

DEVELOPMENT OF THERMODYNAMIC MODEL WITH GOPAL'S CONSTANTS FOR THE INHIBITION OF GAS HYDRATES FORMATION IN GAS PIPELINE

ABSTRACT

Hydrate deposition remains a very willful one in the oil and gas industry and costs the industry billions of dollars worldwide for prevention and remediation in pipelines and flowlines. An economic and environmentally friendly solution to the prevention of hydrate formation is prohibitively expensive.

In this study, a thermodynamic model for hydrate inhibition in gas pipelines by applying the Joule Thomson Expansion phenomenon was developed. The model is a function of the specific gravity, initial and final temperatures, and the initial and final pressures. This developed model comes with the Gopal's constants that make the model trainable to fit data from various expansion processes.

The results obtained for sweet gases were compared with that presented by the Gas Processors Suppliers Association (GPSA) and an error of less than 5% ($R^2 = 0.9629$) was observed. The effect on sour gases was also considered. The pseudo-reduced temperature ranges from $1.05 < T_r < 3.0$ and the pseudo-reduced pressure ranges from $0.2 < P_r < 5.4$. But at extreme values of both pressure and temperature, the result of the proposed model deviates significantly from that of GPSA. The robustness of this model and its ease of use makes it applicable for real-time calculations in the transportation and processing of natural gases.

Keywords: Joule Thomson Expansion, Real Gas Equation, Gas Hydrate Formation, Hydrate Inhibition, Sweet Gas, Sour Gas

1. INTRODUCTION

Natural gas hydrates are crystalline ice-like structure of water lattice with cavities which contain guest gases. These crystalline compounds belong to a group of solids called clathrates and are formed from mixtures of water and low molecular weight gases at high pressures and low temperatures. In the oil and gas industry, gas hydrates are a problem in production and gas transmission pipelines serious because they plug pipelines and process equipment.

Hydrate growth in pipelines and flowlines has received considerable attention in recent years [1, 2]. Gas hydrate crystals resemble ice or wet snow in appearance [3, 4, 5] but do not have ice's solid structure, much less dense, and exhibit physical properties that are generally associated with water compounds [6]. The main framework of their structure is water and hydrocarbon molecule occupies the void space in a crystalline network held together by chemically weak bonds with the water [7, 8]. This framework is ice like in nature; however, unlike ice, it has void space and a network structure.

In 1810, Sir Humphrey Davy discovered the formation of hydrates. This was characterized by identification of the species that could form hydrates and the pressure and temperature conditions at which the formation occurred. In 1934, hydrates were the cause of plugged natural gas pipelines [9]. Since then, the oil and gas industry had been willing to investigate the problem of hydrate formation. The hydrate formation can be prevented by heating the cold unprocessed stream well above the hydrate formation region. If the gas water content and pressure is kept constant during heating, the gas would become undersaturated, thereby eliminating one of the conditions necessary for hydrate formation. Hence applying heat, insulating the pipelines, and using chemical additives as inhibitors, are means to keep the operating conditions out of the hydrate-formation region. Hydrate formation is known to mostly occur at valves, orifices, back pressure regulators, flow provers (i.e. flow measurement device) or chokes due to large pressure changes that further result in temperature drops is known as the Joule-Thomson effect. The best method for determining the conditions of hydrate formation is to experimentally measure the formation at the temperature, pressure and composition of interest. Literature is replete on experimental investigations of hydrate formation conditions [6, 9, 10, 11]. Hydrate formation prediction methods are needed to interpolate between measurements because it is impossible to satisfy the infinite number of conditions for which the measurements are needed. However, such experimental endeavours are both time consuming and expensive, relative to industrial needs for several hydrate formation conditions. The accuracy of estimating the natural gas hydrate is extremely important for optimizing the cost of piping systems and processing units. Good knowledge and full understanding of how hydrates could form will assist a lot in developing an accurate and simplified model for inhibiting and remediating its formation in the natural gas pipeline.

In 1959, [12] developed the first thermodynamic model for the formation of gas hydrates using statistical thermodynamics. Though the model has inaccuracies, it provided the fundamental concepts for further study [5, 13, 14]. Gopal's constants were left out in the original thermodynamic model. The study of [16] on thermodynamics statistical model on structure-H hydrate was based on the original work of [12], while an extension of the method of [16] for hydrate prediction generalized for structure-I and -II hydrates was done by [13]. There method use hydrate equilibrium curve to point out the highest possible temperature at which hydrate can exist at a given pressure.

Hydrate formation can be prevented using one or a combination of the following: use of kinetic low dosage hydrate inhibitors (KLDHIs), displace hydrate-prone fluids with dead fluids before the hydrates can form, addition of hydrate inhibitor such as Methanol (MeOH) or Mono Ethylene Glycol (MEG), Injection of Low Dosage Hydrate Inhibitors(LDHI), Removal of water from the hydrocarbon stream or operating at pressure and temperature conditions outside the hydrate-stable region via heating, heat conservation, pressure control, etc. These inhibitors are needed in large amounts and places severe demands on logistics of transportation, storage capacity and injection [17], while pipe heating will add cost and complication to the pipeline.

In this work, a thermodynamic model for hydrate inhibition in gas pipelines by applying the Joule Thomson Expansion phenomenon was developed. The model incorporates that the Gopal's constant, is a function of the specific gravity, initial and final temperatures, and the initial and final pressures.

2. METHODOLOGY

The methodology employed is to analytically establish a relationship between the hydrate formation temperature and the minimum initial temperature for permissible expansion. The minimum initial temperature for permissible expansion is the least temperature needed for expansion which would not result in the formation of hydrates. The principles of cyclic rule,

Maxwell's generalized thermodynamic relations, real gas equation and compressibility correlation were applied in the development of this present model. For simplification, it was assumed that natural gases with the same specific gravity have the same constituents in identical proportions.

2.1 Cyclic Rule

The Joule-Thomson coefficient (μ_{JT}); Joule-Thomson constant (μ_T) and Isobaric specific heat capacity (C_p) are as shown in equations (1) to (6)

$$\left(\frac{dT}{dP}\right)_H \cdot \left(\frac{dP}{dH}\right)_T \cdot \left(\frac{dH}{dT}\right)_P = -1 \quad (1)$$

$$\left(\frac{dT}{dP}\right)_H = -\left(\frac{dH}{dP}\right)_T / \left(\frac{dH}{dT}\right)_P \quad (2)$$

$$\left(\frac{dT}{dP}\right)_H = \mu_{JT} \quad (3)$$

$$\left(\frac{dH}{dP}\right)_T = \mu_T \quad (4)$$

$$\left(\frac{dH}{dT}\right)_P = C_p \quad (5)$$

$$\left(\frac{dT}{dP}\right)_H = -\frac{\mu_T}{C_p} \quad (6)$$

For each of the differential variables, a corresponding relation was developed. From the generalized Maxwell's thermodynamic equations, we can obtain the Joule Thomson constant as shown in the equations (7) – (8):

$$\mu_T = T \left(\frac{dS}{dP}\right)_T + V \quad (7)$$

$$= -T \left(\frac{dV}{dT}\right)_P + V \quad (8)$$

From the general gas equation (9)

$$PV = nZRT \quad (9)$$

$$V = \frac{ZRT}{P} \quad (10)$$

Differentiating equation (10), gives:

$$\left(\frac{dV}{dT}\right)_P = \frac{ZR}{P} + \frac{RT}{P} \left(\frac{dZ}{dT}\right)_P + V \quad (11)$$

Substituting equations (10 and 11) into equation (8) and simplify gives:

$$\mu_T = -\frac{RT^2}{P} \left(\frac{dZ}{dT}\right)_P \quad (12)$$

The specific heat capacity of a gas at constant pressure is given as:

$$Cp_{ideal} = a + bT + cT^2 + dT^3 \quad (13)$$

An ideal gas maintains a constant specific heat capacity regardless of its pressure as long as the temperature is constant. But natural gas is far from ideal, therefore, the deviation from the ideal is accounted for by the residual specific heat capacity which is the temperature derivative of the residual enthalpy. The mathematical description of the process is as follows:

$$C_{p_{\text{real}}} = \frac{\delta H_{\text{real}}}{\delta T} \quad (14)$$

$$H_{\text{real}} = H_{\text{ideal}} + H_{\text{residual}} \quad (15)$$

$$C_{p_{\text{real}}} = \frac{\delta H_{\text{ideal}}}{\delta T} + \frac{\delta H_{\text{residual}}}{\delta T} \quad (16)$$

$$= C_{p_{\text{ideal}}} + \frac{\delta H_{\text{residual}}}{\delta T} \quad (17)$$

$$C_{p_{\text{residual}}} = C_p(\Delta P_{\text{pr}}, \Delta T_{\text{pr}}) \quad (18)$$

From thermodynamics of **residual properties**, we know that;

$$\Delta H = T\Delta S + V\Delta P \quad (19)$$

$$\left(\frac{dH}{dP}\right)_T = \mu_T = -\frac{RT^2}{P} \left(\frac{dZ}{dT}\right)_P \quad (20)$$

with the Integration, gives

$$\frac{dH}{dT} = -RT^2 \int P^{-1} \left(\frac{d^2Z}{dT^2}\right)_P dp - 2RT \int P^{-1} \left(\frac{dZ}{dT}\right)_P dp \quad (21)$$

$$C_{p_{\text{residual}}} = -RT^2 \int P^{-1} \left(\frac{d^2Z}{dT^2}\right)_P dp - 2RT \int P^{-1} \left(\frac{dZ}{dT}\right)_P dp \quad (22)$$

2.2 Gopal's Z-factor Correlation

In 1977, [15] found a method to categorize the different portions of the Standing-Katz correlation of the gas Compressibility factor as a function of the pseudoreduced temperature and pressure, which is of the form:

$$Z = Pr(ATpr + B) + CTpr + D$$

where the values of the coefficients A, B, C and D are dependent on the pseudoreduced temperature. This gives a set of thirteen equations as presented below:

$$\left(\frac{dZ}{dT}\right)_P = APr + C \quad (23)$$

$$\left(\frac{d^2Z}{dT^2}\right)_P = 0 \quad (24)$$

Equation (22) becomes:

$$C_{p_{\text{residual}}} = -2RT/Tc \int P^{-1} (APr + C)_P dp \quad (25)$$

$$= -\frac{2RT}{T_c} \int \left(\frac{A}{P_c} + \frac{C}{P} \right) dp \quad (26)$$

$$= -\frac{2RT}{T_c} \left[\frac{A(P_2 - P_1)}{P_c} + C \ln \left(\frac{P_2}{P_1} \right) \right]$$

Combining equations (13) and (26), gives:

$$C_{p_{\text{real}}} = a + bT + cT^2 + dT^3 - \frac{2RT}{T_c} \left[\frac{A(P_2 - P_1)}{P_c} + C \ln \left(\frac{P_2}{P_1} \right) \right] \quad (27)$$

Having developed an equation for the isobaric Heat capacity of real gases, we can express the Joule-Thomson Coefficient as a differential equation by a combination of the derived relations given in equations (2), (20) and (27) to obtain:

$$\left(\frac{dT}{dP} \right)_H = \frac{-\frac{RT^2}{P} \left(\frac{dZ}{dT} \right)_P}{a + bT + cT^2 + dT^3 - \frac{2RT}{T_c} \left[\frac{A(P_2 - P_1)}{P_c} + C \ln \left(\frac{P_2}{P_1} \right) \right]} \quad (28)$$

$$\left(\frac{dT}{dP} \right)_H = \frac{-\frac{RTTr(APr+C)}{P}}{\left[a + bT + cT^2 + dT^3 - \frac{2RT}{T_c} \left[\frac{A(P_2 - P_1)}{P_c} + C \ln \left(\frac{P_2}{P_1} \right) \right] \right]} \quad (29)$$

Solving the differential equation employing separation of variables, we obtain;

$$a \left[\frac{1}{T_1} - \frac{1}{T_2} \right] + b \ln \left(\frac{T_2}{T_1} \right) + c(T_2 - T_1) + \frac{d(T_2^2 - T_1^2)}{2} - \frac{2R}{T_c} \left[\frac{A(P_2 - P_1)}{P_c} + C \ln \left(\frac{P_2}{P_1} \right) \right] * \ln \left(\frac{T_2}{T_1} \right) = \frac{R}{T_c} \left[\frac{A(P_2 - P_1)}{P_c} + C \ln \left(\frac{P_2}{P_1} \right) \right] \quad (30)$$

$$a \left[\frac{1}{T_1} - \frac{1}{T_2} \right] + b \ln \left(\frac{T_2}{T_1} \right) + c(T_2 - T_1) + \frac{d(T_2^2 - T_1^2)}{2} - g_p \left\{ \ln \left(\frac{T_2}{T_1} \right)^2 + 1 \right\} = 0 \quad (31)$$

2.3 SOLUTION TO DEVELOPED MODEL

The equation (31) presents the initial temperature T_1 as the variable of interest, Initial minimum allowable temperature, which was obtained iteratively using the Newton-Raphson approach. In this study, Excel's solver add-on was adopted. The model was used to fit the data by employing the initial and final conditions of two expansion processes. This reduces the developed model to a 2 x 2 matrix equations which when solved simultaneously gave the values of A and C (the terms of the Gopal's constant) as 0.11 and 0.16 respectively.

2.3.1 Effect of Acidic Gases

As a function of the pseudocritical temperature and pressure, the model was modified for both natural gas and gas condensates by adopting models that modify the gas's pseudocritical temperature and pressure. Sour gas (gas containing H_2S in the amount above the acceptable industry limits) type is selected for this study and is modified in its pseudocritical properties. The Wichert-Aziz correction method, equations (32) and (33) was used to adjust for the pseudo-critical temperature and pressure

$$T'_{PC} = T_{pc} - \varepsilon \quad (32)$$

$$P'_{PC} = \frac{P_{pc}T'_{pc}}{T_{pc}+F(1-F)\varepsilon} \quad (33)$$

$$\varepsilon = 120[E^{0.9} - E^{1.6}] + 15[F^{0.5} - F^{4.0}] \quad (34)$$

3. RESULTS AND DISCUSSION

The results for the initial minimum allowable temperature from developed model (equation 31) was compared to that of GPSA which is only applicable to sweet gas (a non-H₂S-bearing gas) using data from five different gas streams with varying composition for the sweet gas of specific gravities (0.6 to 1.0), and that for sour gas of specific gravities (0.6 to 0.7) with varying acidic gas compositions.

The results as shown in Table 1 and Figure 1 revealed that both models agree quite favourably with R² of 0.9629 about the initial temperatures of the gases given the other parameters remain constant.

Table 1: Predicted and Actual (GPSA) values of initial minimum temperature for permissible expansion of different gas specific gravities.

Initial Pressure (psia)	Final Pressure (psia)	SG = 0.6		SG = 0.7		SG = 0.8		SG = 0.9		SG = 1.0	
		Predicted Temp. (°F)	Actual (GPSA) Temp. (°F)	Predicted Temp. (°F)	Actual (GPSA) Temp. (°F)	Predicted Temp. (°F)	Actual (GPSA) Temp. (°F)	Predicted Temp. (°R)	Actual (GPSA) Temp. (°F)	Predicted Temp. (°F)	Actual (GPSA) Temp. (°F)
3800	380	181.3	163.0	196.6	180.0	209.3	195.0	219.6	210.0	231.3	215.0
3600	360	174.0	160.0	190.3	175.0	203.8	190.0	214.7	205.0	226.7	213.0
3400	340	166.9	158.0	184.1	173.0	198.3	188.0	209.7	203.0	222.2	205.0
3200	320	160.0	153.0	177.9	171.0	192.8	185.0	204.8	200.0	217.7	203.0
3000	300	153.1	150.0	171.9	170.0	187.4	183.0	199.9	197.0	213.1	198.0
2800	280	146.3	145.0	165.8	165.0	182.0	180.0	195.0	195.0	208.6	205.0
2600	260	139.5	140.0	159.8	160.0	176.5	175.0	190.1	190.0	204.0	200.0
2400	240	132.8	135.0	153.8	150.0	171.1	170.0	185.1	185.0	199.4	195.0
2200	220	126.1	121.0	147.7	145.0	165.6	165.0	180.1	180.0	194.8	193.0
2000	200	119.3	123.0	141.6	140.0	160.0	160.0	175.0	175.0	190.0	190.0
1800	180	112.4	116.0	135.3	138.0	154.3	155.0	169.8	170.0	185.1	183.0
1600	160	105.4	110.0	128.9	130.0	148.4	150.0	164.4	163.0	180.0	180.0
1400	140	98.2	90.0	122.3	117.0	142.3	140.0	158.7	155.0	174.7	169.0
1200	120	90.7	-	115.3	100.0	135.8	130.0	152.7	150.0	169.1	156.0
1000	100	82.6	-	107.8	-	128.8	120.0	146.1	140.0	162.9	140.0

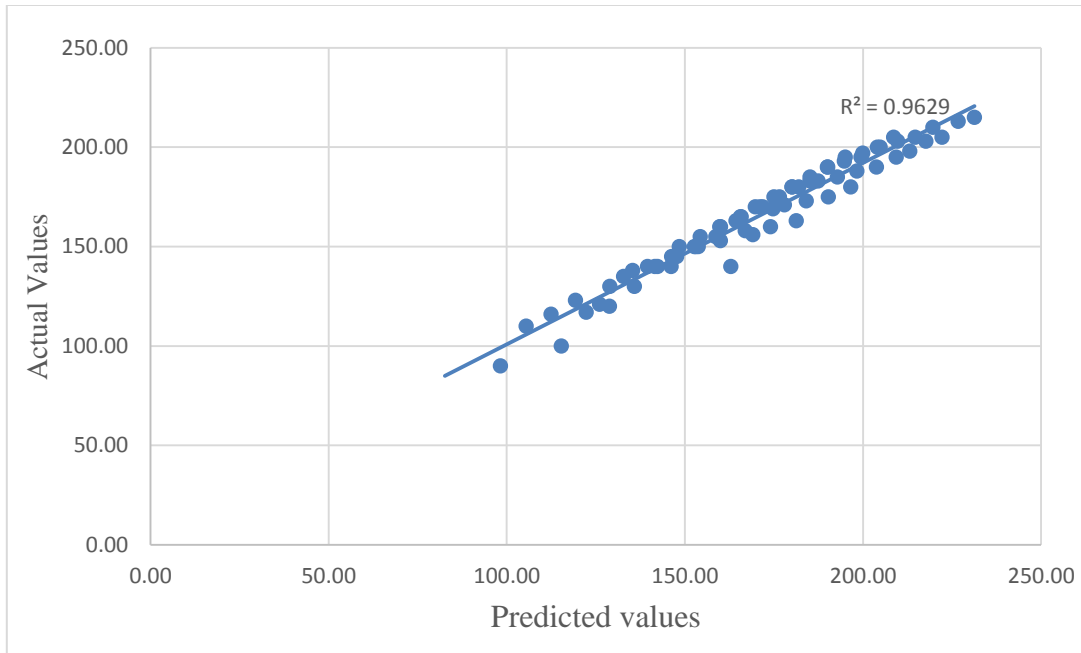


Figure 1: Initial minimum temperature for permissible expansion of sweet gases.

For the sour gases, the pseudocritical properties were adjusted using the Wichert-Aziz correlation and this reflects in the Initial Minimum allowable temperature. Since the presence of acidic gases **does lower the increase in** the hydrate formation temperature, it is only expected that the permissible initial temperature for expansion also increases with the increasing amount of acidic gas content at constant gas gravity as revealed in Figure 2.

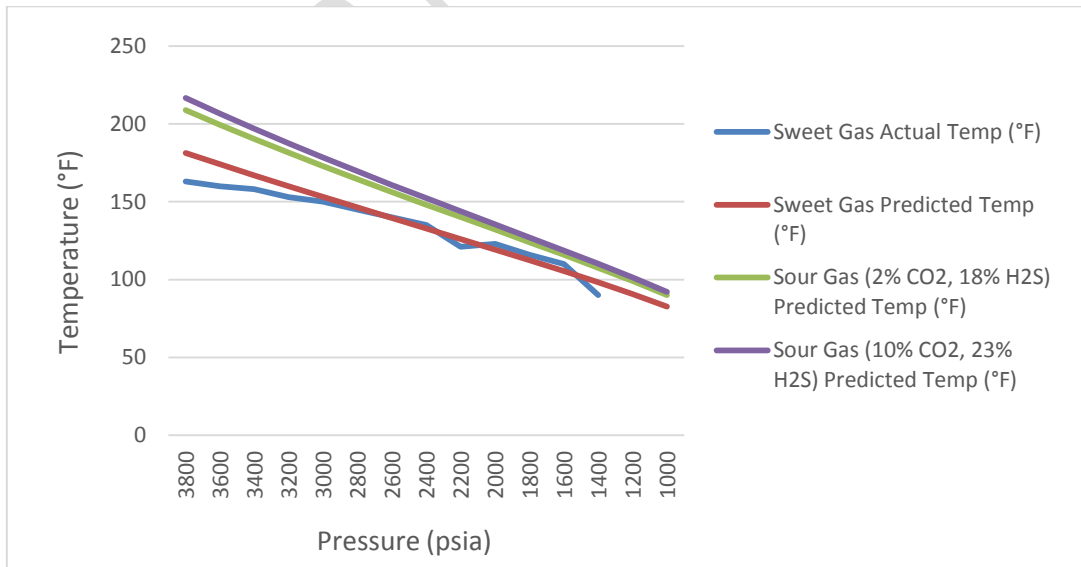


Figure 2: Temperature against Pressure for Sweet and Sour Gases of 0.6 specific gravity

4. CONCLUSION

The study successfully developed a model that describes the Joule-Thomson expansion to explain the drop in gas temperature which depends on Gopal's constant, the gas weight, critical pressure and critical temperature and also applicable to sweet and sour gases.

The model developed has application for real gas systems which comprise of natural gas and gas condensates streams respectively. It is most suitable for smaller members in the paraffin series even though the presence of heavy components might alter the behaviour of these gases when subjected to expansion process, .it is therefore recommended that further studies be performed to account for the presence of heavy components

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by the personal efforts of the authors.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

$$a=8.0211\gamma_g + 3.3359$$

$$b=2.0744 \times 10^{-2} \gamma_g - 4.2441 \times 10^{-3}$$

$$c=-8.1528 \times 10^{-6} \gamma_g + 4.8536 \times 10^{-6}$$

$$d=1.2887 \times 10^{-9} \gamma_g - 1.1626 \times 10^{-9}$$

$$0.55 < \gamma_g < 1 \text{ and } 180^\circ\text{R} < T < 2700^\circ\text{R}$$

γ_g = Specific gravity

$T_1 = T_{in}$:the initial minimum allowable temperature R

$T_2 = T_{out}$:Hydrate formation temperature R

$P_1 = P_{in}$:Initial Pressure psia

$P_2 = P_{out}$:Final Pressure psia

g_p = Gopal's constant and the terms A and C can be used to model the expansion process.

Where

T_{pc} = Pseudo-critical temperature, °R

P_{pc} = Pseudo-critical pressure, psia

T'_{pc} = corrected pseudo-critical temperature, °R

P'_{pc} = corrected pseudo-critical pressure, psia

E = sum of the mole fraction H₂S and CO₂ in the gas mixture

F = mole fraction of H₂S in the gas mixture

ϵ = pseudo-critical temperature adjustment factor.

GPSA = Gas Processors Suppliers Association