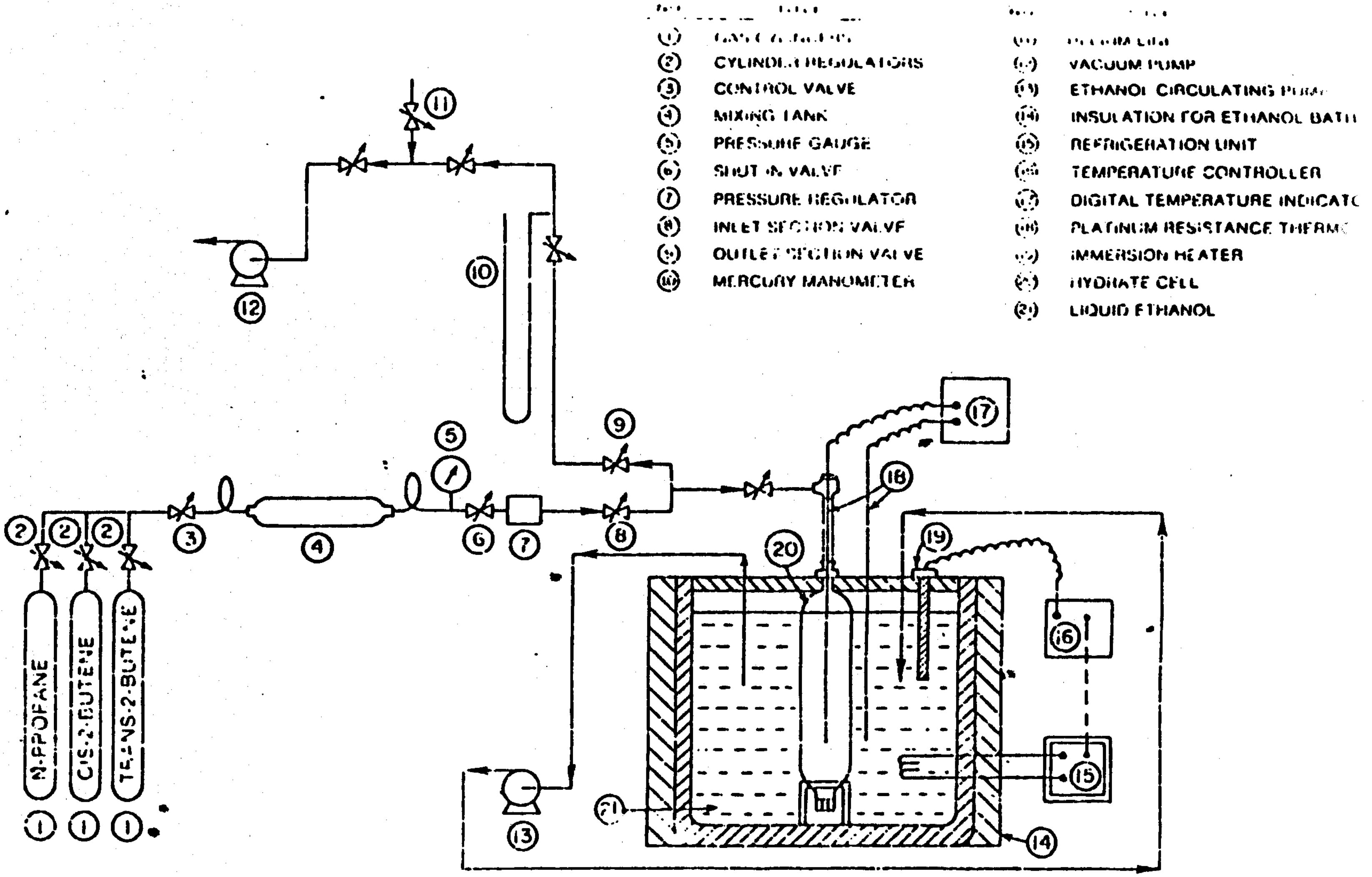
NO.	TITLE
⑫	PLATINUM RESISTANCE THERMOMETER (100 Ω)
⑬	DIGITAL DISPLAY (0.1° K)
⑭	INSULATION
⑮	MERCURY MANOMETER
⑯	VACUUM PUMP

FIGURE 4*: *GRAVIMETRIC APPARATUS FOR DETERMINING HYDRATE DISSOCIATION PRESSURE BELOW THE ICE POINT

After suspending a water sample from the balance, the temperature was set to a value below the ice point and the sample was frozen. After evacuating the system to 0.1 kPa, it was filled with water saturated isobutane to the desired pressure. The evacuation/filling procedure was repeated and the temperature lowered to 200°k overnight. A gain in weight of sample of 3 to 10 mg was observed due to hydrate formation. The temperature was increased to about 5°K colder than the estimated dissociation temperature of isobutane and subsequently increased in small temperature increments (0.3°K) until there was a weight loss of 1 to 2 mg, which corresponded to the dissociation temperature of hydrates.

The method can detect the presence of hydrates even in very little quantities, and problems with phase occlusion are avoided, due to the small quantities involved. The method was used to determine the dissociation pressures of isobutane hydrate and of propane hydrate which are useful in calculating gas-water kihara parameters for these gases.

Kamath (1982) used a modified experimental set up for the studying three phase (VIH) hydrate equilibrium for hydrates of cis and trans-isomers of 2-butene below the ice point (Figure 5). The main hydrate cell was a 300 cc SS sampling cylinder, tightly closed at the bottom end and completely immersed in an insulated ethanol bath. A 0.3175 cm resistance thermometer was inserted into the sampling cylinder and was connected to the top end of the cell through a 0.635 cm tube. The bath was equipped with all necessary auxillaries such as a refrigeration unit for cooling, an immersion heater for heating the bath, a temperature controller for controlling bath temperature, a circulating pump for ethanol circulation (to reduce temperature gradients) and 2 platinum resistance thermometer which was inserted in the bath connected to a digital temperature display unit. One resistance thermometer was placed in the hydrate cell about 5 cm above bottom and the other was immersed in the bath near the hydrate- forming cell.



Modified Experimental Apparatus

FIGURE 5: EXPERIMENTAL SETUP FOR STUDY OF THREE PHASE HYDRATE EQUILIBRIUM

The inlet section of the system had three gas cylinders of propane, cis 2-butene and trans-2-butene respectively with standard pressure regulators and a mixing tank for collecting gas from each cylinder. From the mixing tank, the gas could be passed to the sampling cylinder through the annular tubing inlet section. The outlet section was provided with a mercury manometer, a vacuum pump to evacuate the system, provisions for taking gas samples for analysis and a helium cylinder for pressuring the isolated sample before chromatographic analysis and also as a carrier gas in gas chromatograph.

Initially, a 0.3175 cm tube was introduced into the sampling cylinder, extending up to the top quarter of hydrate cell, and its other end was connected to a conical flask containing distilled water. With the hydrate cell bath temperature maintained at 263°K, the system was pressure tested and a vacuum was applied to boil the water in the conical flask and distill it into the experimental cell. This resulted in the formation of about 50cc of finely divided ice crystals in the hydrate cell. The 0.3175cm tube was then replaced by a 0.3175 cm Platinum resistance thermometer, a pressure test conducted and the entire system was evacuated for 3 hours.

Kamath et al (1984) developed an experimental technique for measuring rates of heat transfer to a solid hydrate phase decomposing into gas and liquid phases simultaneously under controlled pressures and temperatures. As shown in Figure 6, the apparatus consisted of two pressure vessels A and B, designed for pressures up to 13.8 MPa and provided with a removable top flange and a permanent bottom flange. Vessel B was used to form hydrate cores and was provided with a pressure gauge, a coiled tube jacket around it for cooling and independent cooling manifold at the bottom. A temperature gradient was maintained in the hydrate vessel by keeping coolant in manifold colder than that in coils. Vessel A was used to separate the gas and water overflow from vessel B during hydrate dissociation and was

NO.	TITLE	NO.	TITLE
1	GAS FLOW METER	26	TEMPERATURE CONTROLLER SENSOR
2	PRESSURE GAUGE	27	BACK PRESSURE REGULATOR
3	JERGUSON GAUGE	28	PLATINUM RESISTANCE THERMOMETER
4	GAS DISPERSION TUBE	29	MAIN GAS STORAGE TANK
5	HEATER USED WITH TEMPERATURE CONTROLLER	30-31	PRESSURE REGULATORS
6	CIRCULATING PUMP	32	PRESSURE GAUGE
7	COOLING MANIFOLD	33	HEATER
8	PISTON WITH GAS INLET THROUGH CENTER	34	COOLING COILS
9-23	CONTROL VALVES	35-36	COOLANT CIRCULATING PUMPS
24	COOLANT RESERVOIR	37	GAS COLLECTING TANK
25	REFRIGERATION UNIT		

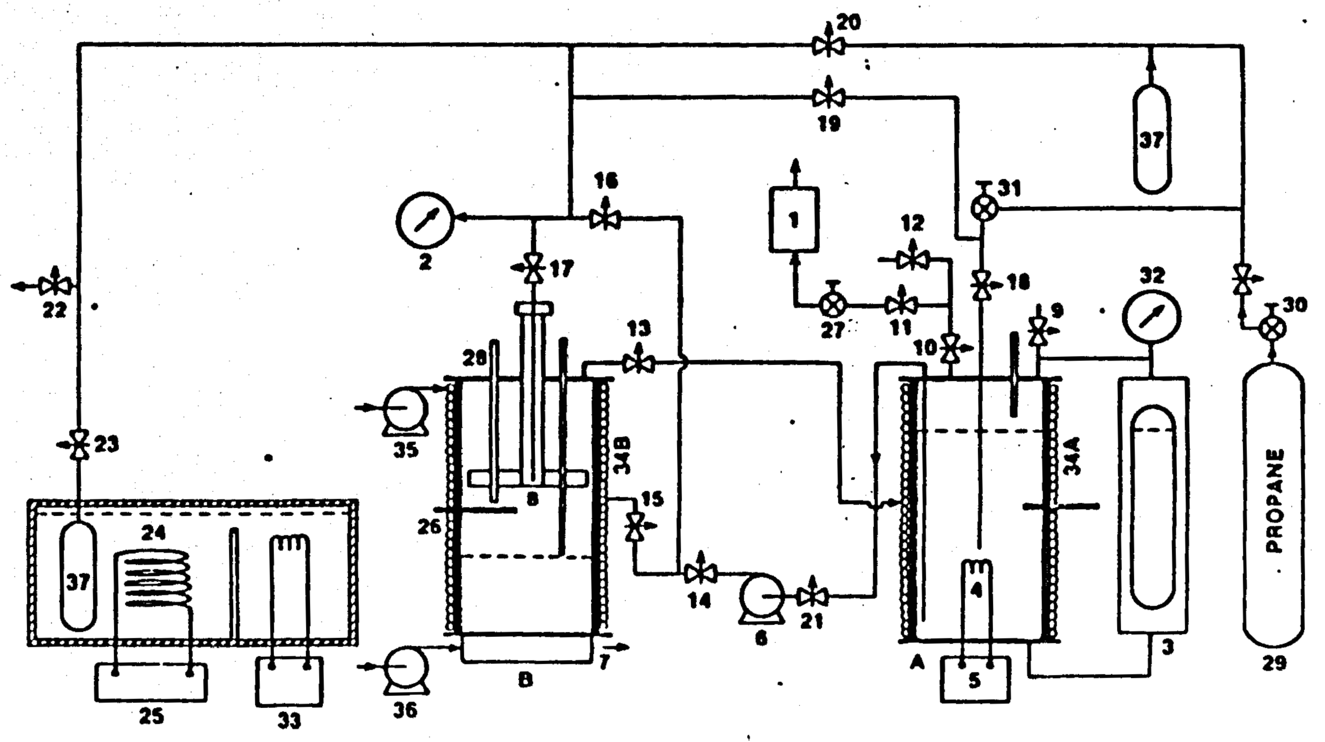


FIGURE 6: EXPERIMENTAL APPARATUS FOR STUDY OF THREE PHASE HEAT TRANSFER DURING HYDRATE DISSOCIATION

provided with a pressure gauge, a heater to maintain bulk water temperature greater than that of hydrate, a Jerguson gauge as a liquid level indicator and a circulating pump to circulate warm water to vessel B for dissociating hydrates. The gas liberated during dissociation was separated from water in vessel A and passed subsequently through a wet test meter.

To form hydrates, a known quantity of frost was added to vessel B, maintained at very low temperatures, in four portions with successive compaction of each of the portions by the piston (to ensure uniform void fraction of 0.4 - 0.5). With bottom frost maintained at 250°K, vessel B was closed evacuated and saturated with a known quantity of liquid propane. The temperature gradient in the frost zone saturates the frost completely and ensures that it is saturated from bottom upwards. To prevent any premature melting of frost, the frost temperature is maintained lower than 273.15°K. After complete saturation of frost, vessel B temperature was raised to 274°K and maintained for more than 24 hours, to promote nucleation and formation of hydrates. Excess propane was distilled off by reducing pressure of vessel B below that of vapor pressure of propane but higher than dissociation pressure of hydrates.

Recently, Paranjpe et al (1987) have studied effect of salinity on phase behavior of gas hydrates for different binary and ternary mixtures of methane, propane, isobutane and n-butane, using an experimental set up similar to that used by Kamath et al (1982). As shown schematicaly in Figure 7, the hydrate cell consists of a windowed Jerguson gauge of capacity 50cc and capable of withstanding pressures up to 20 MPa, suspended in a constant temperature, insulated both by a lever connected to an in-line gear motor for agitation. The windowed bath is provided with a refrigeration unit, an immersion heater and temperature controller, thermo couples and temperature readout device. The salt

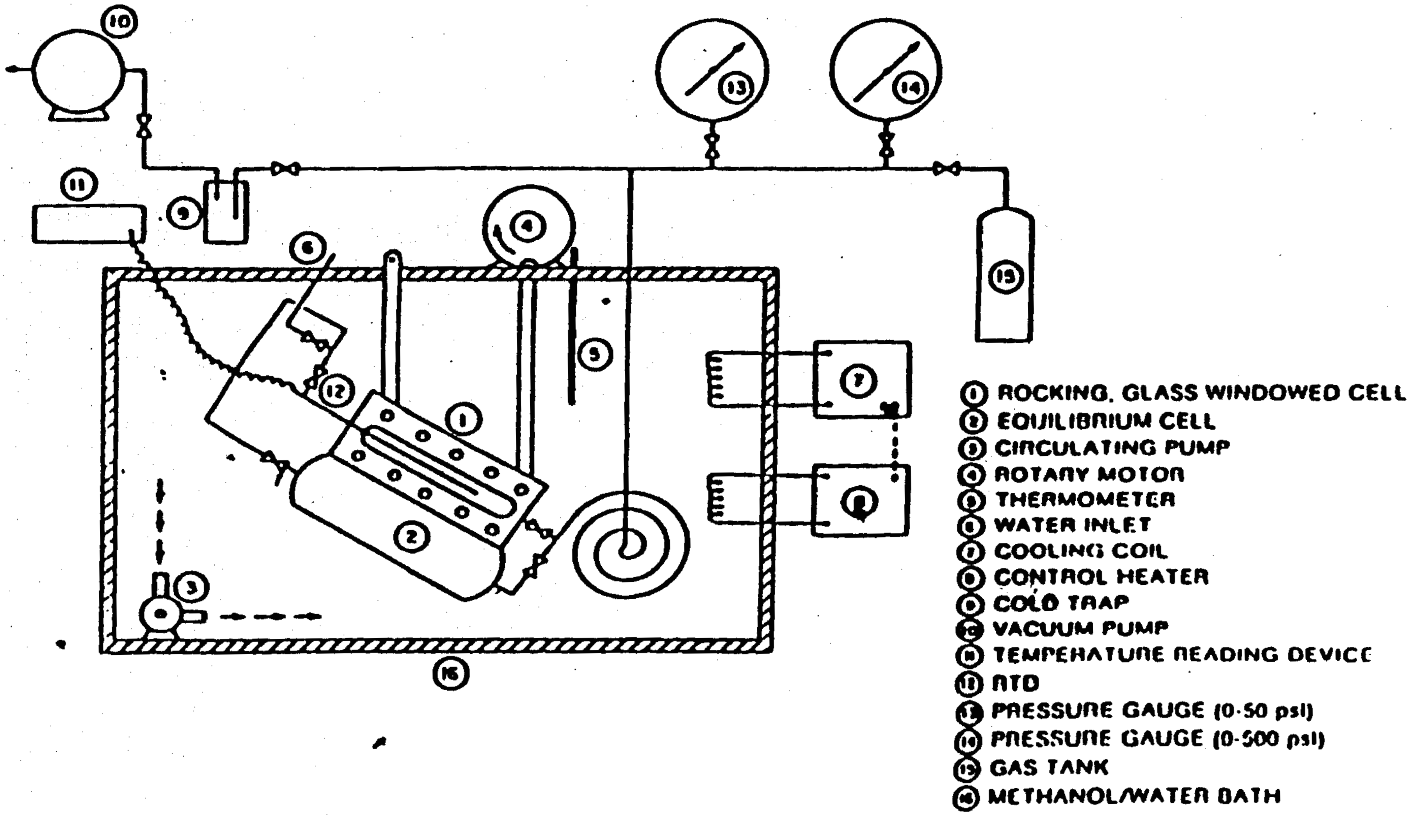


FIGURE 7: EXPERIMENTAL APPARATUS FOR DETERMINATION OF HYDRATE PHASE EQUILIBRIUM

concentrations were measured using Beckmann thermal conductivity bridge and gas analysis was done using a gas chromatograph.

Experiments on hydrate phase equilibrium for several binary and ternary mixtures of methane, propane, isobutane and n-butane were carried out to study the effect of heavier components like isobutane and n-butane on phase behavior of hydrates and are important for accurate prediction of zone of hydrate stability for in-situ hydrates. Also, the effect of salinity on three phase (VL_1H) and four phase (VL_1L_2H) equilibrium conditions for mixtures of propane and n-butane of two different salt concentrations was studied and the data were used to calculate hydrate numbers by extending the Miller and Strong Method (1946) to gas mixtures.

The experimental set up can also be employed for studying the hydrate formation in presence of crude oil, which is discussed below.

Hydrate Formation in Presence of Crude Oil

Recent studies (Collett, 1985) have indicated that gas hydrates are present in conjunction with heavy oils and tar sands in the southwest up-dip continuation of West Sak and Ugnu formations in the Kuparak river unit, North Slope of Alaska. With the advent of ARCO-Alaska's thermal recovery pilot plant in the West Sak sands (OGI Report, 1983), it is of increasing importance to establish hydrate phase equilibrium conditions for light gases, brine and oils found in such regions.

The experimental procedure for determining the three phase (VL_1H_1VIH) and four phase (VL_1L_2H) hydrate forming conditions of crude oil-natural gas mixture will be the same as that for gas-water mixtures (Patil, 1987). In this case, the bubble point curve for crude oil-natural gas mixture can also be determined along with the pressure-temperature-gas and oil compositions.

The crude oil mixture and the gas mixture has to be added quantitatively from the recombination apparatus, which recombines dead oil with its lighter components, to the main hydrate chamber containing water or brine. The bubble point pressure can then be determined for various temperatures by first fixing the temperature and pressurizing the hydrate cell until only a very small gas bubble remains. After allowing sufficient for equilibration by rocking the hydrate cell, the pressure can be increased in steps at certain time intervals until the bubble clearly disappears at the bubble point pressure. The temperature of the system is then lowered until a large quantity of hydrate dissociates from the mixture of oil and water. The hydrate cell is treated until very few crystals are left. The system slowly cooled to the predetermined temperature and the four phase water-liquid hydrocarbon-vapor-hydrate equilibrium pressure is determined. The above procedure can then be repeated to obtain data under well mixed equilibrium conditions.

Past studies (Katz, 1971) have shown that the presence of hydrates along with oil can denude a crude oil of its natural gas constituents, resulting in a decrease in production due to viscosity increase and pore blockage and due to radial lowering of vapor pressure of oil (Holder, 1976). The above experimental apparatus can also be used to quantify the effect of hydrate formation on crude oil properties and to predict denuding effects due to hydrate formation by employing the following procedure.

Initially, the various properties of the oil to be tested, like viscosity, specific gravity, bubble point pressure, gas composition and crude oil composition are measured. Hydrates can then formed in presence of crude oil by following the same procedure as used by Holder (1976), and the pressure and temperature conditions for hydrate formation can be determined. At the end of the experiment, the oil can be separated from hydrates and the above properties determined. This data can be employed to quantify the effect of hydrates on crude oil properties and denuding of oil, and can be useful for developing guidelines for thermal recovery studies, e.g. thermal recovery in West Sak and Ugnu reservoirs.

Study of Hydrate Cores in Unconsolidated Sands

The recovery of natural gas hydrates in the Arctic can be accomplished by the use of hydrate dissociating agents like methanol, brine, hot water, steam injection or by depressurization method when hydrates coexist with a gas cap. To develop methods for hydrate recovery, baseline experimental data are essential. Kamath (1984) studied hydrate dissociation in laboratory sythesized hydrate cores by hot water injection method. For modelling hydrate recovery by different methods, a similar study for other dissociation mechanisms is necessary as also the study of hydrate formation and dissociation in consolidated or unconsolidated sand cores. The following procedure can be followed for hydrate core studies and for studying effect of hydrate formation or dissociation on change in permeability of porous rock.

1. Form hydrates in unconsolidated sand cores.
2. Measure permeability of hydrate cores and study effect of hydrate saturation on permeability of cores.
3. Measure hydrate formation rates under varying gas flow rate, pressure, temperature conditions and study kinetics of hydrate formation.
4. Measure hydrate dissociation rates, heat transfer rate and quantify convection effects during dissociation of hydrates like brine, hot water, and steam injection and depressurization, since previous hydrate models have neglected the convection effect and considered heat conduction as the sole mechanism of heat transfer.

The experimental set up (Figure 8) consists of a specially designed hydrate cell equipped with a cooling jacket through which coolant is circulated. The bath circulator can be maintained at a constant temperature with the help of a temperature controller. The core holder has three parts to monitor the pressure drop across the hydrate core for permeability determination. In addition, three temperature ports are provided to obtain temperature profiles in the hydrate zone and dissociated zone during the dissociation run, and the entire core holder well insulated, to minimize heat losses to the surrounding area. The inlet gas in core holder passes through the bottom port by means of three concentric tubes connected to three gas spargers within the core. Such a design provides a flexible mechanism to overcome problems of core plugging due to hydrate formation. The flow rates of inlet gas and outlet gas-water mixture can be measured by online gas flow meters, whereas a mass flow controller can be used to keep the inlet gas flowrate constant. The outlet gas is compressed and recirculated back into the core holder with a gas compressor, and the downstream pressure of the coreholder is kept constant with a back pressure regulator. Other auxillary units of the setup include: a gas-water separator, wet test gas flow meter to measure gas production during dissociation, injection fluid reservoir with liquid level indicator, a steam generator, etc.

The core is initially packed with 20 mesh size sand of known porosity and is saturated with water after evacuation. The core is then saturated by methane flowing at a constant rate from a cylinder. From the pressure drops and gas flow rates, absolute permeabilities can be computed. The outlet gas is then compressed to a pressure higher than the core holder pressure thus maintaining the flow of gas in the system. The gas flow rate is controlled by means of flow control and monitored by means of a flow meter. Two inline filters are installed at either end of core holder, housing a teflon membrane which prevents water from escaping from

1. Temperature Controller
2. Methanol Bath
3. Refrigeration Coils
4. Heater
5. Digital Temp Indicator
6. Core Holder
7,8,9. Pressure Transducers
10. To Methanol Bath
11. Pressure Indicator
12. Gas Flow Meter
13. Gas Cylinder
14. Wet Test Flow Meter
15. Water Tank
16. Gas Water Separator
17. Back Pressure Regulator
18. Pressure Gauge
19. Back Pressure Regulator
20. Moist Trap
21. Temperature Control
22. Gas Flow Meter
23. Gas Flow Control
24. To Vaccum Pump
25. Water Flow Meter
26. Water Pump
27. Pressure Vessel

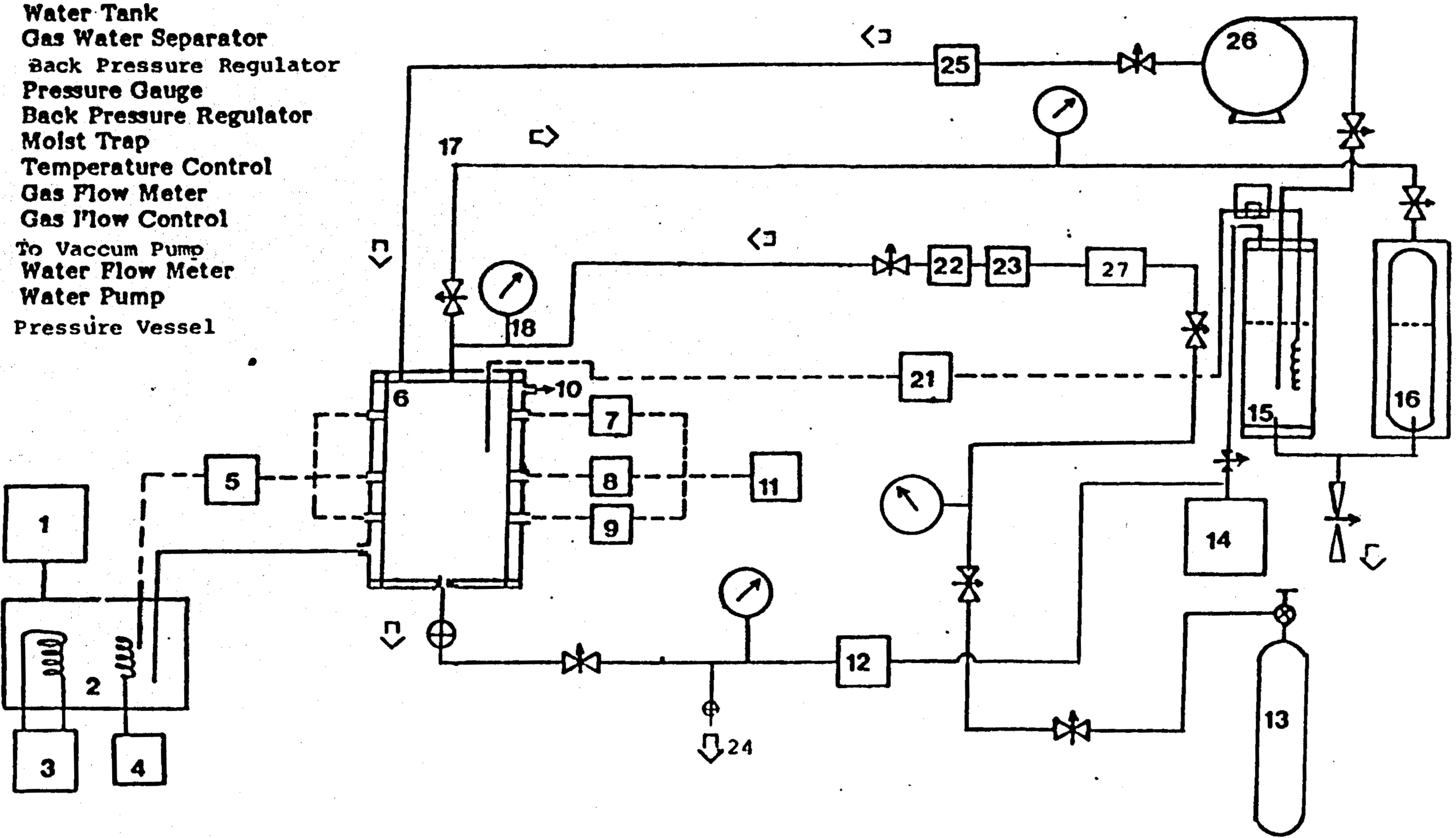


FIGURE 8: EXPERIMENTAL SETUP FOR STUDY OF HYDRATE CORES IN UNCONSOLIDATED SANDS

the core holder during hydrate formation.

8. THERMODYNAMICS OF GAS HYDRATES

Several methods have been reported in literature for the prediction of hydrate phase equilibria. One of the earliest methods suggested for prediction of dissociation pressures, the pressure at which the nucleation of hydrate crystals begins, was the K value method of Katz (1944). In this method, analogous to vapor-liquid equilibria, the hydrate equilibria is characterized by a vapor-solid equilibrium constant K_{vsi} given by,

$$K_{vs,i} = \frac{y_i}{x_i} \qquad \text{.................} \quad (11)$$

whey yi and xi are the vapor phase and solid phase mole fractions, respectively, of the ith component on a dry basis. K_{vs} is a function of temperature and pressure and can be calculated from experimental hydrate data by using the criteria

$$\sum_i \frac{y_i}{K_{vsi}} = 1 \qquad \text{................} \quad (12)$$

However, this method is no longer used as it suffers from the disadvantages that the experimental data has been used to determine and extrapolate K_{vsi} values are not accurate and they do not distinguish between the two hydrate structures. Also, K_{vsi} is not a function of gas composition. The K value charts have very large errors associated with predictions.

The first attempt of theoretical studies on hydrates was reported in the late 50's and early 60's when Van der Waals and Platteau (1959) presented a basic statistical model for predicting hydrate equilibrium based on the crystal structure of hydrates. Their model was based on the following assumptions:

a. Each hydrate cavity can be occupied by either zero or one gas molecule only and this molecule is localized within the cavity.

b. The cage is much larger in all dimensions than the largest dimension of the gas molecule, i.e., the gas molecule entrapped has the same rotational freedom as it would in the gas phase and does not distort the cavity. This assumption is not valid for larger molecules like propane and isobutane.

c. The mutual interaction between the solute (gas) molecules is negligible and the only interaction of the solute is with its nearest neighbor (water) molecules. In other words, the partition function for the motion of a gas molecule in its cage is independent of the number of types of gas molecules present. The distribution of the energy levels occupies by the molecules of a species are described by the work partition function.

d. The free energy contribution of the host (water) molecules is not affected by the mode of occupation of cavity by dissolved gases.

e. All the assumption of classical statistics are valid. The water-solute interaction is accurately described by a certain potential function, e.g., the Leonard Jones or the spherical core Kihara potential function.

Consider a hydrate crystal containing N_Q molecules of Q and occupying a volume V at temperature T and crystalized while in equilibrium with the solutes A . . . , J . . . , M having absolute activities $\lambda_A, \ldots \lambda_M$. Then the chemical potential of a solvent (water) molecule in the hydrate phase is given by

$$\Delta\mu_H = \mu_B - \mu_H = -RT \sum_{j=1}^{2} v_j \, ln \left(1 - \sum_i \theta_{ij}\right) \qquad \ldots\ldots\ldots\ldots\ (13)$$

where μ_H and μ_B are the chemical potential of the occupied and the unoccupied lattice water, respectively, R is the universal gas constant, υ_j is the ratio of the number of j cavities to the number of water molecules in the hydrate phase. The variable θ_{ij} is the fraction of the j cavities occupies by an i type gas molecule, and is give by the Langmuir isotherm

$$\theta_{ij} = \frac{C_{ij} f_i}{1 + \sum C_{ij} f_j} \qquad \text{.............} \quad (14)$$

where f_i is the gas phase fugacity of the ith gas species and can be determined by the method of Prausnitz and Chuch (1968). C_{ij} is the Langmuir constant whose value depends only on temperature and potential function parameters and is given by

$$C_{ij} = \frac{4\pi}{RT} \int_{cell\ radius} exp. \left[- \frac{w_{ij}(r)}{RT} r^2 dr \right] \qquad \text{.............} \quad (15)$$

where r is the radial position of solute in the cavity, $w_{ij}(r)$ is the smoothed cell potential function.

Since chemical potential of water in equilibrium hydrate phase is equal to that in water rich liquid or ice phase (μ_w), we have

$$\Delta\mu_H = \Delta\mu_w = \mu_B - \mu_w \qquad \text{.............} \quad (16)$$

Van der Waals modelled the gas-water interaction using the Leonard-Jones 12-6 potential function and found the dissociation pressure predictions were not quite accurate using literature values of LJ 12-6 constants. Later, Mckoy et al (1963) succeeded in predicting more accurately, the dissociation pressures of polyatomic gases by employing the Kihara potential function, which is given by

$$\Gamma\ (\upsilon)_{H2O-gas} = 4\varepsilon\left(\frac{\sigma}{r-2a}\right)^{12} - \left(\frac{\sigma}{r-2a}\right)^{6} \mathit{for}\, r > 29$$

$$= \infty \qquad\qquad \mathit{for}\, r \leq 29$$

. . . . (17)

where

ε = Kihara energy parameter

r = Intermolecule separation between gas and water molecules.

a = radius of core of gas molecule.

σ = Kihara distance parameter.

Figure 9 shows the Kihara potential function σ, ε/K, and a. Tee et al (1968) have developed correlations for estimating the parameters of the Kihara potential function. However, use of these correlations does not predict hydrate forming conditions accurately. Kobayashi and Katz (1955), Barduhn and Lee (1978) and Nagata and Kobayashi (1960), instead of employing second virial coefficient data, used a semi-empirical approach for predicting hydrate dissociation pressures of methane, Ar and N_2 by fitting the potential function parameters to experimental data. In 1972, Parrish and Prausnitz (1972) extended Kobayashi's work by fitting the potential function parameters and developed a generalized method of prediction of fifteen gases and their mixtures. Though their predictions of pure component data were very accurate, the predictions for mixture dissociation pressure were slightly in error.

In the above cases, it is assumed that the water molecules surrounding the gas molecules are evenly distributed over a sphere whose diameter is average of the

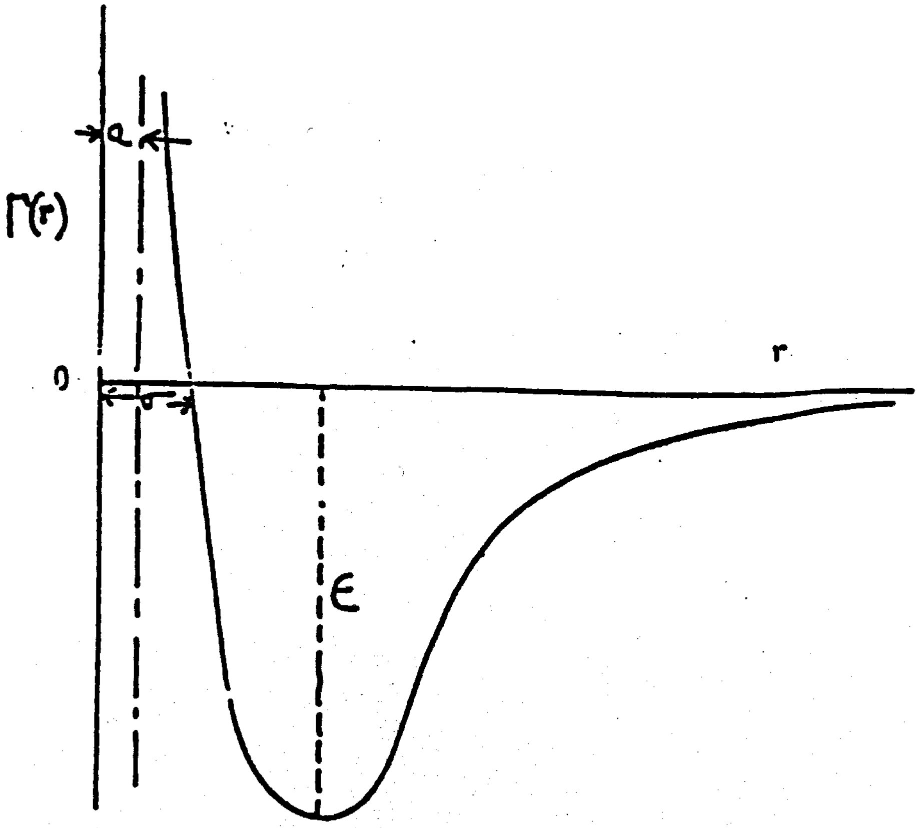


FIGURE 9: KIHARA POTENTIAL FUNCTION

actual cage dimensions. Fester et al (1966) calculated the sum of all gas-water interactions individually by employing the Monte Carlo approach, but with little improvement in the accuracy of the results.

Holder (1976) and Holder and Godbole (1982) employed the Parrish and Prausnitz method for predicting the dissociation pressures of methane, ethane and propane mixtures and obtained optimum values of the different parameters involved in the hydrate model. Ng and Robinson (1977) added another adjustable parameters to obtain improved prediction of multi-component dissociation pressures, and also for prediction of conditions of hydrate formation from condensed systems.

Although the basic van der Waal model based on structure of hydrates, contributed significantly to the theory of hydrate compounds the original model has undergone many modifications in the last decade. In the Van der Wall model it is assumed that only the neighboring interactions between gas and water molecules are important. John and Holder (1981, 1982) and John et al (1985) critically examined hydrate phase equilibrium theory of Van der Waal and Plateau and found that the equilibrium calculations were significantly affected by the interactions of the guest molecules with those host molecules of the hydrate lattice, which are not in their immediate vicinity. They also defined second and third shells of water molecules for the four cavities of hydrate structures. For large asymmetric guest molecules whose internal motion is likely to be restricted, they used a modified semi-empirical method for calculating Langmuir constants which gave improved predictions of hydrate equilibrium. However, this method suffers from the disadvantage that each gas species has to be treated according to its shape, i.e., linear, spherical, etc. A study was also made of restrictions to molecular rotations and of molecular locations within hydrate cavities caused by them.

John et al (1985) have suggested that the overall cell potential is represented by assuming three different shell contributions to the overall gas water interactions and is given by

$$w(r) = w_1(r) + w_2(r) + w_3(r) \qquad \ldots\ldots\ldots\ldots\ (18)$$

where w_1, w_2, w_3 represent first, second and third shell of water molecule, respectively.

To account for the asymmetric gas-water interactions for non-spherical gas molecules like n- and isobutane, Holder and John et al (1985) introduced a novel approach called the Qstar correlation method for determination of true Langmuir constant. Q represents an empirical correction factor for Langmuir constant due to restricted motion of gas molecules and the corresponding state correlation for Q function is given by

$$Q = exp.\left[-Ao\left\{w\left(\frac{\sigma}{R-a}\right)\left(\frac{\varepsilon}{KT}\right)\right\}^n\right] \qquad \ldots\ldots\ldots\ldots\ (19)$$

where Ao and n are empirical parameters and depends on the particular cavity. The true Langmuir constant C is then given by

$$C = C^* Q^* \qquad \ldots\ldots\ldots\ldots\ (20)$$

This approach is recommended for hydrate phase equilibrium studies as it provides sufficiently accurate predictions.

Kamath (1982) used the Q star correlation method developed by John and Holder (1982) and extended it to optimize Kihara parameters for n-Butane from their experimental data.

9. DETECTION AND EVALUATION OF IN-SITU NATURAL GAS HYDRATES

A. INTRODUCTION

Natural gas hydrates have been studied in the past primarily to determine how to avoid their formation in natural gas transmission lines (Hammerschmidt, 1935). Also, the in-situ natural gas hydrates represent a potential drilling hazard and as such their detection of vital importance in regions where they occur. In addition, they may in the future provide a valuable resource for natural gas. Significant quantities of gas hydrates have been detected in many permafrost regions of the world, in West Siberia (Makagon, 1970), in the Mckenzie Delta of Canada, and on the North Slope of Alaska, as well as in the warmer offshore regions such as the Gulf of Mexico, Blake Bahama Outer Ridge and Mid-American Trench. The existence of hydrates in these areas has been confirmed from well log responses in the Mckenzie Delta (Bily and Dick, 1974), Prudhoe Bay and Kuparuk field (Osterkamp and Payne, 1981) as well as retrieved from Gulf of Mexico (Brooks et al, 1984). Also, extensive gas hydrates can exist in many areas beneath the sea floor (Makagon, 1970). The occurrence of hydrates in deep sea sediments in essentially tropical regions like the Gulf of Oman and off the northern coast of Columbia and Panama has also been indicated in drilling operations and seismic data. Bily and Dick (1974) provided one of the most conclusive studies on the occurrence and detection of in-situ natural gas hydrates wherein they incorporated well logs, including dual indvction, sonic and mud logs as potential hydrate detection devices.

B. MEANS OF DETECTION OF HYDRATE FIELDS

In spite of the fact that the present detection techniques serve to identify the location of hydrate fields, with the increased interest in naturally occurring hydrates, there is a greater need for improved detection and evaluation methods.The various techniques used to detect the hydrates in the earth are discussed in the following paragraphs.

1. *Hydrate Stability Determination*

The simplest and quickest way to check the zone of possible gas hydrate occurrence is to examine the zone of gas hydrate stability. For gas hydrates to be stable at a given depth, the earth temperature at that depth should be lower than the equilibrium temperature of hydrates corresponding to the pressure and gas composition conditions. However, the existence of gas hydrate stability conditions is not a necessary and sufficient condition for the existence of hydrates. For hydrates to occur, gas and water should coexist in the zone of hydrate stability.

The stability of gas hydrates in the earth and in the outer regions depends upon several factors such as mean annual surface temperature, geothermal gradients above and below the base of permafrost, salinity, subsurface pressures, gas composition, permafrost depth, pore pressure conditions and soil particle effects. The geothermal gradients and subsurface temperatures in Arctic North Slope regions can be obtained from previous studies (Osterkamp and Payne, 1981) and (Lachenbruch et al, 1985; Lachenbruch et al, 1982; Blanchard and Tailleur, 1982; Ferrigna, 1965; Brewer, 1958; McCarthy, 1952). Also, several thermodynamic studies on the measurement of pressure-temperature relationships for different gas hydrates reported in literature are used for hydrate stability determination (Deaton and Frost, 1946; Kobayashi and Katz, 1955; Wu et al, 1976; Kamath, 1982). Table 11 gives the values of mean annual surface temperature (T_S), permafrost base depth (Z_p), geothermal gradient within permafrost (Gfr), and geothermal gradient below the base of the permafrost (Gth) in the Prudhoe Bay and Kuparuk - West Sak fields. Godbole et al (1986) have presented a nomogram for the determination of zone of methane hydrate stability (ZMHS) for specific conditions of mean annual surface

TABLE 11: GEOTHERMAL PROPERTIES FOR PRUDHOE BAY AND KUPARAK-WEST SAK FIELDS

PARAMETER	PRUDHOE BAY	WEST SAK AND KUPARAK FIELD
1) Annual Surface Temperature, °C	-10.9	-9.3
2) Permafrost Depth, m	630	682
3) Geothermal Gradient Within Permafrost, °C/100m	1.66	1.75
4) Geothermal Gradient Below Permafrost, °C/100m	2.86	3.03

temperature (Ts), salinity, geothermal gradients (Gfr and Gth). Osterkamp and Payne (1981) and Zoeller (1984) suggested that subsurface pressure for the shallow unit on the North Slope can be assumed to be in a hydrostatic equilibrium (0.435 psi/ft or 9.84 kPa/m) and have a developed a nomogram assuming a hydrostatic variation in pressure. Sensitivity analysis indicates that the zone of hydrostatic stability increases by about 2.75 percent per percent increase in pressure gradient above hydrostatic value.

Evrenos (1971) has shown that the presence of salts in the formation fluids not only depresses the permafrost base temperature but also depresses the equilibrium by hydrate temperature and thus reduces the zone of hydrate stability. An increase in mean annual surface temperature and geothermal gradients lowers the zone of hydrate stability. Similarly, the reduction in ZHS is about 2.3% per 1,000 ppm increase in salinity.

Gas composition strongly influences hydrate stability conditions. The stability of methane hydrate is increasingly affected by the addition of ethane, propane and isobutane. Addition of CO_2 has an effect similar to ethane. A recent study by Kamath et al (1984) of 46 representative wells on the North Slope of Alaska has shown that the presence of small quantities of lighter hydrocarbons like propane, butane, etc. increases the stability of hydrates considerably and needs to be incorporated in the future calculations of hydrate stability.

2. *Drilling Response*

Severe and gasification, drill stem tests, ore sample studies, etc. can be applied for the detection of hydrates. Cores have been retrieved in Prudhoe Bay (Northwest Eileen State Well #2), Leg 84 of Blake Bahama Outer Ridge (Sloan, 1983) and in the Gulf of Mexico and the offshore region of Guatemala, for core sample studies, etc.

Present techniques like pressure core barrel can be applied for determining the type of hydrate deposit (massive, laminated, modular, etc.).

3. *Seismic Profiling*

Shipley et al (1979) have presented data which show that many anomalous reflections from the continental slopes and rises have characteristics which can be explained by the formation of gas hydrates. Direct sampling of these horizons is needed to identify them conclusively and to substantiate the physical conditions of formation. It is found that acoustic wave velocities in hydrated sediments are much higher than in hydrate free sediments and can be utilized for detecting the presence of hydrates in suboceanic environment. Tucholke et al (1977) have studied gas hydrate horizons detected in seismic profiler data from the Western North Atlantic, wherein reflecting horizons have anomaously high amplitude. It has been found that these horizons cut across bedding planes in the sediment and are restricted to areas where seismic strata up landward.

4. *Wire Line Log Evaluation*

Logging of hydrate intervals with conventional logs provides significant information for hydrate identification. High acoustic velocities on sonic logs, high resistivity deflection or dual induction logs, high gas on mud logs, expanded well bore on caliper logs are some of the indications of presence of hydrates. Direct log readings can often lead to misinterpretation of hydrate zones as either free gas zones or permafrost zones, particularly if decomposition has occurred during drilling. Log correlation and analysis provides additional proof of occurrence of hydrate zones. Goodman et al (1982) have presented five log analysis methods for specific application to in-situ hydrates. In this study, a correlation technique based on temperature log has been presented.

Collett and Economides (1983) have reviewed the use of well logs in the detection of hydrates. Collett et al (1983) have presented a technique for confirming the distinction between ice and hydrate, as well as quantification of hydrate deposits, which involves the use of neutron porosity transtime cross plot along with Pickett cross plot. Similar to the neutron porosity correction factor. Collett et al (1984) have outlined a transtime porosity correction factor. They showed that the ratio of compressional velocity in boise core saturated with structure I hydrate to that in boise core saturated with ire at -5°C is 1.18, e.g., an apparent porosity of 0.28 in hydrate saturated zone would be corrected as 0.335. They also evaluated a series of matrix porosities and sonic-velocities for eighteen units in Kuparuk B-1 production well. For a mixture of hydrate-water coexistence, it is possible to calculate the average water saturation, and hence, the average hydrate saturation by use of Pickett cross plots. A similar study of hydrates in Canada is being presently conducted by Judge (1984) and coworkers. In general, the best method for identification and quantification of gas hydrate deposits is to first determine the zone of hydrate stability, and then further determination of hydrates within stability zone by use of well logs.

GEOLOGIC ANALYSIS OF GAS HYDRATE DEPOSITS

Malone et al (1986) have evaluated the geologic factors that control the formation and detection of gas hydrates within offshore (Blake Outer Ridge), as well as onshore (North Slope of Alaska environments). In their study, they concluded that more detailed geology and reservoir data on the known hydrate occurrences, a detailed study of reservoir conditions and laboratory research a detailed analysis of individual targets with high potential for hydrate occurrence and greater drilling to recovery more samples, were necessary for geologic analysis of potential gas hydrate deposits.

10. GAS PRODUCTION FROM HYDRATE RESERVOIRS

The first step in the production of gas from hydrates is the dissociation of hydrates to gas and water. This transformation can be represented as:

$$C_nH_{2n+2}xH_2O\,(s) \rightarrow C_nH_{2n+2}(g) + xH_2O\,(l) - \Delta Hn$$

$$(\Delta H_n = +\,10 - 20\,kcal)$$

where $C_n\,H_{2n+2}$ represents either methane, ethane or propane and x is called hydrate number and is a measure of the number of moles of water/mole of gas in the hydrate phase. Table 6 gives typical values for x.

The positive value of ΔH indicates that 10-20 kcal of heat must be added to the hydrate reservoir per mole of methane dissociated, a part of which is used in heating up the reservoir to dissociation temperature and the remaining heat is available for achieving the above transformation. In addition, there are heat losses to overburden and underburden formations, and wellbore heat losses. It has been found that heat obtained by burning gas produced from hydrates is nearly ten times that required to dissociate them. Thus, we can conclude that from a thermodynamic point of view, production of gas from hydrates is energy efficient.

The most important factors to be considered for assessing the feasibility of gas production from hydrates are the form in which they exist in the reservoir and the extent of their saturation in the reservoir rock pores (Holder et al, 1984). Hydrates can exist either in association with gas, water, ice, or as 100% hydrates. Other factors which should be considered are reservoir rock properties of hydrated and hydrate free zones, and heat losses, if any, to overburden and underburden formations.

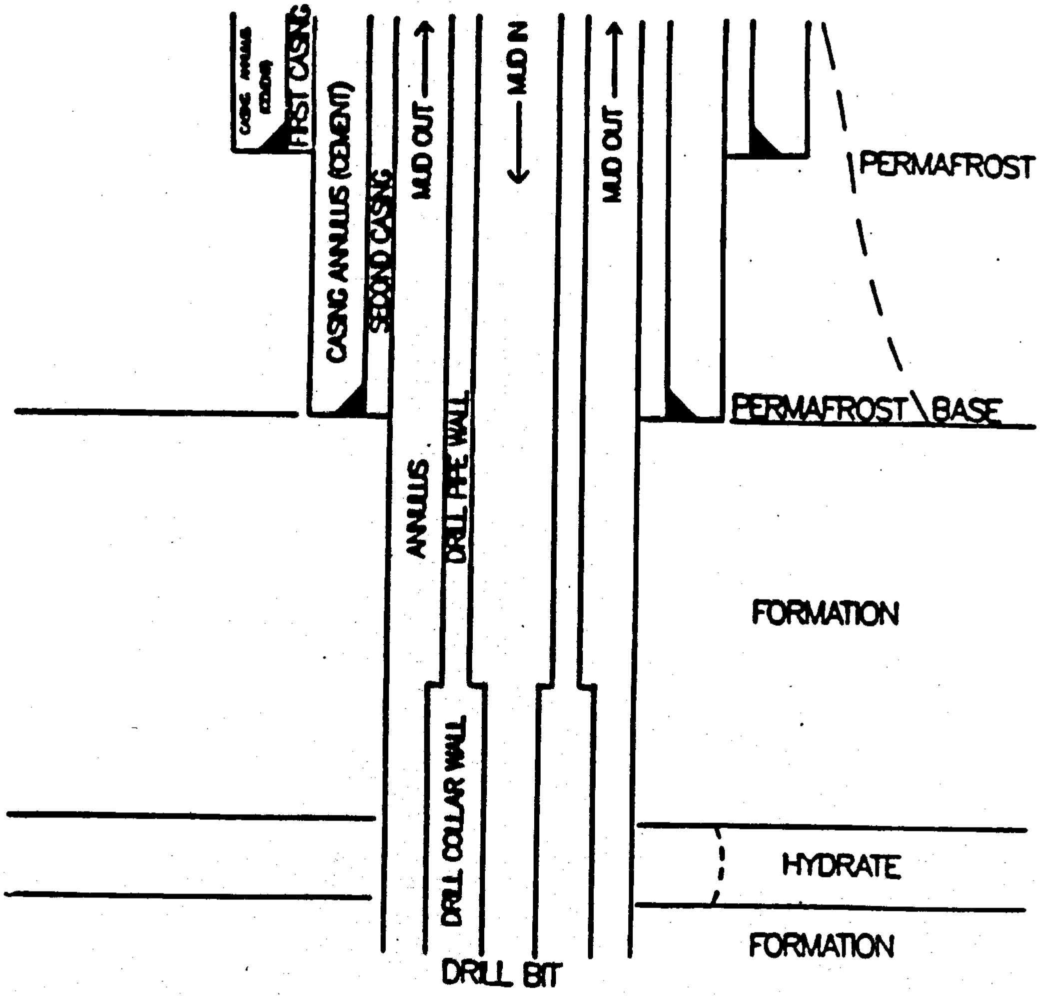
The quantity of gas that can be produced from a hydrate reservoir will also depend upon how the dissociation of hydrates affects the porosity, permeability, formation structure, etc. of the reservoir. The hydrated gas may be present in the reservoir in consolidated or unconsolidated media. The reservoir character may change drastically with dissociation of hydrates into gas and water (ice). Hence, in order to apply the conventional production techniques to a hydrate reservoir, it is necessary to compare the technical and economic aspects of the various production methods.

Various techniques have been put forward for the production of gas from gas hydrates. These include thermal recovery by injection of steam, hot water, hot brine or fire flooding, depressurization and injection of hydrate inhibitors like methanol or glycol (Halleck et al, 1982; McGuire, 1981; Holder et al, May 1982; Holder et al, Nov. 1982; Bayles et al, 1984; Kamath et al, 1985). These are discussed in the following paragraphs.

a. *Thermal Recovery*

In this method, the dissociation of hydrates to gas and water is accomplished by providing thermal energy in the form of steam, hot water, hot brine or by fire flooding. From a thermodynamic point of view, thermal recovery technique has been found to be viable (Holder et al, 1982), but it may pose problems in the severe conditions where hydrates occur.

Gas production by thermal recovery is illustrated here by considering steam injection. A schematic diagram of thermal recovery by steam injection is shown in Figure 10. Steam is injected into the hydrate reservoir at a specific rate and at a specific temperature in a cyclic manner. Each cycle is considered to be made up of steam injection stage, hydrate dissociation stage and gas production stage



<u>FIGURE 10:</u> ***<u>SCHEMATIC DIAGRAM OF A WELL IN THE ARCTIC REGION</u>***

Bayles et al (1984) have developed a model to determine the limits of expected gas production for such single well cyclic steam process. Their results indicate that deeper reservoirs and reservoirs with higher hydrate filled porosity and higher zone thickness result in better gas production, and higher energy efficiency ratios.

McGuire (1981) has developed two models for the production of methane hydrate by hot water injection. The frontal sweep model envisages a production scheme which is similar to steam flooding of a heavy oil reservoir and predicts highly optimistic gas production rates. The fracture flow model simulates gas production from low permeability hydrate reservoirs and predicts the lower limit of hydrate gas production.

Recently, Kamath and Godbole (1985) have suggested the use of hot brine for gas production from hydrate reservoirs. The use of hot brine instead of steam results in lower heat losses, reduced reservoir heating and lower hydrate dissociation energy. For economic viability, they recommended that the hydrate reservoir should possess a porosity of, at least, 15%, minimum hydrate zone thickness of 25 feet, high brine salinity, brine temperature between 250°F and 600°F, and minimum brine injection rates of 5,000 BPD.

Kamath et al (1985) have studied the effect of hydrate dissociation during thermal recovery of heavy oils by steam drive on the North Slope of Alaska. It was found that the presence of hydrates is beneficial for heavy oil recovery and results in improved reservoir heat efficiency, cumulative oil production and higher oil to steam ratio. Also, the generation of gas due to hydrate dissociation results in a higher reservoir pressure, reduced oil viscosity, reduced gravity override and provides gas drive mechanism. However, there is a decrease in steam zone efficiency due to significant loss of steam in dissociated zone.

b. Depressurization

Another method for dissociating hydrates to gas and water is by reduction of pressure. In order that heat flows to the hydrates, a temperature gradient has to be generated between the hydrates and the surrounding media. This is accomplished by reduction of pressure which causes dissociation of hydrates to gas and hence a lowering of temperature of remaining hydrates. The generation of gas in turn, raises the pressure to the vapor pressure of hydrates at the new lower temperature, thus establishing a temperature gradient.

Holder et al (1982) have simulated gas production from a reservoir containing stratified layers of gas hydrates and free gas. The hydrate zone was assumed to be impermeable and hence acted as a gas cap. They showed that the contribution of gas from dissociation of hydrates to the total gas production, increases with production time, and can even reach up to 40% of total production.

McGuire (1981) has presented a depressurization production scheme wherein a fracture is deliberately generated to increase the permeability of the hydrate zone. As per the model, the rate of gas production is a strong function of permeability in the ice zone but is independent of permeability in the hydrate zone. McGuire (1981) has also suggested a *salt-free* technique for melting the ice or hydrate surrounding the fracture and for maintaining the salt concentration in the area sufficient to prevent refreezing for the life of the well. This may enable the production of hydrate gas feasible even temperatures well below 0°C which might not be possible by conventional fracturing techniques.

So far, gas production from a hydrate reservoir only has been considered. Recently, Burshears et al (1986) presented a 2 phase, 3-dimensional, variable composition numerical model for gas production from a conventional gas reservoir in contact with hydrates. They concluded that it is possible to dissociate hydrates without any external energy source. The production of gas from the gas reservoir causes pressure reduction which, in turn, results in dissociation of hydrates to gas and water by depressurization and consequently a further increase in gas production. Thus, an expected low rate of pressure decrease during production of conventional oil and gas might indicate the existence of hydrates. However, for depressurization the initial temperature of the reservoir should be near or above 32°F. Otherwise, the hydrate would dissociate to gas and ice, which being impermeable prevents further dissociation of hydrates.

C. *Unconventional Techniques of Gas Production From Hydrates*

A number of unconventional techniques for producing gas from hydrates have been suggested which include solvent injection, salt frac and in-situ combustion. The injection of solvents like methanol or glycols into a hydrate reservoir causes the hydrate to dissociate. An advantage of this technique is that the solvent can be recovered in a production well and recycled.

Another method suggested (McGuire et al, 1981) is the salt frac technique which improves the effectiveness of steam or solvent injection by using salt as a proppant. In the presence of salts, the hydrate stability curve shifts to the left, thus reducing the hydrate dissociation temperature in the thermal injection or reducing the quantity of solvent necessary for hydrate dissociation in the solvent injection technique.

In case of the in-situ combustion method, methane and oxygen are injected into the reservoir and ignited. As a result of controlled combustion of methane within the reservoir, the hydrates dissociate to produce gas.

Some of the unconventional extraction techniques suggested are dissociation of hydrates by microwaves and electrical waves, water jet drilling, burial of radioactive wastes for providing thermal energy for dissociation, reservoir depressurization and sea floor mining (METC Topical Report, 1984).

Some other production techniques suggested by Russian scientists (Krason, 1985) are given below:

- a. By utilizing heat of the formation, e.g., reduction of formation pressure in hydrate deposits by removing fluids.
- b. Reduction of the equilibrium temperature of hydrate dissociation
  - i. by addition of substances that dissolve gas released due to hydrate dissociation, thereby decreasing the partial pressure of gas above hydrates;
  - ii. by injection of non-hydrate forming gases like air.
- c. Simultaneous injection of hot water, believed to exist beneath the hydrate zone and at temperatures above 50°C for dissociation of hydrate.

For marine gas hydrate deposits;

- a. Suction dredging of sediments saturated with hydrate has been suggested. The slurry containing gas, hydrates and sediments are transported to the surface where gas is then separated. However, for producing gas from marine gas hydrate deposits, it is necessary to remove the upper layers of sediments devoid of hydrates, excavate the sediment poorly saturated with hydrate and develop the producing deposits at tens to hundreds of meters from the sea bottom.

Geological Implications

In addition to the temperature and pressure conditions in the hydrate reservoir, geological parameters play an important role in determining the amount of hydrates formed. This, in turn, affects the producibility of gas from a reservoir. One of the most important factors which affects the heat necessary for hydrate dissociation and the flow rate of dissociated gas is reservoir porosity. The efficiency of thermal injection and the thermal properties of the hydrates are determined by the thermal properties of the hydrate reservoir like heat capacity and enthalpy of reservoir media, etc.

Holder et al (1980) have studied the effect of geological parameters on gas production from in-situ gas hydrates by steam injection recovery technique. Their study indicates that the geological and thermal conditions of the hydrate reservoir play an important role in maximizing thermal recovery of gas by hydrate dissociation.

11. DRILLING IN THE PRESENCE OF HYDRATES

The occurrence of hydrates in wells drilled in the polar region has been well documented. In the past, drilling through hydrate zones has resulted in problems of mud control due to severe mud gasification (Bily and Dick, 1974; Franklin, 1979), and the decomposition of hydrates during drilling has resulted in several gas kicks in the Mckenzie Delta and fires on seismic rigs (Judge, 1984). In addition, fizzed drill cuttings, wellbore freeze up, casing collapse and near blowout situations (Makagon, 1965; Franklin, 1979) have been reported. The low permeability of hydrate reservoirs prevents mud loss and results in the formation of a protective clay coating on well walls. Therefore, drilling through hydrate reservoirs results in decomposition of hydrate and also heats up near-hole hydrate containing rocks. The intergranular bonds weaken, the rock collapses, forming an intensive cavity and may lead to violent degassing, tool sticking and mud blowout (Makagon, 1983).

While drilling through a zone of naturally occurring hydrates, they are exposed to an increased temperature and thereby dissociate into gas and water, providing gas influx in the wellbore. In addition, the introduction of gas for cleaning hole cuttings or for lubrication of the drill bit, reduces hydrostatic pressure of the mud column which further accelerates hydrate dissociation in the vicinity of the wellbore. Rapid dissociation of the hydrate zone can introduce a large gas influx from the dissociated hydrate zone into the wellbore causing a gas kick.

In view of the expected increase in oil and gas exploration in the coming years, particularly in areas of potential hydrate occurrences, it has become increasingly important to use safe drilling practices. One of the standard drilling methods used in the past to overcome severe gasification problems has been to cool the drilling mud and increase the mud density. Though this approach eliminates heat input from the mud to the hydrate zone, it does not succeed in reducing the hydrate zone temperature primarily due to heat flow from deeper formations and also due to the heat exchange between down flowing drill pipe fluid and returning annulus fluid.

Another approach is to use cooler muds while increasing mud weights. In this case, the dissociation of hydrates during drilling can raise the shut-in pressures under closed in BOP stacks to levels sufficient to fracture formation below the casing shoe. Also, as a result of gas evolution, there is a reduction in mud density, which facilitates entry of free gas from other exposed holes into the drill hole. Goodman (1978) has analyzed the decomposition of hydrates during drilling considering thermal effects only as governed by the pressure-temperature equilibrium curves of hydrates. Factors affecting decomposition of hydrates include mud inlet temperature, flow rate, drilling schedule, geothermal gradient, well configuration, soil properties, etc.

In contrast to the foregoing methods which aim at inhibiting dissociation of in-situ hydrates, Franklin (1980) suggested promotion of the dissociation while the drill pipe is in hole by using lower weight muds. The gasified mud on returning to wellhead is subjected to degassing, cooling and recirculated. Furthermore, the penetration rate is reduced to maintain the gas volume in proportion to the capacity of the available equipment. For replacement of drill bit or for logging purposes, hydrate dissociation can be interrupted by employing heavier muds. This approach has been effectively used for drilling through hydrates in the Canadian Arctic.

Coring hydrates with conventional core equipment can be dangerous with a pressure core barrel. It is necessary to use cool drilling mud. Otherwise, special equipment would be needed at the surface to control the temperature of the hydrate filled core barrel during depressurization (Bily and Dick, 1974). For drilling to deeper depths, hydrate zones should be preferably cased off.

Goodman et al (1979) have simulated the drilling process of a Panacrtic well in the arctic offshore which can be used for controlling hydrate dissociation during tripping and setting of the casing. To control the hydrate gas influx, increase the dissociation temperature should be increased by using higher mud weights. This causes a change in hydrate equilibrium conditions, so that further decomposition is prevented. Goodman (1978) has provided guidelines for the type of muds to be used in arctic conditions. Thompson (1985) presented a model for determination of downhole mud temperatures to be used while drilling through non-hydrate zones.

Roadifer et al (1987) have presented an unsteady state, two dimensional (r-z) cylindrical coordinate finite difference simulator for modeling the dissociation of hydrates during drilling, for establishing guidelines for controlling the hydrate dissociation rate and the gas influx at wellbore, and for handling gas realized at the surface. The model determines dissociation rates, gas influx rates for given mud weight, mud temperature and specific reservoir conditions. Furthermore, it enables the determination of optimum mud weight and mud temperature for a given capacity of a degassing unit. Three methods have been suggested to control hydrate dissociation during drilling. These include: reducing mud temperature, increasing circulation rate and increasing mud weight. The specific method or combination to be used depends upon several factors like feasibility, economics and reservoir parameters.

Based on the wellbore heat transfer models of Keller et al (1973), Marshall and Bentsen (1982) and the wellbore hydraulics for newtonian fluids. Bingham plastics and power law fluids (Bourgoyne et al, 1986), Roadifer et al (1987) coupled the wellbore heat transfer and hydraulics with their hydrate dissociation model to model the hydrate dissociation under a wider range of drilling conditions. The model can be used to predict the effects of a wide range of drilling parameters on wellbore temperature, pressure, and subsequently the hydrate dissociation rate for arctic terrestrial, arctic subsea and subtropic subsea locations. They concluded that for preventing hydrate dissociation:

a. Turbulent flow conditions should be maintained in the annulus.

b. Run the casing after potential hydrate zones have been penetrated, if permafrost problems can be avoided.

c. There should be no casing run to the platform in subsea locations if it is feasible.

For promotion of hydrate dissociation:

a. Flow through the annulus should be laminar.

b. The casing should be run to the maximum depth above potential hydrate zones, where feasible.

A series of plots and nomographs have been presented for the determination of potential hydrate zones, selection of drilling parameters, or design of surface equipment for safe drilling through potential hydrate zones. Figure 11 (Godbole et al, 1987), Figure 12 and Figure 13 can be used to determine depths to which hydrates may be expected in arctic subsea and subtropic subsea locations. Figure 14 gives a nomogram for estimating parameters for drilling through hydrates. These can be used for predicting temperature and pressure necessary to keep hydrate dissociation within safe limits of drilling equipment, or vice versa, for design of surface degassing equipment for maximum temperatures and minimum pressures expected to occur over the hydrate zone.

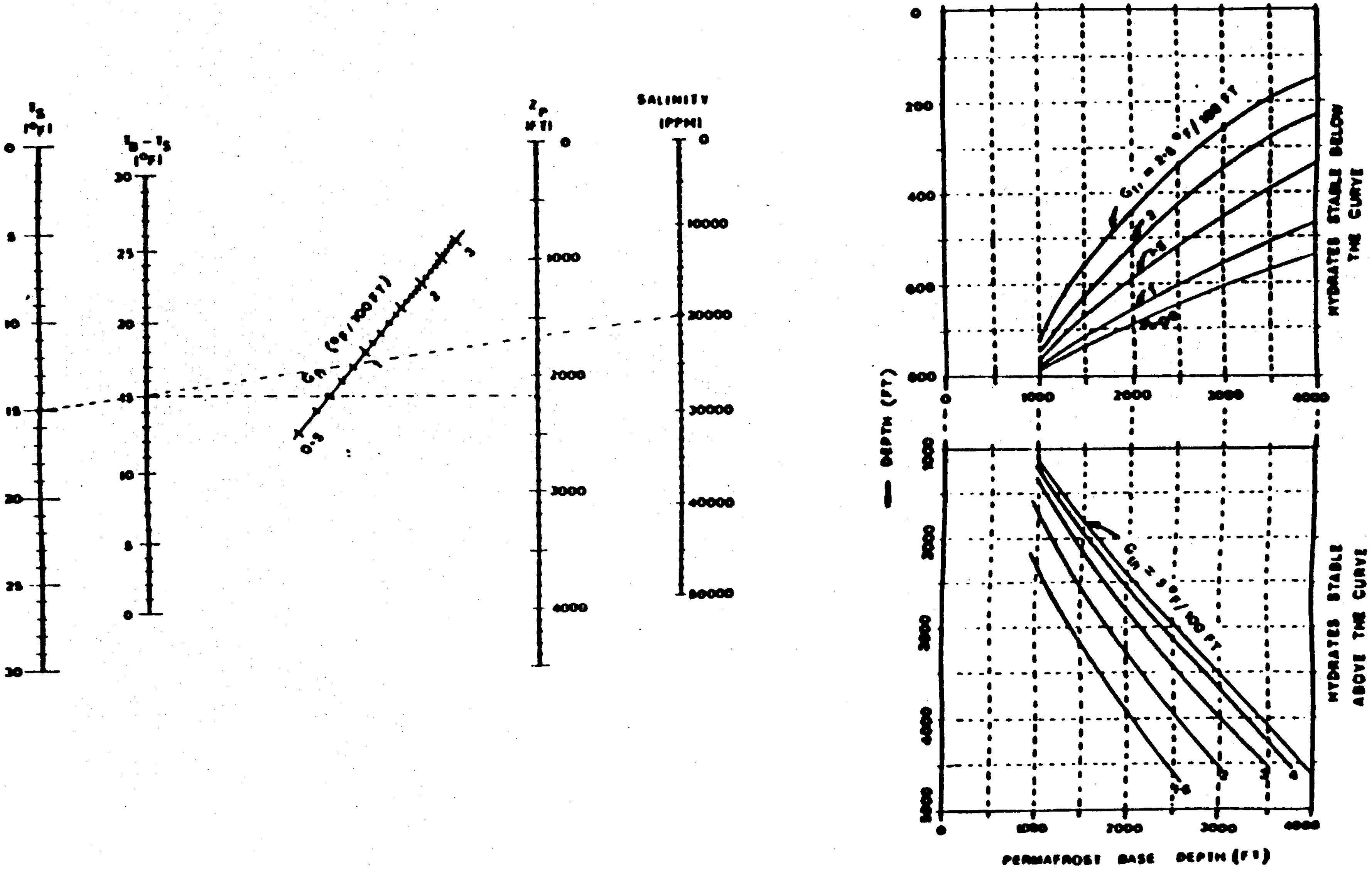


FIGURE 11: NOMOGRAM TO DETERMINE HYDRATE STABILITY IN ARCTIC ONSHORE REGIONS

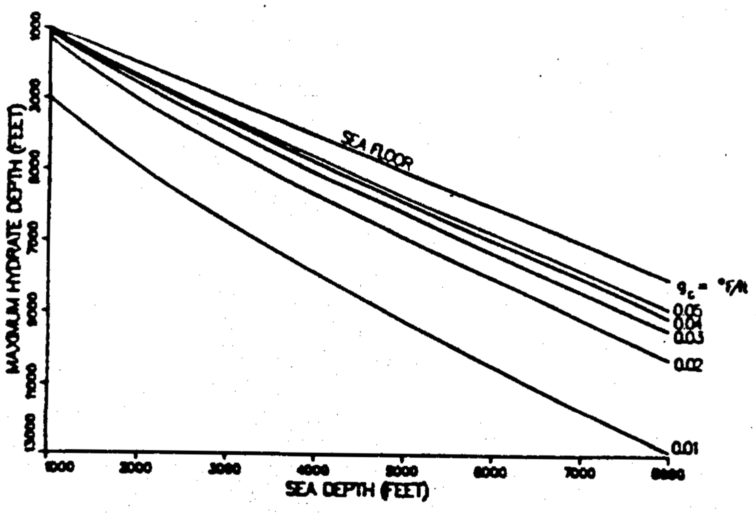


FIGURE 12: ZONE OF HYDRATE STABILITY IN THE ARCTIC SUBSEA REGION

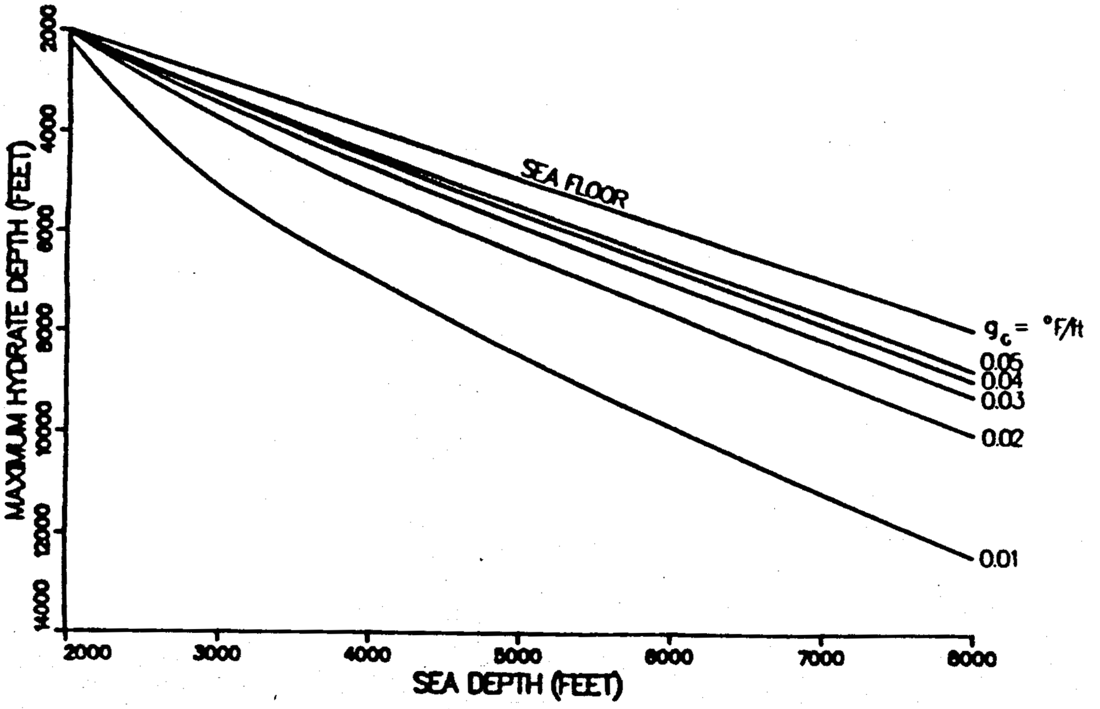


FIGURE 13: ZONE OF HYDRATE STABILITY IN THE SUBTROPIC SUBSEA REGION

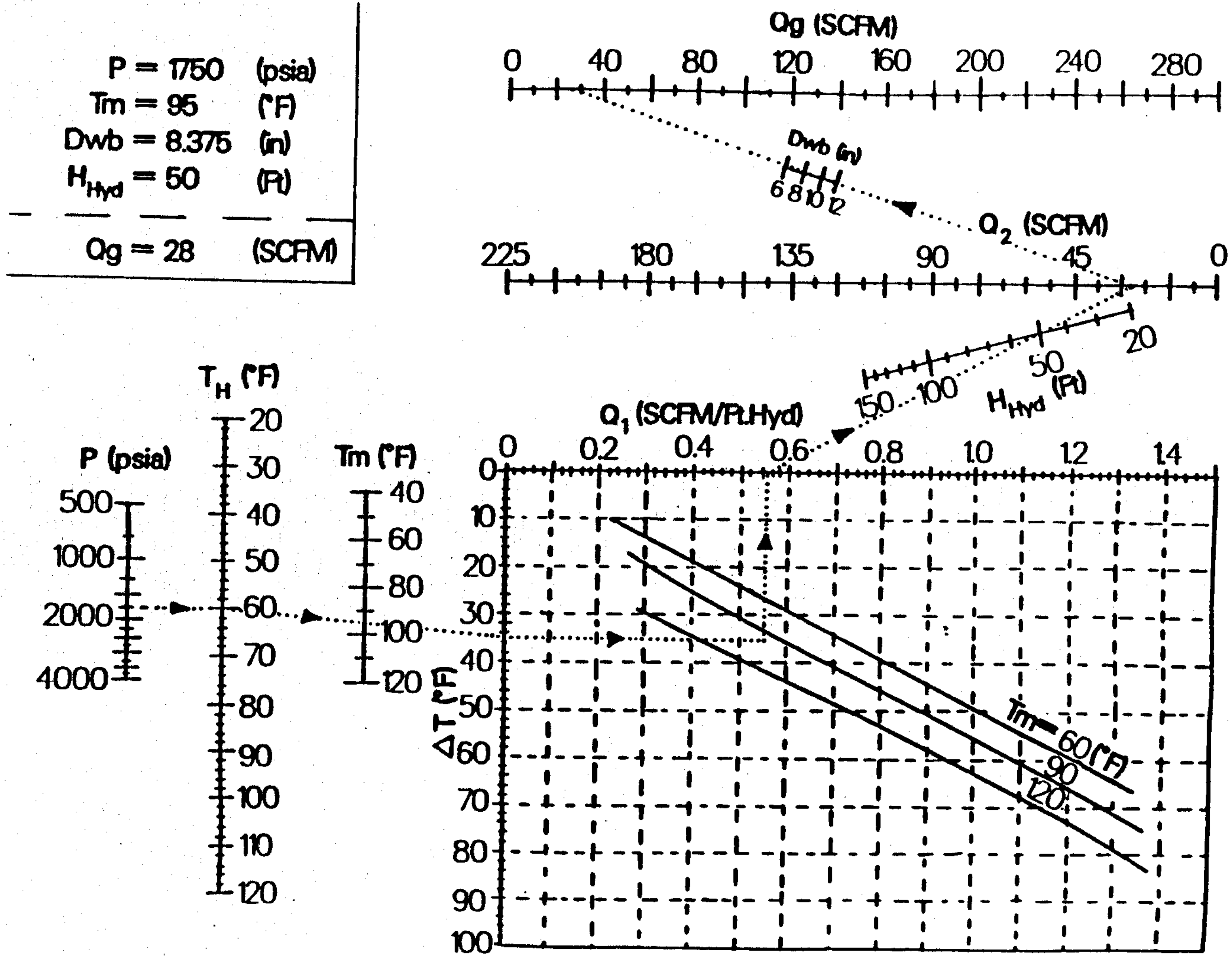


FIGURE 14: NOMOGRAM FOR ESTIMATION OF PARAMETERS WHILE DRILLING THROUGH HYDRATES

12. POTENTIAL OF HYDRATES AS AN ENERGY RESOURCE

The presence of in-situ natural gas hydrates in Arctic and suboceanic regions has been well documented. Potentially huge deposits of hydrates have been identified in cold regions such as Arctic Alaska, the preliminary estimates for Alaskan onshore and offshore regions being approximately 500 million cubic feet of gas-in-place. (Holder et al, 1984). Hydrates possess several characteristics which make them an attractive alternate source of energy for the future. First of all, hydrates represent a concentrated form of natural gas i.e. one cub feet of hydrate can contain as high as 160-180 ft^3 of natural gas. Secondly, they possess an energy content comparable to that of heavy oil. Thus, the energy content of a hydrate reservoir is approximately 45,000 to 60,000 Btu/cubic feet of hydrate. Also, from a thermodynamic viewpoint, the recovery of gas from a hydrate reservoir is an energy efficient process. Thus, only 10% of the energy recoverable from the gas is consumed in recovering it from hydrates.

It is well established that hydrates contain about 10 to 15 weight % natural gas, depending upon the gas composition, and hence they can be considered as a potential energy source in the future if they can be economically recovered. In addition, even the most conservative estimates of natural gas in hydrate form are significantly greater than the conventional gas deposits. Though several recovery schemes like thermal recovery, depressurisation, inhibitor injection etc. have been suggested to recover gas from the hydrates, they have not been found to be economically attractive primarily due to the abundant supplies of conventional gas. With the depletion of the conventional gas resources, there will be an increasing need to develop production technologies to harness this resource, particularly because of its widespread occurrence.

For hydrate production to be feasible, it appears that free gas should be laterally associated with hydrated gas and that too extensively (Franklin, 1980). For recovering natural gas, Panarctic suggested a novel approach, wherein the dissociation of hydrates is influenced by the free gas laterally associated with it. By employing low weight muds and proper degassing equipment on the surface, they tried to promote early dissociation, while the drill pipe was in the hole. Recently, Roadifer et al (1987) have studied the effect of varying drilling parameters for safe drilling through potential hydrate zones and have provided guidelines for promoting and preventing dissociation.

The heat required to convert the hydrates to gas and water is about 60-120 kJ/mole of gas, which is nearly 10 percent of the heating value of the gas. However, the hydrate dissociation process maybe accompanied by large heat losses to overburden and under formations, which can make the gas production uneconomical. Holder et al (1986) have compared the economics of gas production from hydrate deposits by thermal recovery and depressurisation techniques, on the North Slope of Alaska. Their analysis indicates that thermal techniques are uneconomical even with multiple zones, though depressurisation technique might be feasible. For producing gas from offshore hydrate deposits by the depressurisation technique, the break-even-prices are lower.

For developing viable gas recovery techniques from hydrates, it is necessary to study, in detail, the in-situ nature of hydrates, characteristics of the media in which they occur (like porosity, permeability of hydrated and unhydrated zones), extent of hydrate saturation in the pores of the reservoir, heat requirements for hydrate dissociation and problems associated with production due to low permeabilities and cold environment.

13. PREVENTION OF HYDRATE FORMATION

Though gas hydrates were discovered way back in 1810, the study of gas hydrates did not have any indrect industrial bearing until in 1936. Mammerschmidt (1934) discovered that the plugging of natural gas pipelines was primarily due to the formation of gas hydrates. It was then that the research of hydrates received an impetus and efforts were made to develop techniques to prevent formation of hydrates in natural gas pipelines.

One of the first attempts to study hydrate inhibition technique was in the late 50's, when Scauzillo (1956) investigated the effectiveness of both liquid hydrocarbons and glycols in inhibiting the formation of gas hydrates. He conducted hydrate inhibition tests on three mixtures of natural gas and a saturated hydrocarbon oil in presence of excess brine, and also, on two mixtures of the residue gas and an absorber oil in presence of excess distilled water. He concluded that the hydrate formation temperature of gas was lowered if liquid hydrocarbons are also present in natural gas, and that hydrate formation can be inhibited by glycol solutions. It was also found that the combined effect of liquid hydrocarbons and the aqeous glycol solutions approach additive properties with decrease in gas/oil ratio.

In the late 1970's, Mobil reported the installation of a new methanol injection system to prevent production loss due to hydrate formation in the long flow lines between wells and production platforms in the Gulf of Mexico (Bleakley, 1970). A detailed analysis of the various techniques indicated that the most economically viable technique for prevention of hydrate formation was that of methanol injection directly at the well site. The system was so designed as to inject the optimum amount of methanol at each well head. The injection system was required to be operated only during the colder months of the year since no hydrate formation was found to occur below the Gulf water temperatures of 68°F. Also, no attempt was made to recover the injected methanol, as it was found to be economically unattractive.

Recently, Menten et al (1981) have proposed a theoritical method to predict the effect of inhibitors on the conditions of formation of natural gas hydrates. The method can be used to preduct the effect of inhibitors (like KC1, $CaCl_2$, CH_3OH and C_2H_5OH) using existing hydrate parameters and literature data and can be readily extended to other inhibitors and gas mixtures.

To prevent hydrate formation in measuring and regulating equipment, certain precautions have to be taken. It is possible to avoid down time and a lot of operational problems by proper design and handling procedures in gas production e.g. avoiding unnecessary pressure and temperature drops, insulation of piping to keep gas temperature above hydrate zone, providing isolation and blowdown valves with points for methanol injection etc.

It is possible to predict change in conditions of hydrate formation and hydrate prevention from generalized graphs showing effect of pressure and inhibitor solution concentration on the hydrate formation conditions for different gases (Makagon, 1981). For gases of different compositions at different pressures, it is found that the hydrate formation temperature is lowered by different amounts by injecting an inhibitor solution of a specified concentration.

Koledezni and Arshinov (1970) have discussed the method of hydrate inhibitor injection in the bottom hole well bore vicinity at Messoyakha field. They suggested that 30% calcium chloride solution be used as inhibitor in summer and a mixture of methanol and calcium chloride in winter, the quantity of inhibitor being calculated taking into consideration the capacity of the casing. A cyclic procedure of inhibitor injection, followed by oil production is followed, where the frequency of inhibitor injection can be determined by field experimentation. They also suggested that if hydrates existed in well bore hole, it was necessary to inject inhibitor continuously to avoid formation of hydrates.

14. Environmental Problems due to Hydrate Formation & Dissociation

If hydrates are present in conjunction with oil or free gas, although they provide a potential source of free gas, they also affect the produceability of the crude oil or natural gas reservoir. The formation of gas hydrates in oil and gas reservoirs drastically reduces the permeability of the reservoir to oil and gas flow.

In addition, a crude oil may be denuded of its lighter components, due to formation of hydrates. This not only increases the viscosity of the oil but also reduces the efficiency of the recovery processes. (Holder et al, 1976, Verma et al, 1974). Also, it has been reported that there have been gas blowouts in coal mines due to accumulation and decomposition of gas hydrates in porous media, (Makogen, 1978).

Topham (1984 a,b) has reported that the formation of hydrates in deep sea environment may result in an oil well blowout due to channelling of gas in the form of hydrated plumes of hydrocarbon gases. This reduces the buoyancy of the otherwise fast rising bubble plumes, thereby causing extensive damage.

Recently, Godbole et al (1987) have analysed the hydrate formation and dissocation from bubble plumes rising in deep sea waters. The zones of hydrate formations in deep waters have been determined for various potential arctic offshore exploration areas. A new hydrodynamic model for the hydrate forming bubble plumes has been developed which includes spherical as well as elliptical bubble shapes with appropriate drag coefficients. The model also addresses the ultimate fate of the oil after the hydrated plume dissociates back into gas.

Apart from these there are other problems due to hydrate formation or dissociation in the reservoir or near well bore.

Hydrate dissociation can cause soil compaction due to phenomena similar to thaw subsidence in permafrost.

Hydrate formation can cause freeze back pressure phenomena and cause damages to the well bore.

15. OTHER USES OF HYDRATES

One of the principal areas in which hydrates can be potentially used is in the desalination fo sea water (Knox et al, 1961, Barduhn et al, 1962). In this approach, pure water is separated from its solution in a solid form by reacting with hydrating agents like propane, methl bromide, Freon 22 etc, to form a gas hydrate. As hydrates are stable above 0oC, refrigeration costs can be reduced in processes that use freezing methods to desalineate sea water.

Gas hydrates can be used as a form of underground storage of natural gas (Parent, 1968), who found that the storage of natural gas as a solid was more safer than as liquid. Child (1964) suggested that hydrates can be used in transporting and storing radioactive gases such as Krypton, which itself is capable of forming hydrates. makagon (1974) suggested that hydrates could be used as gas blowout preventer in coal mines as well as in fog and cloud dispersion.

16 NOMENCLATURE

a	Kihara Special Core Radius
b	Structure dependent parameter for specific heat
Cij	Langmuir constant for an ith molecule in a jth cavity
L_1	Water rich liquid phase
L_2	Hydrocarbon rich liquid phase
M	Hydrocarbon gas M
N	Integer Constant
n	Hydrate number
P	Dissociation pressure, kPa or psi
R	Gas Constant, Joule/mole.K
Rj	Radius of cavity j
r	radial distance from centre of cavity
T	temperature, °C or °K
V	Vapour phase
f	gas phase - fugacity
Wij	smoothed cell potential function
Vj	ratio of number of j cavities to the number of water molecules in hydrate phase
I	rate of formation of nuclei
Dw	diffusivity of water through hydrate film
V_T	radial growth rate of surface film hydrate
Mw	water diffusion rate
Dw	Diffusivity of water through hydrate film
STP	Standard Temperature and Pressure
a_s	interfacial area

Greek Letters

Δ	indicates difference in property
ε	gas-water Kihara energy parameter, joule/molecule
μ	chemical potential of water, joule/mole
σ	Kihara distance paramater, pm
θ	Fractional occupancy of the cavity
ω	Accentric factor of gas molecule
τ	Hydrate growth time
γ	overall order of reaction w.r.t. pressure
χ	absolute activities
ζ	density in hydrate phase

Subscripts

1	In pure water
2	in aqueous solution
g	gas phase
h	Hydrate Phase
i	Gas Species, i
j	Cavity type j
liq	liquid phase
$solid$	solid (ice) phase
w	water or ice phase
B	unoccupied water phase

17. REFERENCES

1. Allen, K.W. and Jeffrey, G.A.: *On the Structure of Bromine Hydrate,* J. Chem. Phys., 38, 2304. (1963).

2. Aoyagi, K., Song, K.Y., Sloan, E.D., Pharmawardhana, P.B. and Kobayashi, R.: *Improved Measurements and Correlation of the Water Content of Methane Gas in Equilibrium with Hydrates,* Proc. 58th Ann. GPA Convention, Mar. 19-21, 1979, Denver, CO.

3. Aoyagi, K., Song, K.Y., Kobayashi, R. Sloan, E.D. and Pharmawardhana, P.B.: Research Report RR-65, GPA, Dec. 1980.

4. Baner, R.M. and Ruzicka, D.I.: *Non-Stoichiometric Clathrate Compounds of Water, Part 6, Kinetics of Formation of Clathrate Phases,* Trans. Faraday Soc. 58:2202-2271 (1964).

5. Barduhn, A.J. and Lee, W.C.: *Thermodynamic Properties of F-22 (CHClF2) Hydrate for Use in Desalting,* Desalination, Vol. 25, pp. 151-162 (1978).

6. Barduhn, A.J., Towlson, N.S., and Hu, Y.C.: *The Properties of Some New Gas Hydrates adn Their Use in Demineralizing Sea Water,* AIChE Journal, May 1962, Vol. 8 (No. 2), pp. 176-183.

7. Barduhn, A.J.,: *Distillation by Crystallisation Processee,* Chem. Eng. Prog. 63(1), 98 (1967).

8. Barrer, R.M. and Ruzicka, D.J.: *Non-Stoichiometric Clathrate Compounds of Water, Part 6 - Kinetics of Formation of Clathrate Phases,* Transactions of the Faraday Society, Vol. 58, pp. 2262-2271 (1982).

9. Barrer, R.M. and Edge, and A.V.J.: *Gas Hydrates Containing Argon, Krypton and Xenon: Kinetics and Energetics of Formation and Equilibria,* Proceedings of the Royal Society of London, Vol. 300A, pp. 1-24 (1967).

10. Barrer, R.M. and Ruzicka, D.J.: *Non-Stoichiometric Clathrate Compounds of Water,* Trans. Faraday Society, Vol. 58, No. 6, p. 2262 (1962).

11. Bayles, G.A., Sawer, W.K., Anada, H.R., Reddy, S. and Malone, R.D.: *A Steam Cycling Model for Gas Production from a Hydrate Reservoir,* paper presented t the Winter National American Institute of Chemical Engineers Meeting, Atlanta, GA (Mar. 11-14, 1984).

12. Bily, C. and Dick, J.W.L.: *Naturally Occurring Gas Hydrates in the McKenzie Delta, N.W.T.,* Bulletin of Canadian Petroleum Geology, V. 22, No. 3, pp. 340-352 (1974).

13. Blanchard, D.C. and Tailleur, I.L.: *Temperature and Interval Geothermal-Gradient Determinations from Wells in National Petroleum Reserve in Alaska,* U.S. Geological Survey Open File Report, No. 82-391, p. 79 (1982).

14. Bleakley, W.B.,: *Mobil's Methanol-Injection System Prevents Gulf-Hydrate Formation,* The Oil and Gas Journal, December 7, 1970, pp. 65-67.

15. Bourgoyne, A.T., Jr., Chenevent, M.E., Millheim, K.K., and Young, F.S., Jr.: Applied Drilling Engineering, SPE Textbook Series, Vol. 2 (1986).

16. Bozzo, A.T., Misiano - Sheng Chen, Kass, J.R., Barduhn, A.J.: *The Properties of the Hydrates of Chlorine and Carbon Dioxide* (1973), Paper 206 presented at the Symposium of European Federation of Chemical Engineers on Fresh Water from the Sea, Sept. 9-16, 1973, Heidelberg, Germany.

17. Brewer, M.C.: *Some Results of Geothermal Investigations of Permafrost in Northern Alaska*, Trans. of the American Geophysical Union, V. 39, No. 1, pp. 19-26 (1958).

18. Brooks, J.M., Kennieutt, M.C., Fay, R.R., McDonald, T.J. and Sassen, R.: *Thermogenic Gas Hydrates in the Gulf of Mexico*, Science, V. 225, pp. 409-411.

19. Brown, J.F., Jr.,: *Inclusion Compounds*, Sci. Amer. 207, 82 (1962).

20. Byk, S.Sh. and Fomina, V.I.: *Gas Hydrates*, Russian Chemical Reviews, Vol. 37 (6), pp. 469-491 (1968).

21. Byk, S.Sh., Fomina, V.I. and Skurgat, E.N., 992 Prom. No. 8,30 (1955).

22. Campbell, J.M. and McLeod, H.O.: Trans, AIME, 222, 590 (1961).

23. Carson, D.B. and Katz, D.L.,: *Natural Gas Hydrates*, Trans. AIME, Vol 160 (1962), p. 150.

24. Cecootti, D.J.: *Crystallization of Gas Hydrates from Vapor Phase*, Industrial and Engineering Chemistry Fundamentals, Vol. 5 (1), p. 106 (1966).

25. Cherski, N.V. and Makogen, Y.F.,: *Solid Gas World Reserves are Enormous*, Oil Gas Invest., 10 (8), 82 (1970).

26. Cherski, N.V. and Pondarev, E.A.,: *Thermal Dissociation of Gas Hydrate Deposits*, Dokl, Akad. Nauk SSSR. 203,550 (1972).

27. Chinworth, H.E. and Katz, D.L.: *Refrig. Eng.*, 541, 349 (1947).

28. Churchill, S.W. and Evans, L.B., : *Coefficients for Calculation of Freezing in a Semi-Infinite Region*, Trans ASME, J. Heat Transfer, 93,236 (1971).

29. Clark, E.C., Ford, R.M. and Glew, D.N., Canad. J. Chem., 62,2027 (1964).

30. Claussen, W.F.: *Suggested Structures of Water in Inert Gas Hydrates*, Journal of Chemical Physics, Vol. 19, pp. 662-665 (1951).

31. Collett, T.S., Godbole, S.P. and Ehlig-Economides, C.: *Quantification of Gas Hydrates on North Slope of Alaska*, Proceedings of the 35th Annual Meeting of Canadian Institute of Mining, Calgary, Canada (June 10-12, 1984).

32. Collett, T.S.: *Detection and Evaluation of Natural Gas Hydrates from Well Logs, Prudhoe Bay, Alaska*, M.S. Thesis, University of Alaska - Fairbanks (1983).

33. Collett, T.S. and Ehlig-Economides, C.: *Detection and Evaluation of the In-Situ Natural Gas Hydrates in the North Slope Region, Alaska*, a paper presented at the 1983 California Regional Meeting held in Ventura, CA, SPE #11673 (March 23-25, 1983).

34. Cook, J.G. and Leaist, D.G.: *An Exploratory Study of the Thermal Conductivity of Methane Hydrate*, to be published.

35. Cooper, A.K., Scholl, D.W., Marlow, M., Childs, J., Redden, G., Kvenvolden, K. and Stevenbon, A.: *Hydrocarbon Potential of Aleutian Basin, Berring Sea*, Amer. Assoc. Petro. Geol. Bull., Vol. 63 (11) Nov. 1979, p. 1079-2087.

36. Davidson, D.W., El-Defrawg, M.K., Fuglem, M.O., and Judge, A.A.: *Natural Gas Hydrates in Northern Canada*, Proceedings of the Third International Conference on Permafrost, Edmonton, Canada, Vol. 1 (1976).

37. Deaton, W.M. and Frost, E.M.: *Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines*, U.S. Bureau of Mines, Monograph 8:108 (1946).

38. Deaton, W.M. and Frost, E.M., Gas, 16. No. 6,28 (1960).

39. Deaton, W.M. and Frost, E.M., Amer. Gas Assoc., Dallas (Texas) (1960-9).

40. Deaton, W.M. and Frost, E.M., Amer. Gas Assoc., Dallas (Texas) (1961).

41. Deaton, W.M. and Frost, E.M.: U.S. Department of the Interior, Bureau of Mines, Monograph 8, 1966.

42. de Boer, R.B.,: *Hydrate Formation in Cormorant South Subsea Oil Well*, Shell Internationale Research Moatschappij, B.V., Publication 668, Oct. 1983.

43. de Forcrand: *Composition of Hydrates of Gases*, Compt. Rend., Vol 134 (1902), pp.835, (J. Chem. Soc.) Vol. 82, pp. 666.

44. Diepen, G.A.M. and Scheffer, F.E.C., Rec. Trans. Chim., 69,593 (1950).

45. Dillon, W.P.,: *Unconventional Gas Hydrate Seals May Trap Gas Off Southeast U.S.*, Oil Gas Journal, Jan. 7, 1980, p. 126.

46. Dobrynin, V.M., Korokajer, U.P., Plyuschev, D.V.,: *Gas Hydrates*, IIASA Conf., 4th, Montreal, Canada (1979).

47. Dyadin, Y.A. and Aladko, L.S.: *Compositions of Clathrate Hydrates of Bromine*, Inst. of Inorg., Chem., Academy of Science of the USSR, Siberian Branch. Translated from Journal Strukturnoi Khimit 18(1), pp. 51-57 (1977).

48. Evrenos, A.L., Heathman, J. and Ralstin, J.: *Impermeation of Porous Media by Forming Gas Hydrates In-Situ*, Journal of Petroleum Technology, Vol. 23, p. 1059 (1971).

49. Ewing, J.I. and Hollister, C.D.,: *Regional Aspects of Deep Sea Drilling in the Western North Atlantic*, in C.D. Hollister, et al; eds. Initial Reports of the Deep Sea Drilling Project II, U.S. GPO, Washington, p. 951, 1972.

50. Falabella, B.J.: *A Study of Natural Gas Hydrates*, (unpublished Ph.D. Dissertation, University of Massachusetts - 1975).

51. Faraday, M.: *On Fluid Chlorine*, Philosphical Royal Society London Transactions, Vol. 22A, pp. 160-189 (1823).

52. Ferriana, O.J., Jr.: *Permafrost Map of Alaska*, U.S. Geological Survey, Misc. Geology Map I-445 (1965).

53. Franklin, L.J.: *Hydrates in the Arctic Islands*, Articles, Proceedings of Workshop on Clathrates (Gas Hydrates) in the National Petroleum Reserve in Alaska, Menlo Park, CA, edited by Bowsher, A.L. (July 16-17, 1979).

54. Franklin, L.J.: *In-Situ Hydrates: A Potential as Resource*, Petroleum Engineers International, pp. 112-122 (Nov. 1980).

55. Garg, S.K., Davidson, D.W., Gough, S.R., Reepmester, J.A.: *The Confirmation and Reorientation of Enclathrated 1,2 - dichloroethane*, Can. J. Chem. 57,635 (1979).

56. Garg, S.K., Majid, Y.A., Ripmeester, J.A. and Davidson, D.W.: *Reonentation and Diffusion of Water Molecules in Xeron Hydrate and Other Structure Clothrate Hydrates*, Mol. Phys. (1977), Vol. 33, No. 3.729-736.

57. Godbole, S.P. and Kamath, V.A., *Simulation of Thermal Recovery of Heavy Oil in the Presence of Hydrates*, Proceedings of the Unconventional Gas Recovery Contractors Review Meeting (DOE) held in July 28-29, 1987, Morgantown, WV (1987).

58. Godbole, S.P., *Dissociation pressures of propane and i-butane Hydrates below the Ice Point*, M.S. Thesis, University of Pittsburgh, Chemical & Petroleum Engineering Department. (1981).

59. Godbole, S.P., Kamath, V.A., and Ehlig-Economides, C.E.: *In-situ Natural Gas Hydrates in Alaska*, to be published SPE Formation Evaluation (1987).

60. Godbole, S.P., Kamath, V.A. and Mutalik, P.N. *Hydrate Formation as a Barrier to Environmental Problems in Deep Ocean Oil Well Blowout*, to be submitted to Chemical Engineering Communications.

61. Godbole, S.P., Kamath, V.A., and Ehlig-Economides, C.E.: *Natural Gas Hydrates in the Alaskan Arctic*, to be published SPE Reservoir Engineering (1987).

62. Goodman, M.A.: *World Oil's Handbook of Arctic Well Completions*, World Oil, pp. 13-15 (1978).

63. Goodman, M.A. and Franklin, L.J.: *Thermal Model of New Concept for Hydrate Control During Drilling*, Paper presented at the Canadian Permafrost Conference (1981).

64. Goodman, M.A. and Guissani, A.P.: *Detection and Evaluation Methods for In-Situ Gas Hydrates*, SPE/DOE #10831 (1982).

65. Gough, S.R.: *The Clathrate Hydrate of 2-Methylpropanol: Dielectric Evidence*, Can. J. Chem., 56 202S (1978).

66. Gough, S.R., Garg, S.K., Ripmeester, J.A. and Davidson, D.W.: *Dielectric Relaxation and NMR Studies of Two Clathrate Hydrates of Dimethyl Ether*, J. of Phy. Chem. 81 (23), (1977).

67. Grantz, A., Boucher, A., Whitney, O.J.,: *Possible Solid Gas Hydrates and Natural Gas Deposits Beneath the Continental Slopes of the Beaufort Sea*, U.S. Geol. Surv.Circ. 733:17 (1978).

68. Hafemann, D.R. and Miller, S.L.: *The Clathrate Hydrates of Cydopropane*, J. Phys. Chem., 73(5) (1969), pp. 1392-1397.

69. Hafemann, D.R. and Miller, S.L.: *The Deuterohydrate of Cydopropane*, J. Phys. Chem. 73(5) (1969), pp. 1398-1601.

70. Halleck, P.M., Byrer, C.W., McGuire, P.L., Judge, A.S., Corlett, P.C., Barrclough, B.: Group Discussion, Proc. Methane Hydrate Workshop, Morgantown, WV, pp. 663-72 (Mar. 29-30).

71. Hammerschmidt, E.G.: *Formation of Gas Hydrates in Natural Gas Transmission Lines*, Industrial and Engineering Chemistry, Vol 26, p. 851 (1934).

72. Hawkins, R.E. and Davidson, D.W.: *Dielectric Relaxation in the Clathrate Hydrates of Some Cylic Ethers*, Journal of Phys. Chem. 70(6) (1966) p. 1889.

73 Holder, G.D., Kamath, V.A. and Godbole, S.P.: *The Potential of Natural Gas Hydrates as an Energy Resource*, Annual Review of Energy, pp. 427-45 (1984).

74. Holder, G.D., Angert, P.F., John, V.T., and Yen, S.: *A Thermodynamic Evaluation of Thermal Recovery of Gas from Hydrates in the Earth*, J. Pet. Tech. (34), p. 1122 (May, 1982).

75. Holder, G.D., Angert, P.F., John, V.T., Yen, S.: *A Thermodynamic Evaluation of Thermal Recovery of Gas Hydrates in the Earth*, J.Petr. Technol., 34:1127-32 (1982).

76. Holder, G.D., Angert, P.F., Godbole, S.P.: *Simulation of Gas Production from a Reservoir Containing Both Gas Hydrates and Free Natural Gas*, Proc. Soc. Petr. Eng. Meet., New Orleans, LA, SPE 11105 (Sept. 26-29).

77. Holder, G.D., John, V.T. and Yen, S.: *Geological Implications of Gas Production from In-Situ Gas Hydrates*, SPE/DOE 8929, Paper presented at the 1980 SPE/DOE Symposium on Unconventional Gas Recovery held in Pittsburgh, PA (May 18-21, 1980).

78. Holder, G.D., Katz, D.L., and Hand, J.H.: *Hydrate Formation in Subsurface Environments*, American Association of Petroleum Geologists Bulletin, Vol. 60 (6), pp. 981-994 (1976).

79. Holder, G.D. and Godbole, S.P.: *Dissociation Pressures of Isobutane and Propane Hydrates Below the Ice Point*, AIChE Journal, Vol. 28, p. 830 (1982).

80. Holder, G.D., Malone, R.D. and Lawson, W.F., *Effects of Gas Composition and Geothermal properties on the Thickness and Depth of Natural Gas Hydrate Zones*, Journal of Petroleum Technology, September 1987, pp. 1167.

81. Holder, G.D. and Godbole, S.P., *A Gravimetric Technique for Determining Dissociation Pressures of Gas Hydrates Below the Ice Point*, AIChE Journal, V. 28(6). pp. 930-34 (Nov. 1982).

82. Holder, G.D., Corbin, D. and Papodopoulos, K.D.,: *Thermodynamic and Molecular Properties of Gas Hydrates from Mixtures Containing Methane, Argon and Krypton*, Ind. Eng. Chem. Fundam., 1980, 19, 2828.

83. Holder, G.D., Stephenson, J.L., Joyce, J.I., John, V.T., Kamath, V.A. and Malekar, S., Ind. Eng. Chem. Proc. Des. Dev., Vol. 22 (1983), p. 170.

84. Holder, G.D.,: *Multiphase Equilibria in Methane-Ethane-Propane-Water Hydrate Forming Systems*, Ph. D. Dissertation, School of Chemical Engineering, U. of Michigan (1976).

85. Holder, G.D. and Hand, J.M.,: *Multiphase Equilibria in Hydrates from Methane, Ethane, Propane and Water Mixtures*, AIChE J, Vol. 28 (1982), pp. 440-447.

86. Holder, G.D. and Manganiello, R.J.: *Hydrate Dissociation Pressure Minima in Multicomponent Systems*, Chem. Engg. Sci., 37 (1), pp. 9-16 (1982).

87. Holder, G.D. and Kamath, V.A..: *Experimental Determination of Dissociation Pressures For Hydrates of Cis and Trans Isomers of 2-Butene Below the Ice Temperature*, J. Chem. Thermodynamics, 1982, 14, pp. 119-1128.

88. Holder, G.D. and Kamath, V.A.: *Hydrates of methane + Cis-2-Butene and Methane & Trans-2-Butene*, J. Chem. Thermodynamics, 1984, 16, pp. 399-600.

89. Holder, G.D. and Grigoriou, G.C.: *Hydrate Dissociation Pressure sof (Methane + Ethane + Water): Existence of a Locus of Minimum Pressures*, J. Chem. Thermodynamics, 1980, pp. 1093-1104.

90. Hollister, D.C. Ewang, J.I. et al, *Initial Reports of the Deep Sea Drilling Project* U.S. GPO, Washington, D.C., p. 951 (1972).

91. Jhaveri, J. and Robinson, D.B.: *Hydrates in the Methane-Nitrogen System*, Can. J. Chem. Engg. 63 (2) p. 75 (1965).

92. John, V.T.: *Improved Predictions of Gas Hydrate Phase Equilibrium*, Ph.D. Dissertation, Columbia University, School of Engineering and Applied Science (1981).

93. John, V.T. and Holder, G.D.: *Contribution of Second and Subsequent Water Shells to the Potential Energy of Guest-Host Interactions in Clathrate Hydrates*, Journal of Physical Chemistry, Vol. 86, pp. 455-459 (1982).

94. John, V.T., Papadopoulos, K.D., and Holder, G.D.: *A Generalized Model for Predicting Equilibrium Conditions for Gas Hydrates*, AIChE J., Vol. 31, No. 2, p. 252 (1985).

95. John, V.T. and Holder, G.D.: *The Hydrates of Methane + N-Butane Below the Ice Point*, J. Chem. Engg. Data, Vol. 27 (1982, p. 18.

96. Judge, A.S.: *Natural Gas Hydrates in the Mckenzie Delta-Beaufort Sea Areas of North Canada*, AIChE Meeting (Mar. 1984).

97. Kamath, V.A.: *Study of Heat Transfer Characteristics During Dissociation of Gas Hydrates in Porous Media*, (unpublished Ph.D. Dissertation, School of Engineering, University of Pittsburgh - 1983).

98. Kamath, V.A., Godbole, S.P., Ostermann, R.D. and Collett, T.S.: *Evaluation of the Stability of Gas Hydrates in Northern Alaska*, Cold Regions Science and Technology Vol. 14, p. 107 (1987).

99. Kamath, V.A.: *Dissociation Pressures of Hydates of Propane, Cis-2-Butene, Trans-2-Butene, Propane/n-Butane, and Propane/Trans-2-Butane Mixtures Below the Ice Point*, M.S. Thesis, University of Pittsburgh, School of Chemical Engineering (1982).

100. Kamath, V.A. and Godbole, S.P.: *Evaluation of Hot Brine Stimulation Technique for Gas Production from Natural Gas Hydrates*, Proceedings of the SPE Regional Meeting, CA, SPE 13596 (Mar. 1985).

101. Kamath, V.A., Godbole, S.P. and Baena, C.J.: *Effect of Dissociation of Hydrates During Thermal Recovery of Heavy Oils on the North Slope, Alaska*, Paper presented at the 60th Annual Technical Conference and Exhibition of SPE, Las Vegas, NV, SPE 14224 (Sept. 1985).

102. Kamath, V.A., Godbole, S.P. and Meherdad, N., *Permeability Measurements in Hydrate Saturated Cores*, under preparation (1987).

103. Kamath, V.A., Holder, G.D. and Argert, P.F.: *Three Phase Interfacial Heat Transfer During the Dissociation of Propane Hydrates*, Chem. Engg. Science, Vol. 39 (10), pp. 1635-1442 (1984).

104. Kamath, V.A. and Holder, G.D.: *Dissociation Heat Transfer Characteristics of Methane Hydrates*, AIChE J., 33 (2), 347 (1987).

105. Kamath, V.A., Holder, G.D. and Ng. H.Y.: *The Hydrates of Propane/N-Butane, Propane/Trans-2-Butane, Propane/IsoBUtane, Hs-2-Butane and Trans-2-Butane, Below the Ice Point*, Paper presented at the Annual AIChE Meeting, Los Angeles, CA (Nov. 1982).

106. Kaplan, L.R., ed.: *Natural Gases in Marine Sediments*, Review of Gas Hydrates with Implications for Ocean Sediments by J.H. Hand, D.L. Katz, and V.K. Verma, New York, Plenum Press, Chap. 3 (1974).

107. Kasper, J.S.,: *Clathrate Structure of Silicon Na_8Si_{46} and Na_xSi_{136} (NC11)*, Science, Dec. 1965, p. 1713.

108. Katz, D.L. et al: *Handbook of Natural Gas Engineering*, McGraw-Hill Book Company, New York (1959).

109. Katz, D.L.: *Depths to Which Frozen Gas Fields (Gas Hydrates) May Be Expected,* Journal of Petroleum Technology, V. 23, pp. 419-423 (1971).

110. Katz, D.L.: *Predictions of Conditions for Hydrate Formation in Natural Gas,* American Institute of Mining and Metallurgical Engineering Transactions Technical Publication No. 1748 (1944).

111. Katz, D.L.: Dornell, D., Kobayashi, R., Poettmann, F., Weinaug, C.F., Vary, J.A. and Elenbaas, J.R.: Handbook of Natural Gas Engineering, McGraw-Hill Book Company, N.Y. (1959), (Chris).

112. Keller, H.H., Couch, E.J., and Berry, P.M.: *Temperature Distribution in Circulating Mud Columns,* Society of Petroleum Engineers Journal, pp. 23-30 (Feb. 1973).

113. Knox, W.G., Hess, M., Jones, G.E. and Smith, H.B.: *The Hydrate Process,* Chemical Engineering Progress, Vol. 57, No. 2, pp. 66-71 (February 1961).

114. Kobayashi, R. and Katz, D.L.: *Metastable Equilibrium in the Dew Point Determination of Natural Gases in the Hydrate Region,* Petroleum Transactions of AIME, pp. 262-263, Technical Notes #294 (1955).

115. Kobayashi, R., and Katz, D.L.: *Methane Hydrates at High Pressure,* Trans AIME, 186, 66 (1949).

116. Kobayashi, R. and Katz, D.L.: *Metastable Equilibrium in the Dew Point Determination of Natural Gases in the Hydrate Region,* Trans. AIME, 206, (1955).

117. Kobayashi, R. and Katz, D.L.: Trans AIME, 206, 51 (Aug. 1955).

118. Kobayashi, R. and Katz, D.L., Trans. AIME, p. 86,66 (1969).

119. Kobayashi, R. and Katz, D.L., J. Petrol. Technol., No. 3,66 (1969).

120. Kobayashi, R., Withrow, H.J., Williams, G.B. and Katz, D.L.: *Gas Hydrates Formation with Brine and Ethanol Solutions,* Proc. of 13th Annual Convention, Natural Gasoline Assoc. of America, 27 (1957).

121. Koledezni, P.A. and Arshinov, S.A.: *The Technology of Hydrate Inhibitors Injection at Messoyakha Field,* Russian Journal of Gas Business, No. 11, 1970, Moscow.

122. Krason, J. and Kiesnike, M., *Gas Hydrates in the Russian Literature*, Vol. 5, U.S. DOE, Fossil Energy Report, METC, Oct. 1985, pp. 111-112.

123. Kvenholden, K.A. and McMenamin, M.A.: *Hydrates of Natural Gas: A Review of Their Geological Occurrence,* U.S. Geological Survey Circular 825, p. 11 (1980).

124. Kvenholden, K.A. and McDonald, T.J.: *Gas Hydrates of the Middle American Trench,* DSDP/IPODLeg 84: in R. Von Huene, J. Aubouin et al, Initial Reports DSDP186, U.S. Gov't. Printing Office, Washington, D.C.

125. Lachenbruch, A.H.: *Temperature and Depth of Permafrost on the North Slope of Alaska,* paper presented at the 60th Annual Meeting AAPG Pacific Section Convention (May 22-24, 1985).

126. Lachenbruch, A.H., Sass, J.H., Marshall, V. and Moses, T.H.: *Permafrost Heat Flow and Geothermal Regime* at Prudhoe Bay, Alaska, J. Geophys. Res. 87(B11), pp. 197-200 (1971).

127. Laughlin, A.R.: *Water Content in Natural Gas,* presented at the Gas Conditioning Conference, Norman, Oklahoma, 1969.

128. Laulhere, B.M. and Briscoe, C.F., Gas, 15(9), 21 (1939).

129. Lawson, W.F.: *Acoustic Velocity and Electrical Property Measurements in the DSDP Methane-Hydrate Core,* U.S. DOE, presented at AIChE Winter National Meeting, March 12, 1986, Atlanta, Georgia.

130. Leas, W.J.: *Relative Permeability to Gas,* Petroleum Transactions AIME, Vol. 189 (1950) p. 65.

131. Maini, B.B. and Bishnoi, P.R.: *Experimental Investigation of Hydrate Formation Behavior of a Natural Gas Bubble in a Simulated Deep Sea Environment,* Chemical Engineering Science, Vol. 36, pp. 183-198 (1981).

132. Makagen, Y.F.: *Detection of a Pool of Natural Gas in a Solid (Hydrate Gas) State,* Doklady Akad Naut SSSR, V. 196, pp. 197-200 (1971).

133. Makagen, Y.F., Cieslewez, W.J.: trans, Hydrates of Natural Gas, Tulsa, Oklahoma: Pennwell Publishing Co. (1981).

134. Makagen, Y.F.: *Influence of Transition of Gas-Water Systems in the Earth's Crust on the Technology of Well Drilling and Operation,* proceedings of the Eleventh World Petroleum Congress, Vol. 3, Production, pp. 141.

135. Makagen, Y.F.: *Hydrate Formation in Gas Bearing Strata Under Permafrost,* Gozou. Promst., Vol. 5 (1965).

136. Makagen, Y.F.: *Hydrates of Natural Gas.* Translated from Russian by W.J. Cestwicz, Geoexplorer Association, Inc. (1978). Denver, Colorado.

137. Malone, R.D., Mroz, T.H. and Dominic, K.L.: *Geologic Analysis of Gas Hydrate Deposits,* SPE #15224 (1985).

138. Marshall, D.W. and Bentsen, R.G.: *A Computer Model to Determine the Temperature Distributions in a Wellbore,* Journal of Canadian Petroleum Technology, pp. 63-75 (Jan.-Feb. 1982).

139. Marshall, D.R., Saito, S.H. and Robayashi, R., AIChE J., 10,22 (1964).

140. Mathews, M.: *Logging Characteristics of methane Hydrates,* The Log Analyst, pp. 26-63 (May-June, 1986).

141. McCarthy, G.R.: *Geothermal Investigations on the Arctic Slope of Alaska,* Trans. of the American Geophysical Union, V. 33, No. 4, pp. 589-593 (1854).

142. McCarthy, E.L., Boyd, W.L. and Reid, L.S.: Trans AIME, 189,261 (1950).

143. McKetta, J.J. and Katz, D.L., I.E.C. 40, 853 (1968).

144. McKetta, J.J., Wehe, A.H.: Pet. Refiner, 37,153, (Aug. 1958).

145. McKoy, V. and Sinanogly, O.: *Theory of Dissociation Pressures of Some Gas Hydrates*, Journal of Chemical Physics, Vol. 38, pp. 2946-2956 (1963).

146. McGuire, P.L.: *Methane Gas Production by Thermal Stimulation*, paper presented at the Fourth Canadian Permafrost Conference, Alberta (Mar. 2-6, 1981).

147. McGuire, P.L.: *Methane Hydrate Gas Production: An Assessment of Conventional Production Technology as Applied to Hydrate Gas Recovery*, Los Alamos Sci. Lab. Rep. LA-91-MS, Los Alamos, NM.

148. Menten, P.D., Parrish, W.R., and Sloan, E.D.: *Effect of inhibitors on Hydrate Formation*, Ind. Chem. Process Des. Dev., Vol. 20 (1981), pp. 399-401.

149. METC Topical Report: *Gas Hydrate Project*, Morgantown Energy Technology Center, Topical Report (Feb. 1984).

150. Miller, B. and Strong, E.K.: *Hydrate Storage of Natural Gas*, American Gas Association, Vol. 28, No. 2 (1969), pp. 63-67.

151. Miller, S.L. and Smythe, W.S.: *Carbon Dioxide Clathrate in Martian Ice Cap*, Science, Vol. 170, pp. 531-532 (October 30, 1970).

152. Nair, N.K. and Adamson, A.W.: *Physical Adsorption of Vapors on Ice III, Argon, Nitrogen and Carbon Monoxide*, The Journal of Physical Chemistry, Vol. 74, No. 10, pp. 2229-2230 (May 14, 1970).

153. Nagata, L. and Kobayashi, R.: *Prediction of Dissociation Pressures of Mixed Gas Hydrates from Data for Hydrates of Pure Gases with Water*, Industrial and Engineering Chemistry Fundamentals, Vol 5, p. 466 (1966).

154. Nagata, L. and Kobayashi, R.: *Calculation of Dissociation Pressures of Gas Hydrates Using the Kihora Model*, I & EC Fundamentals 5 (3) (1966).

155. Ng., H.J. and Robinson, D.B.: *The Role of N-Butane in Hydrate Formation*, AIChE J, Vol. 22, No. 4 (1976), p. 636.

156. Ng., N.Y.: *Hydrates of Isobutane and Propane, Isobutane Mixtures and the Determination of Isobutane Composition*, M.S. thesis, University of Pittsburgh, (1983), School of Chemical Engineering.

157. Noafer, L.J. and Katz, D.L.: *Gas Hydrates of Hydrogen Sulphide - Methane Mixtures*, Trans AIME, 201,237 (1956).

158. Osterkamp, T.E. and Payne, M.W.: *Estimates for Permafrost Thickness from Well Logs in Northern Alaska*, Cold Regions Science and Technology, Vol. 5, pp. 13-27 (1981).

159. Otto, F.D. and Robinson, D.B.: *A study of Hydrates in the Methane-Propylene-Water System*, AIChE J. 6(6), (1960.

160. Paranjpe, S.G., Patil, S.L. and Kamath, V.A., *Hydrate Formation in Crude Oils and Phasee Behavior of Hydrates in Mixtures of Methane, Propane, Isobutane and n-Butane*, to be presented at the third Chemical Conference of the North American Continent to be held in Toronto, Ontario, from June 5-11, 1988.

161. Paranjpe, S.G., Patil, S.L., Kamath, V.A. and Godbole, S.P., *Hydrate Equilibria for Binary and Tertiary Mixtures of Methane, Propane, Isobutane, and n-Butane: Effect of Salinity*, SPE 16871, presented at the 62nd Annual Technical Conference and Exhibition of SPE held in Dallas, TX, Sept. 27-30, 1987.

162. Parent, J.D.; *The Storage of Natural Gas as Hydrate*, Inst. Gas Tech. Rep., Bull. #1, 16 (1968).

163. Parrish, W.R., and Prausnitz, J.M.: *Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures*, Industrial and Engineering Chemistry - Process Design and Development, Vol. 11, pp. 26-34 (1972).

164. Patil, S.L.: *Measurements of Multiphase Gas Hydrate Phase Equilibria: Effect of Inhibitors and Heavier Hydrocarbon Components*, M.S. Thesis, University of Alaska, Fairbanks, Petroleum Engineering Department (1987).

165. Pauling, L. and Marsh, R.E.: *The Structure of Chlorine Hydrate*, National Academy of Science Proceedings, Vol. 28, pp. 112-117 (1952).

166. Pearson, C., Murphy, J., Halleck, P., Hermes, R. and Mathews, M.: *Sonic & Resistivity Measurements on Berea Sandstone Containing Tetrahydrofuran Hydrates: A Possible Analog to Natural Gas Hydrate Deposits*, Earth & Space Sciences Division, Las Almos National Laboratory, (1983).

167. Pharmarwardona, M.W.C.: *Thermal Conductivity of the Ice Polymorphs and the Ice Hydrates*, The Journal of Physical Chemistry, Vol. 87, No. 21, 1983.

168. Pinder, K.L: *A Kinetic Study of the Formation of the Tetrohydrofuran Gas Hydrate*, Canadian Jounral of Chemical Engineering, pp. 271-274 (October 1965).

169. Prausnitz, J.M., Chueh, P.L.: *Computer Calculations for High Pressure Vapor-Liquid Equilibria*, Prentice Hall, Inc., Englewood Cliffs, New Jersey (1968).

170. Reamer, H.H., Selleck, F.T., Sage, B.H.: Trans. AIME, 195, 197 (1952).

171. Records, L.R. and Seely, D.H.: Trans, AIME, 192,61 (1951).

172. Roadifer, R.D., Godbole, S.P. and Kamath, V.A.: *Thermal Model for Establishing Guidelines for Drilling in the Arctic in the Presence of Hydrates*, SPE Paper 16361, presented at the SPE California Regional meeting held in Ventura, CA, April 8-10, 1987.

173. Roadifer, R.D., Godbole, S.P. and Kamath, V.A.: *Estimation of Parameters for Drilling in Arctic and Offshore Environmental in the Presence of Hydrates*, SPE Paper 16671, presented at the 62nd Annual Technical Conference and Exhibition of the SPE held in Dallas, TX (Sept. 27-30, 1987).

174. Roberts, O.L. , Brownscombe, E.R. and Hower, E.S.: *Constitution Diagrams and Composition of Methane and Ethane Hydrates*, Oil and Gas Journal, Vol. 39 (1960), pp. 30-37.

175. Roberts, O.L., Brosonscome, E.R. and Howe, L.S., Petrol. Engr. 12, No. 6,56 (1961).

176. Robinson, D.B. and Mehta, B.R.: *Hydrates in the Propane -CO_2-Water System*, Journal of Canadian Petroleum Technology, Jan-Mar 1971, p. 33.

177. Robinson, D.B. and Huton, J.B.: *Hydrate Formation in Systems Containing Methane H_2S and CO_2*, Journal of Canadian Petroleum Technology, Jan-Mar 1967, p. 6.

178. Ross, R.G.: *Clathrate and Other Solid Phases in the Tetrohydrofuran - Water System: Thermal Conductivity and Heat Capacity Under Pressure*, Can. J. Chem., 60, 1982, p. 881.

179. Ross, R.G.: *Unusual PT Dependence of Thermal Conductivity for a Clathrate Hydrate*, Nature, Vol. 290, 26 Mar. 1981, p. 322.

180. Rouher, O.S. and Barduhn, A.J.: *Hydrates of Iso and Normal Butane and Their Mixtures*, Desalination, Vol. 6, (1969), pp. 53-57.

181. Sada, E.: *Surface Tension of Some Molten Salt Hydrates by the Pendant Drop Technique*, J. Chem. Engg. Data, 1986, 79, pp. 117-119.

182. Scauzillo, F.R.: *Inhibiting Hydrate Formations by Hydrocarbon Gases*, Chemical Engineering Progress, Vol. 52 (No. 8), August, 1956, pp. 324-328.

183. Schneider, G.R. and Farrer, J., Tech.: *Office of Saline Water Research Development*, Program Report. #2929 (1968).

184. Schroeder, W.: *Gas Hydrates: A Review*, Samml. Chem. and Chemical Technolgoy Vortrage, Vol. 29, p. 1 (1927).

185. Selim, M.S. and Sloan, E.D.: *Modelling of the Dissociation of an In-situ Hydrate*, SPE 13597, Paper presented at the SPE California Regional Meeting, Bakersfield, CA, March 27-29, 1985.

186. Selim, M.S. and Sloan, E.D.: *Hydrate Dissociation in Sediment*, SPE 16859, Paper presented at the 62nd Annual Technical Conference and Exhibition of the SPE held in Dallas, TX, September 27-30, 1987.

187. Selleck, F.T., Carmichael, L.T. and Sage, B.H., Ind. Eng Chem. 66,2219 (1952).

188. Sharma, G.D., patil, S.L., Kamath, V.A. and Godbole, S.P., *The Potential of Natural Gas in the Alaskan Arctic*, to be presented at the SPE 1988 California Regional Meeting, March 23-25, 1988, Long Beach, California.

189. Shipley, T.H., Houston, M.H., Buffler, R.T., Shaup, F.J., McMillen, K.J., Ladd, J.W., and Worzel, J.L.: *Seismic Evidence for Widespread Possible Gas Hydrate Horizons on Continental Slopes and Rises*, The American Association of Petroleum Geology Bulletin, V. 63, No. 12, pp. 2,204-2,213 (Dec. 1979).

190. Sloan, E.D.: *Measurement of In-Situ Hydrate Thermodynamic Properties*, GRI Final Report (1983).

191. Sloan, E.D., Khoury, R.M. and Kobayashi, R.: *Water Content of Methane Gas in Equilibrium with Hydrate*, Ind. Eng. Chem., 15, 318 (1976).

192. Sloan, E.D.: Progress Report on Project 775-A-82, NGL-Hydrate Two Phase Systems, Prepared for GPA Meeting, March 1982.

193. Snell, L.E., Otto, F.D. and Robinson, D.B.: *Hydrates in Systems Containing methane, Ethylene, Propylene & Water*, AIChE J, 7(3) (1961).

194. Song, K.Y. and Kobayashi, R.: *Measurement and Interpretation of the Water Content of a Methane-Propane Mixture in the Gaseous State in Equilibrium with Hydrate*, I and EC, Fundam., 1982, 21, pp. 391-395.

195. Song, K.Y. and Kobayashi, R.: *Measurements & Interpretation of the Water Content of a Methane-Propane (5.31 Mol%) Mixture in the Gaseous State in Equilibrium with Hydrate*, Paper prepared for submission to I.E.C. Fundamentals, 1981.

196. Sortland, L.D. and robinson, D.B.: *The Hydrates of Methane and Mixaflouride*, Can. J. of Chem. Engg. (1964).

197. Stackelberg, Von, M. and muller, H.R.; *Test Gas Hydrates*, Zeit Electro Chemistry, Vol. 28, pp. 25-49 (1954).

198. Stoll, R.D., Ewing, J., Bryan, G.M.: *Anomoalous Wave Velocities in Sediments Containing Gas Hydrates*, J. Geophys., Res., Vol. 76, p. 2090 (1971).

199. Stoll, R.D. and Bryan, G.M.: *Physical Properties of Sediments Containing Gas Hydrates*, Lamant-Doherty Geological Observatory, Vol. 23, p. 1059 (1971).

200. Stoll, R.D.: *Effect of Gas Hydrates in Sediments, Natural Gases in Marine Sediments*, Ed. from Kaplan, I.R., Plenum Press (1976).

201. Tee, L.S., Gototh, S. and Stewart, W.R.: *Molecular Parameters for normal Fluids*, Industrial and Engineering Chemistry Fundamentals, Vol. 5, pp. 363-368 (1986).

202. Tester, J.W., Vjvins, R.L., and Herrich, C.C.: *Use of Monte Carlo in Calculating Thermodynamic Properties of Water Clathrates*, AIChE Journal, 18 (6), 1220 (1972).

203. Tester, J.W. and Wiegandt, H.F: *The Fluid Hydrates of methlene Chloride and Chloroform: Their Phase Equilibria and Behavior as Influenced by Mexane*, AIChE J, Vol. 15 (2), 1969, pp. 239-244.

204. Thompson, M.: *The Prediction and Interpretation of Downhole Mud Temperature While Drilling*, Paper presented at the 60th Annual Technical Conference and Exhibition of the SPE held in Las Vegas, NV, SPE Paper #14180 (Sept. 1985).

205. Topham, D.R.: *The Formation of Gas Hydrates on Bubbles of Hydrocarbon Gases Rising in Seawater*, Chemical Engineering Science, Vol. 39, No. 5, pp. 821-828 (p. 986).

206. Tophane, D.R.: *The Modelling of Hydrocarbon Bubble Plumes to Include Gas Hydrate Formation*, Chemical Engineering Science, Vol. 39, No. 11, pp. 1613-1622 (1984).

207. Tucholke, B.E., Bryan, G.M. and Ewing, J.I.: *Gas Hydrate Horizons Detected in Seismic Profiler Data from the Western North Atlantic*, American Association of Petroleum Geologists Bulletin, 61(5), pp. 698-707 (1977).

208. Uchida, T. and Hayano, I.: *Hydrate Formation in Isobutane or a Butane Isomer-water Systems at a Given Temperature*, Desalination, Vol. 3 (1967), p. 373.

209. Ullerich, J.N., Selim, M.S., Sloan, E.D.: *Theory and Measurement of Hydrate Dissociation*, AIChE Journal, Vol. 33, No. 5, p. 747 (May 1987).

210. Unruh, C.H. and Katz, D.: *Gas Hydrates of CO2-Methane Mixtures*, Trans. AIME, 186, 83 (1949).

211. Van Cleff A. and Diepen, G.A.M.: *Gas Hydrates of Nitrogen and Oxygen-I*, Recueill, 79 (1960) pp. 582-586.

212. Van Cleff.A. and Diepen, G.A.M.: *Gas Hydrates of Nitrogen and Oxygen I*, Recueil, 86 (1965) pp. 1085-1093.

213. Van Cleff A. and Diepen, G.A.M.: Ethylene Hydrates at High Pressures, Recueil, 81 (1965) pp. 1085-1093.

214. Van der Waals, J.H. and Plateuw, J.C.: *Clathrate Solutions*, Advances in Chemical Physics, Vol. 2 (1959), pp. 1-57.

215. Verma, V.K.: *Gas Hydrates from Liquid Hydrocarbon Water System*, Ph.D. Thesis, University of Michigan, p. 145 (1974).

216. Verma, V.K., Hand, J.H. and Katz, D.K.: *Gas Hydrates from Liquid Hydrocarbons (Methane-Propane-Water System)*; Munich, Germany, Am. Inst. Chem. Engineers -Gesell, Verfahrstechni, V. Cheminingenieurwesen, p. 10 (1974).

217. Verma, V.K. and Holder, C.D.: *Denuding Hydrocarbon Liquid of natural Gas Constituents by Hydrate Formation*, Journal of Petroleum Technology, No. 27, pp. 223-226 (1975).

218. Villard, M., Compt. Rend., 106,1602 (1888-9).

219. Vysniauskas, A. and Bishoi, P.R.: *A Kinetic Study of Methane Hydrate Formation*, Chemical Engineering Science, Vol. 38, No. 7, pp. 1061-1072 (1983).

220. Vysniauskas, A. and Bishoi, P.R.: *Kinetics of Ethane Hydrate Formation,* Chemical Engineering Science, Vol. 40, No. 2, pp. 299-303 (1985).

221. Wagner, J., Erbar, R.C. and Majeed, A.I.: *Aqua + Sim and Phase Equilibria and Hydrate Inhibitor Using the PFGC Equation of State,* GPA Report (1984), pp. 129-136.

222. Weaver, J.S. and Steward, J.M.: In-situ Hydrates Under the Beaufort Sea Shelf, Dome Petroleum Ltd. (1982).

223. Weibe, R., Chem. Rev. 29 675 (1961).

224. Whalley, E.: *Speed of Longitudinal Sound in Clathrate Hydrates,* Journal of Geophysical Research, Vol. 85, NO. B5, Pages 2539-2542, May 10, 1980.

225. Whitten, B.L., Kiefte, M., and Clouter, M.J.: *Determination of Acoustic Velocities in Xerox and Methane Hydrates by Brillouin Spectroscopy,* Geophysical Research Letters, Vol. 9, No. 6, pp. 645-648, June 1982.

226. Wilcox, W.J., Carson, D.B. and Katz, D.L.: *Natural Gas Hydrates,* Ind. Eng. Chem., 33, 662 (1941).

227. Wright, D.A.: *A Kinetic Study of Methane Hydrate Formation from Ice,* M.S. Thesis, School of Engineering, University of Pittsburgh (1985).

228. Wu, B.J., Robinson, D.B. and Ng, H.J.: *Three and Four Phase Hydrate Forming Conditionsin the Methane - Isobutane Water System,* Journal of Chemical Thermodynamics, 8(5):461 (1976).