December 22, 1947

# LETDOWN IN STAGES OF THE CO2 SCRUBBING WATER

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## SUMMARY

During discussions with Dr. R. C. Dressler, the possibility was mentioned of recovering CO /- $H_2$ by letdown in stages of $CO_2$ scrubbing water. It was thought that this principle might have application in the proposed Gas Synthesis Demonstration Plant. One of the principal costs of pressure water scrubbing of $CO_2$ from gases is involved in the losses of CO /- $H_2$. When the scrubbing water is aerated prior to recirculation, this loss is usually quoted to be from 3 to 5% of the gas scrubbed. Since the cost of manufacture of CO /- $H_2$ is a major contributing factor in the cost of manufacturing gasoline by the Fischer-Tropsch process, any saving of gas losses is desirable.

The idea of partial letdown and subsequent recovery of CO /- $H_2$ for recycle is not new. Mention is made of this principle by C. C. Wright and R. F. Michell.[1] However, no reference has been noted to the separation of $H_2S$ and $CO_2$ by means of letdown in stages during the removal off these two constituents from gas streams.

In the present paper, calculations are shown for three cases of stepwise letdown:

a) Letdown to one intermediate stage at 64 psig resulting in a recovery of 81% of the CO /- $H_2$ which otherwise would have been lost in the scrubbing water.

b) Letdown to 3 psig whereby 505 of the CO2 and 98% of the CO /- $H_2$ is recovered for recycle to the gas generator.

c) Letdown in two intermediate stages (64 psig and 10-21 psia) to recover 81% of the CO /- $H_2$ and a second stream representing 50% of the $CO_2$.

[1] The Production of Hydrogen and Synthesis Gas by the Oxygen Gasification of Solid Fuels, presented at the American Chemical Society Meeting, September 15-19, 1947.

It is to be noted that figures, tables and graphs given are the result of calculations. The data, which are the basis for the calculations, were taken mainly from actual plant operation of a $CO_2$ pressure w ater scrubbing operation at the M.O.W. Plant, Louisiana, Missouri, and published solubility data. Although the calculations indicate the general feasibility of such an operation, it is believed that it would be desirable to conduct laboratory trials to confirm the results given. Also, it would be desirable to make a brief economic study of the proposed operation. It appears that the saving may amount to about 3-4% of the CO /– $H_2$, corresponding to 0.2-0.3¢/1000 cu.ft. assuming the $CO_2$ saturation calcu lated from the M.O.W. data.

The data from the M.O.W. $CO_2$ scrubbing p lant, given in Appendix 1, show 51% $CO_2$ saturation. With these figures for a gas of the analysis

0.7% $H_2S$
10.0% $CO_2$
44.7% $H_2$
44.6% CO

the following figures were obtained by calculation, assuming for 100 cu.m. gas at 20°C and 25 ata. water circulation rate of 89 cu.m., corresponding to 0.67 gal/cu.ft.:

a) Letdown to 64 psig (5.5 ata.)

Letdown pressure 64 psig (5.5 ata.)
Cu.ft. per 1000 cu.ft scrubbed gas

| | Dissolved at 25 ata. in the scrubbing water | Released at 5.5 ata. | Remaining dissolved at 5.5 ata. | % of originally dissolved in 5.5 ata. release gas | Analysis of 5.5 ata. release gas |
|---|---|---|---|---|---|
| $H_2S$ | 7 | 0.3 | 6.7 | 4 | 0.5 |
| $CO_2$ | 100 | 8.0 | 92.0 | 8 | 10.0 |
| $H_2$ | 18.1 | 15.0 | 3.1 | 83 | 45.5 |
| CO | 22.9 | 18.4 | 4.5 | 80 | 44.0 |
| Total | 148.0 | 41.7 | 106.3 | 28 | 100 |

51% of the CO + $H_2$ can be recovered by partial letdown of the scrubbing water and the CO + $H_2$ loss reduced from 4.6% to 0.9%. The 5.5 ata. letdown gas can be recycled to the water scrubber, its $CO_2$ content (10%) being the same as that of the original gas, and its $H_2S$ content (0.5%) being even lower.

b) Letdown to 3 psig (1.2 ata.)

Letdown Pressure 3 psig (1.2 ata.)
Cu.ft. per 1000 cu.ft. scrubbed gas

| | Dissolved at 25 ata. in the scrubbing water | Released at 1.2 ata. | Remaining dissolved at 1.2 ata. | % of originally dissolved in 1.2 ata. release gas | Analysis of 1.2 ata. release gas |
|---|---|---|---|---|---|
| $H_2S$ | 7 | 1.7 | 5.3 | 25 | 2 |
| $CO_2$ | 100 | 50.0 | 50.0 | 50 | 54 |
| $H_2$ | 18.1 | 17.7 | 0.4 | 98 | 20 |
| CO | 22.9 | 22.4 | 0.5 | 98 | 24 |
| Total | 148.0 | 91.8 | 56.2 | 62 | 100 |

50% of the originally dissolved $CO_2$ is recovered together with 98% of the CO + $H_2$. The CO + $H_2$ loss in the scrubbing water is 0.1% of that originally present. The 1.2 ata. gas with 54% $CO_2$ content could be recycled into the gasification.

c) Letdown in 2 intermediate stages

Cu.ft. per 1000 cu.ft. scrubbed gas

| | Dissolved at 25 ata. in the scrubbing water | Released at 5.5 ata. (64 psig) | Released at 0.65 ata. 20°C or 1.4 ata. at 60°C | Remaining dissolved |
|---|---|---|---|---|
| $H_2S$ | 7 | 0.3 | 1.8 | 4.9 |
| $CO_2$ | 100 | 8.0 | 49.0 | 43.0 |
| $H_2$ | 18.1 | 15.0 | 3.0 | 0.1 |
| CO | 22.9 | 18.4 | 4.4 | 0.1 |
| Total | 148.0 | 41.7 | 58.2 | 48.1 |

| | % of gas originally dissolved obtained in 5.5 ata. release gas | 0.65 ata. 20°C or 1.4 ata. 80°C release gas | Analysis of release gas First | Second |
|---|---|---|---|---|
| $H_2S$ | 4 | 26 | 0.5 | 3.2 |
| $CO_2$ | 8 | 49 | 10.0 | 84.0 |
| $H_2$ | 33 | 16.5 | 45.5 | 5.1 |
| CO | 80 | 19 | 44.0 | 7.7 |
| Total | 28 | 40 | 100.0 | 100.0 |

In the gas of the first release stage 81% of the dissolved CO + $H_2$ can be recovered and recycled to the $CO_2$ scrubbing. In the second release stage 50% of the originally dissolved $CO_2$ is recovered in a gas with 84% $CO_2$. This gas could be recycled to the gasification zone to increase the $CO/H_2$ ratio. In this case about 25% of the originally present $H_2S$ returns to the gasification zone.

The detailed calculations are given in the following part of the report.

Water Scrubbing of Synthesis Gas

Gas to be scrubbed at 25 ata.

| | | Solubility 20° [1] |
|---|---|---|
| 0.7% $H_2S$ | P $H_2S$ = 0.18 atm., | 2.58 1/1 atm. |
| 10.0% $CO_2$ | P $CO_2$ = 2.5 atm., | 0.878 1/1 atm. |
| 44.7% $H_2$ | P $H_2$ = 11.2 atm., | 0.0182 1/1 atm. |
| 44.6% CO | P CO = 11.12 atm., | 0.0232 1/1 atm. |

Scrubbing at 20°C, solubility of $CO_2$ = 2.2 1/1 or 0.878 1/1 atm., for 100 cu.m. $CO_2$ (= 1000 cu.m. gas) with 51% saturation (see Appendix 1).

1) See TASCHENBUCH FUER CHEMIKER UND PHYSIKER

$\frac{100}{2.2 \times 0.51}$ = 89 cu.m. $H_2O$ are required.

Then 89 cu.m. $H_2O$ dissolve:

| | | % by Vol. |
|---|---|---|
| (89 x 0.18 x 2.58 = 41.3 cu.m.) | 7 cu.m. $H_2S$ (total) | 4.7 |
| (89 x 2.5 x 0.878 = 195 cu.m.) | 100 cu.m. $CO_2$ (total) | 67.6 |
| 89 x 11.2 x 0.0182 | = 18.1 cu.m. $H_2$ (= 4.1%) | 12.2 |
| 89 x 11.12 x 0.0232 | = 22.9 cu.m. CO (= 5.1%) | 15.5 |
| | 148.0 | |

In 1 cu.m. water the following gas quantities are dissolved:

| | |
|---|---|
| $H_2S$ | 0.079 cu.m. |
| $CO_2$ | 1.12 cu.m. |
| $H_2$ | 0.203 cu.m. |
| CO | 0.257 cu.m. |

For the letdown in stages the following figures are obtained ($p = \frac{v}{\lambda + V}$)

| Gas | $\lambda$ = Solub. 1/1 atm. | v | V = 1. $p_{atm}$ = | cu.m. Dissolved ($p \times \lambda$) | cu.m. Released ($p \times V$) | V = 0.1 $p_{atm}$ = | cu.m. Dissolved ($p \times \lambda$) | cu.m. Released ($p \times V$) |
|---|---|---|---|---|---|---|---|---|
| $H_2S$ | 2.58 | 0.079 | 0.022 | 0.057 | 0.022 | 0.029 | 0.076 | 0.003 |
| $CO_2$ | 0.878 | 1.12 | 0.597 | 0.523 | 0.597 | 1.146 | 1.01 | 0.11 |
| $H_2$ | 0.0182 | 0.203 | 0.199 | 0.004 | 0.199 | 1.72 | 0.031 | 0.172 |
| CO | 0.0232 | 0.257 | 0.251 | 0.006 | 0.251 | 2.09 | 0.048 | 0.209 |
| Total | | 1.659 | 1.069 | 0.590 | 1.069 | 4.98 | 1.165 | 0.494 |

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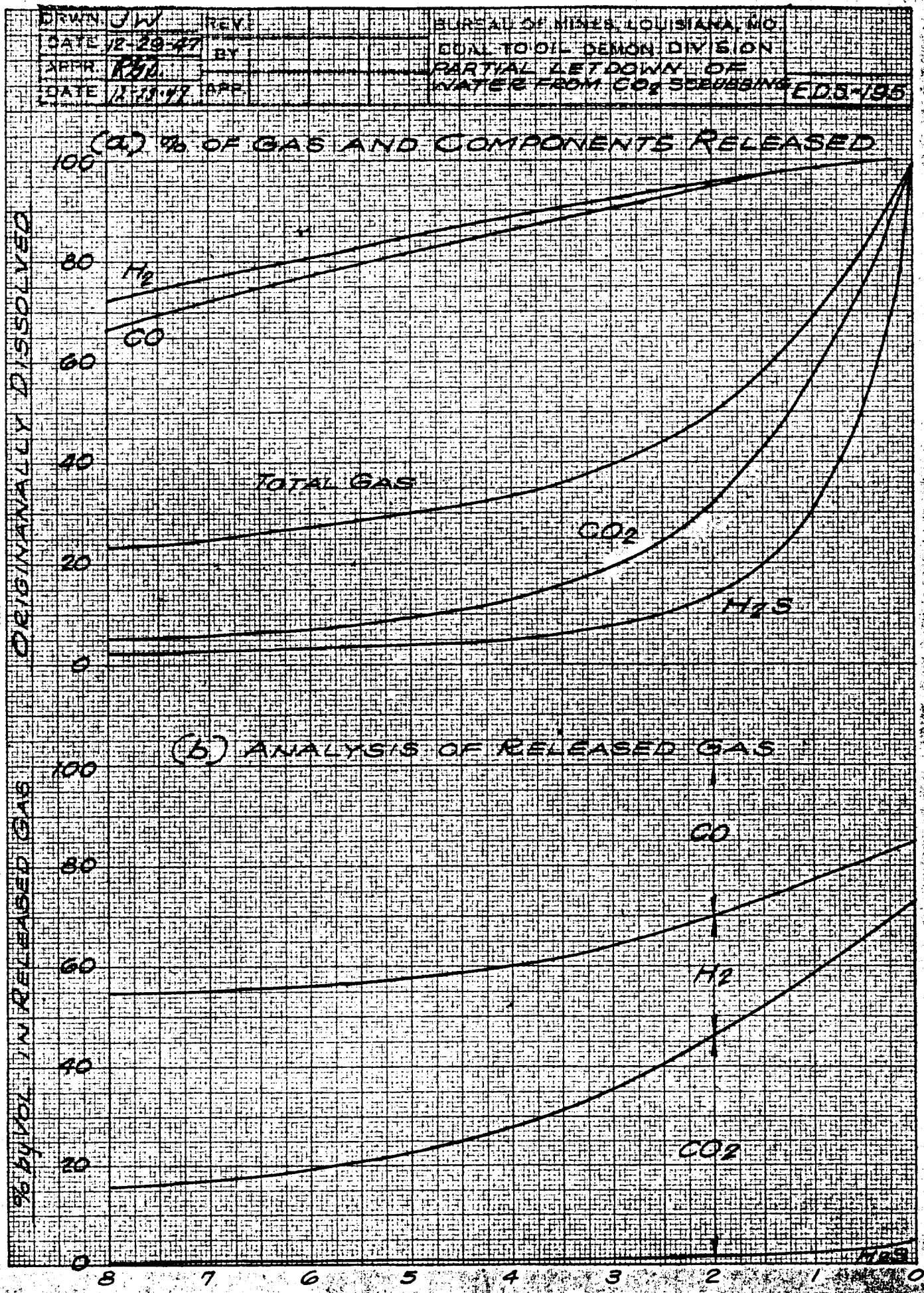
PARTIAL LETDOWN OF WATER FROM $CO_2$ SCRUBBING — ED.5-195



| V = 0 | V = 0.2 | | | V = 0.05 | | | V = 2.0 | | |
|---|---|---|---|---|---|---|---|---|---|
| $P_{atm}$ = | $P_{atm}$ = | cu.m. Dissolved (p x λ) | cu.m. Released (p x V) | $P_{atm}$ = | cu.m. Dissolved (p x λ) | cu.m. Released (p x V) | $P_{atm}$ = | cu.m. Dissolved (p x λ) | cu.m. Released (p x V) |
| 0.031 | 0.028 | 0.073 | 0.006 | 0.030 | 0.0775 | 0.0015 | 0.017 | 0.045 | 0.034 |
| 1.28 | 1.04 | 0.91 | 0.21 | 1.21 | 1.06 | 0.06 | 0.39 | 0.34 | 0.78 |
| 11.15 | 0.93 | 0.017 | 0.186 | 2.98 | 0.054 | 0.149 | 0.101 | 0.002 | 0.201 |
| 11.08 | 1.15 | 0.027 | 0.230 | 3.51 | 0.081 | 0.176 | 0.127 | 0.003 | 0.254 |
| 23.54 | 3.148 | 1.027 | 0.632 | 7.73 | 1.2725 | 0.3865 | 0.635 | 0.390 | 1.269 |

With these data the following figures are obtained:

| Letdown pressure ata. | 23.5 | 7.7 | 5.0 | 3.1 | 1.1 | 0.64 |
|---|---|---|---|---|---|---|
| Released % of Total | 0 | 23.3 | 29.8 | 38.1 | 64.4 | 76.3 |
| $H_2S$ | 0 | 2.5 | 3.8 | 7.6 | 27.9 | 43.0 |
| $CO_2$ | 0 | 5.4 | 9.8 | 18.7 | 53.2 | 70.5 |
| $H_2$ | 0 | 73.3 | 84.7 | 91.6 | 98.0 | 99.0 |
| CO | 0 | 68.5 | 81.4 | 89.5 | 97.7 | 98.8 |
| Letdown gas analysis % $H_2S$ | | 0.4 | 0.6 | 0.9 | 2.1 | 2.7 |
| $CO_2$ | | 15.5 | 22.2 | 33.3 | 55.8 | 61.5 |
| $H_2$ | | 38.5 | 34.8 | 29.4 | 18.6 | 15.8 |
| CO | | 45.6 | 42.4 | 36.4 | 23.5 | 20.0 |
| % $H_2S$/% $CO_2$ | | 2.5 | 2.7 | 2.9 | 3.7 | 4.4 |

From these figures a diagram, Fig. 1, is prepared. It shows under a) which amount of the originally dissolved total gas and of the individual components is released at various letdown pressures. Under b) the analysis of the released gas at various pressures can be seen.

Assuming that by partial release a gas with the same $CO_2$ content (10%) as the originally scrubbed gas shall be obtained, a letdown pressure of 5.5 ata. is required. Then the following figures are obtained from Fig. 1.

| Letdown Pressure | 5.5 ata. (64 psig) | |
|---|---|---|
| | % of originally dissolved in release gas | Analysis of release gas % by Vol. |
| Total | 28 | 100 |
| $H_2S$ | 4 | 0.5 |
| $CO_2$ | 8 | 10 |
| $H_2$ | 83 | 45.5 |
| CO | 80 | 44 |

This means that a recovery of 80% of the originally dissolved CO and $H_2$ is possible. The CO and $H_2$ loss of 4.6% ba sed on CO $\nearrow$ $H_2$ contained in the scrubbed gas can be reduced by 3.7% to 0.9%. The gas released at 5.5 ata. after compression can immediately be recycled to the $CO_2$ scru bbing plant.

In the gasification, assuming that $CO_2$ f rom the water scrubbing is required, the water can be let down either in one step, to obtain a $CO_2$ rich gas, or in two steps to obtain in the first letdown stage a CO /— $H_2$ fraction and in the second a $CO_2$ rich fraction. For the one stage letdown and the recovery of 50% of the originally dissolved $CO_2$ the followin g data are obtained from Fig. 1:

Letdown pressure 1.2 ata. (3 psig)

| | % of originally dissolved in release gas | Analysis of release gas % by Vol. |
|---|---|---|
| Total | 62 | 100 |
| $H_2S$ | 25 | 2 |
| $CO_2$ | 50 | 54 |
| $H_2$ | 98 | 20 |
| CO | 98 | 24 |

Recycling of 50% of the $CO_2$ originally d issolved means a recovery of 98% of the CO $\nearrow$ $H_2$ and recycling of 25% of the $H_2S$.

For the two stage letdown in the first stage a pressure of 5.5 ata. may be assumed. Then the following figures are obtained:

First stage letdown pressure 5.5 ata. (64 psig)

| | % of originally dissolved in release gas | In 1 cu.m. water at 5.5 ata. Dissolved cu.m. | Released cu.m. |
|---|---|---|---|
| Total | 28 | 1.191 | 0.468 |
| $H_2S$ | 4 | 0.076 | 0.003 |
| $CO_2$ | 8 | 1.03 | 0.09 |
| $H_2$ | 83 | 0.034 | 0.159 |
| CO | 80 | 0.051 | 0.206 |

This gives for the second stage letdown the following figures ($p = \frac{V}{\lambda / V}$):

| Gas | $\lambda$ Solub. 1/1 atm. | V | V = 1 Patm = cu.m. Diss. (p x $\lambda$) | Rel. (p x V) | V = 0.5 Patm = cu.m. Diss. (p x $\lambda$) | Rel. (p x V) | V = 0.1 Patm = cu.m. Diss. (p x $\lambda$) | Rel. (p x V |
|---|---|---|---|---|---|---|---|---|
| $H_2S$ | 2.58 | 0.076 | 0.021 | 0.055 | 0.021 | 0.025 0.064 | 0.012 | 0.028 0.073 | 0.003 |
| $CO_2$ | 0.878 | 1.03 | 0.56 | 0.48 | 0.55 | 0.75 0.656 | 0.374 | 1.05 0.925 | 0.105 |
| $H_2$ | 0.0182 | 0.034 | 0.033 | 0.0006 | 0.0334 | 0.066 0.0012 | 0.0328 | 0.29 0.005 | 0.029 |
| CO | 0.0232 | 0.051 | 0.050 | 0.001 | 0.050 | 0.098 0.0023 | 0.0487 | 0.41 0.010 | 0.041 |
| Total | | 1.191 | 0.654 | 0.5366 | 0.6544 | 0.939 0.7235 | 0.4675 | 1.778 1.013 | 0.178 |

With these data the following figures are obtained:

| Second stage letdown pressure ata. | 1.78 | 0.94 | 0.65 | 1.78 | 0.94 | 0.65 |
|---|---|---|---|---|---|---|
| | Released % of dissolved before second stage | | | Released % of total dissolved before first stage | | |
| Total gas | 15 | 39 | 55 | 11 | 28 | 40 |
| $H_2S$ | 4 | 16 | 27.5 | 4 | 15.5 | 26.4 |
| $CO_2$ | 10 | 36 | 53 | 9 | 33 | 49 |
| $H_2$ | 85 | 96.5 | 98 | 14.5 | 16.4 | 16.7 |
| CO | 80.5 | 95.5 | 98 | 16.1 | 19.1 | 19.6 |
| Second stage letdown gas analysis %$H_2S$ | 1.7 | 2.6 | 3.2 | | | |
| %$CO_2$ | 59.0 | 80.0 | 84.0 | | | |
| % $H_2$ | 16.3 | 7.0 | 5.1 | | | |
| %CO | 23 | 10.4 | 7.7 | | | |

If the second stage letdown is made at 60°C instead of the previously assumed 80°C, the following figures result ($p = \frac{v}{\lambda + V}$)

| Gas | $\lambda$ 60° Solub. l/l atm. | v | V = 1 Patm = | cu.m. Diss. (p x $\lambda$) | Rel. (p x V) | V = 0.5 Patm = | cu.m. Diss. (p x $\lambda$) | Rel. (p x V) | V = 0.2 Patm = | cu.m. Diss. (p x $\lambda$) | Rel. (p x |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2S$ | 1.19 | 0.076 | 0.0846 | 0.041 | 0.065 | 0.045 | 0.053 | 0.023 | 0.055 | 0.065 | 0.01 |
| $CO_2$ | 0.359 | 1.03 | 0.76 | 0.27 | 0.78 | 1.2 | 0.43 | 0.60 | 1.84 | 0.66 | 0.37 |
| $H_2$ | 0.018 | 0.034 | 0.033 | 0.001 | 0.033 | 0.066 | 0.001 | 0.033 | 0.16 | 0.003 | 0.03 |
| CO | 0.0149 | 0.051 | 0.050 | 0.001 | 0.050 | 0.099 | 0.002 | 0.049 | 0.24 | 0.004 | 0.04 |
| Total | | 1.191 | 0.88 | 0.313 | 0.878 | 1.41 | 0.486 | 0.705 | 3.00 | 0.732 | 0.45 |

With these data the following figures for the second stage letdown at 60°C are obtained:

| Second stage letdown pressure ata. (at 60°C) | 3.0 | 1.4 | 0.9 | 3.0 | 1.4 | 0.9 |
|---|---|---|---|---|---|---|
| | Released in second stage as % of dissolved before second stage | | | Released in second stage as % of total dissolved before first stage | | |
| Total gas | 41 | 63 | 78.5 | 29.5 | 45.5 | 56.5 |
| $H_2S$ | 14.5 | 30 | 46 | 14 | 29 | 44 |
| $CO_2$ | 36 | 58.3 | 73.8 | 33 | 53.7 | 68 |
| $H_2$ | 91 | 97 | 98 | 15.5 | 16.5 | 16.7 |
| CO | 92 | 96 | 98 | 18.4 | 19.2 | 19.6 |

| Second stage letdown gas analysis | | | |
|---|---|---|---|
| %$H_2S$ | 2.4 | 3.5 | 4.0 |
| %$CO_2$ | 80.5 | 85.2 | 86.5 |
| %$H_2$ | 6.8 | 4.6 | 3.8 |
| %CO | 10.3 | 6.9 | 5.7 |

APPENDIX 1

$CO_2$ Scrubbing, H.O.W., December 14 & 15, 1943

| | | |
|---|---|---|
| Scrubbing water GPM | = 1051 | = 3.97 cu.m./min. |
| Gas SCFT/M | = 3500 | = 99.4 cu.m./min. |
| % $CO_2$ in out gas | 0.23 | |
| Temp. of water | 43°F | = 6°C |
| % $CO_2$ in in gas | 17.3 | |

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40 cu.m. $H_2O$/1000 cu.m. gas with 173 cu.m. $CO_2$

p = 490 psig = 35.4 atm.; $r_{CO_2}$ = 6.12 atm.

Dissolved 173/40 = 4.33 cu.m. $CO_2$/cu.m. $H_2O$

resp. $\frac{4.33}{6.12}$ = 0.708 cu.m./cu.m. x atm.

Solubility 6°C: a) 8.5 cu.m./cu.m. $H_2O$

b) 1.377 cu.m./cu.m. x atm.

Saturation: a) = $\frac{4.33}{8.5}$ = 51%

b) = $\frac{0.708}{1.377}$ = 51%

/mc