

I.1 Calibration Mixtures

The calibration procedure for the gas chromatographs involved the use of three calibrated mixtures provided by Matheson Corp. The contents of each tank as well as a typical value obtained for the response factor ($\frac{\text{mole fraction}}{\text{peak area}}$). The accuracy of the mole fractions in each calibration tank are with 3%.

Table I-1 Calibration Tank #1

<u>Component</u>	<u>mole %</u> x10 ⁻²	<u>mole fraction/peak area</u> x10 ⁻⁸
CO ₂	2.49	
C ₂ H ₄	2.46	8.06
C ₃ H ₈	2.51	7.98
CH ₃ OH	2.52	6.11
		11.73

Table I-2 Calibration Tank #2
Calibrated with HP

<u>Component</u>	<u>mole %</u> x10 ⁻²	<u>mole fraction/peak area</u> x10 ⁻⁸
1-C ₃ H ₁₀	1.99	
1-C ₆ H ₁₂	1.51	7.38
n-C ₆ H ₁₄	1.49	6.5
n-C ₇ H ₁₆	.99	6.1
1-C ₉ H ₁₆	.51	5.4
n-C ₈ H ₁₈	.49	5.14
		4.3

Table I-3 Calibration Tank #1

<u>Component</u>	<u>mole %</u>	<u>mole fraction/peak area</u>
	$\times 10^{-2} (\pm 2\%)$	$\times 10^{-9} (\pm 10\%)$
CO ₂	24.8	8.4
C ₂ H ₄	24.9	8.01
C ₂ H ₆	25.1	7.6
C ₃ H ₆	25.4	6.4
C ₃ H ₈	25.2	6.3
1-C ₄ H ₈	25.6	5.6
n-C ₄ H ₁₀	10.0	5.1
1-C ₅ H ₁₀	20.1	7.7
1-C ₆ H ₁₂	15.0	6.5
n-C ₇ H ₁₄	9.8	5.6

I.2 Flow Corrections:

At very high volumetric flow rates there is a significant pressure drop across the GC sample valve loops. Since the total sample moles injected into the GC column depends upon the total pressure in the sample loops it was necessary to correlate the total moles injected as a function of volumetric flow through the loop.

At flow rates below 60 cc/min (25°C, 1 atm.) the correction is within the experimental error associated with measuring peak areas ($\pm 5\%$) however at higher flow rates the increase in the amount of moles injected becomes significant.

The data shown in Table I-4 represents molar amounts normalized to low flow conditions $\left(\frac{\text{moles injected at flows} > 30 \text{ cc/min}}{\text{moles injected at flow of } 30 \text{ cc/min}} \right)$ for the HP #5730 with the factor installed 1 cc sample loop.

Table I-4 Flow Corrections for the HP #5730 with 1 cc Sample Loop

<u>Flow rate (cc/min)</u> <u>(25°C, 1 atm)</u>	<u>Normalized number</u> <u>of moles injected</u>
20	1.0
60	1.02
113	1.06
234	1.13
365	1.26
600	1.53
860	1.8

Table I-5 Flow Corrections for the Perkin Elmer E3 with 1 cc Sample Loop

<u>Flow rate (cc/min)</u> <u>(25°C, 1 atm)</u>	<u>Normalized number</u> <u>of moles injected</u>
7	1.0
40	1.0
50	1.04
126	1.08
240	1.1
320	1.2
480	1.25
780	1.36

The curves representing the normalized molar amount injected versus the volumetric flow were fit to fourth order polynomials by a non linear least squares routine. The functional forms for each correlation are given below where FR is the flow rate in cc/min at 25°C and 1 atm.

5730 Flow Correction Correlation

$$\begin{aligned} \text{Normalized moles} = & 0.995 + .281 \times 10^{-3} \text{ FR} + .5 \times 10^{-5} \text{ FR}^2 \\ & .148 \times 10^{-7} \text{ FR}^3 + .125 \times 10^{-10} \text{ FR}^4 \end{aligned} \quad \text{I.1}$$

Sigma 3 Flow Correction Correlation

$$\begin{aligned} \text{Normalized moles} = & 0.99 + .337 \times 10^{-3} \text{ FR} + .147 \times 10^{-5} \text{ FR}^2 \\ & -.3628 \times 10^{-8} \text{ FR}^3 + .237 \times 10^{-11} \text{ FR}^4 \end{aligned} \quad \text{I.2}$$

Appendix II: Calculation of Product Yields, CO Conversion and Reaction Rates

The gas chromatographs measure the mole fraction of each component contained in the gas sample loop. The total number of moles in the sample can vary since the FT reaction involves a net decrease in total moles. The mole fraction of component measured by the GC, Y_i , can be related to the mole fraction based on one mole of feed, X_i by the following relation

$$Y_i = \frac{X_i}{F_{out}} \quad \text{II.1}$$

where F_{out} is the total molar flow rate of the effluent stream. F_{out} can be determined by basing the mole fractions on one mole of feed and subtracting out the number of moles lost due to the formation of each FT product.

$$F_{out} = 1 - \sum_{i=1}^m \alpha_i X_i \quad \text{II.2}$$

where m is the number of FT products.

For example, assume that only methane, methanol, ethylene, propylene and 1-pentene, are produced. The reactions corresponding to the formation of these products are as follows.

Table II-1 Example Reactions

<u>Component</u>	<u>Reaction</u>	<u>Moles loss</u>
CH ₄	3H ₂ + CO → CH ₄ + H ₂ O	2
CH ₃ OH	2H ₂ + CO → CH ₃ OH	1
C ₂ H ₄	4H ₂ + 2CO → C ₂ H ₄	3
C ₃ H ₆	6H ₂ + 3CO → C ₃ H ₆	5
C ₅ H ₁₀	10H ₂ + 5CO → C ₅ H ₁₀ + 5H ₂ O	9

In this example F_{out} is given by

$$F_{out} = 1 - 2X_{CH_4} - 1X_{CH_3OH} - 3X_{C_2H_4} \\ - 5X_{C_3H_6} - 9X_{C_3H_{10}}$$

II.3

For each product produced one has an equation defining the value of the measured GC mole fraction Y_i with a normalized mole fraction X_i . For a 3 component product distribution one would have a set of 3 equations shown below

$$Y_1 = \frac{X_1}{F_{out} - \sum_{i=1}^3 \alpha_i X_i} \quad \text{II.4A}$$

$$Y_2 = \frac{X_1}{F_{out} - \sum_{i=1}^3 \alpha_i X_i} \quad \text{II.4B}$$

$$Y_3 = \frac{X_1}{F_{out} - \sum_{i=1}^3 \alpha_i X_i} \quad \text{II.4C}$$

The actual number of components was general 20. The set of linear equations were rearranged in the form

$$X_i = f(y_1 \dots y_{20}, X_1 \dots X_{i-1}, X_{i+1} \dots X_{20}) \quad \text{II.5}$$

for $1 < i < 20$

and solved by using a standard set solver employing matrix inversion.

The percent CO conversion was determined by the following equation

$$\% \text{ CO converted} = 1 - \frac{X_0 - \sum_{i=1}^R \beta_i X_i}{X_0} \quad \text{II.6}$$

where R is the total number of CO consuming reactions

β_i corresponds to the moles of CO consumed in the reaction producing component i

X_i is the normalized mole fraction component i

X_0 is the initial mole fraction of CO in the feed

At this point the careful reader would note that X_i is identical to the yield of component i (Y_i).

The computer program employed in the calculations is included in this appendix. This particular version is a more recent edition provided by coworker Keith Kreitman.


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CSRAT(I)=7(A)/7(I)
TORAT(I)=TCH4(I)/TOT(I)
999 CONTINUE

```

C
C
C

WRITE SUMMARY TABLES

```

WRITE (6,1110)
WRITE (6,1040) TITLE
WRITE (6,1045) XCOI,MZUP,WT
WRITE (6,1120)
DO 120 I=1,INJ
120 WRITE (6,1130) I,TIME(I),TEMP(I),PRESS(I),FLOW(I),TCON(I),TOT(I)
    &,TCH4(I),SA(I),SV(I)
    WRITE (6,1140)
    DO 130 I=1,INJ
130 WRITE (6,1150) I,TCON(I),CH4(I),C2TOC5(I),C6PLUS(I),OH(I),CO2(I)
    &,OB(I),CEVEN(I),COCC(I)
    WRITE (6,1170)
    DO 140 I=1,INJ
140 WRITE (6,1180) I,TCON(I),C2RAT(I),C3RAT(I),C4RAT(I),CSRAT(I)
    &,TORAT(I)
9999 CONTINUE

```

C
C
C

FORMAT STATEMENTS

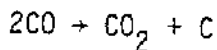
```

1000 FORMAT (I2)
1010 FORMAT ('1',8A10)
1020 FORMAT (8A10)
1030 FORMAT (8F10.5)
1035 FORMAT (/18F10.5)
1040 FORMAT ('0',8A10)
1045 FORMAT (T10,'XCOI= ',F4.2,5X,'MZUP= ',F6.2,5X,'WT= ',F6.4)
1050 FORMAT ('# SET NUMBER ',I2/T10,F4.0,' PSIG',5X,F4.0,' OES C',5X
    &,F4.0,' MIN',5X,F5.1,' CC/MIN')
1060 FORMAT ('# MOLE FRACTIONS'/'# COMPONENT',T19,'#C DATA',T33
    &,'#FLOW CORRECTED',T50,'#NORMALIZED',T64,'#RELATIVE'/'#)
1070 FORMAT (T4,1A10,T20,F6.3,T35,F9.8,T50,F9.8,T65,F6.5)
1080 FORMAT ('#SCHULTZ FLOW'/'# N',8X,'#MOLES',8X,'#SFO'/'#)
1090 FORMAT (I1,I2,5X,F8.3,5X,F8.3)
1100 FORMAT (T10,'#FLOW CORRECTIONS',5X,'#P= ',F6.4,5X,'#S3= ',F6.4)
1110 FORMAT ('#SUMMARY OF RESULTS')
1120 FORMAT ('# SET',T7,'#TIME',T13,'#TEMP',T19,'#PRESS',T26,'#FLOW',T34
    &,'#TCON',T44,'#TOT',T54,'#TCH4',T65,'#SA',T75,'#SV',T43,'#X1000',T53
    &,'#X1000')
1130 FORMAT (T2,I2,T7,F4.0,T13,F4.0,T19,F4.0,T25,F5.1,T32,F7.3,T43,F6.3
    &,T53,F6.3,T63,F5.4,T72,F7.0)
1140 FORMAT ('# SET',T7,'#TCON',T15,'#CH4',T22,'#C2TOC5',T30,'#C6PLUS',T40
    &,'#OH',T47,'#CO2',T56,'#OB',T62,'#CEVEN',T71,'#COCC'/'#)
1150 FORMAT (T2,I2,T6,F5.3,T14,F5.4,T22,F5.4,T30,F5.4,T38,F5.4,T46,F5.4
    &,T54,F5.4,T62,F5.4,T71,F5.4)
1160 FORMAT ('#CONVERSION',F7.3,'# PERCENT')
1170 FORMAT ('# SET',T7,'#TCON',3X,'#C2RAT',3X,'#C3RAT',3X,'#C4RAT',3X
    &,'#CSRAT',3X,'#TORAT'/'#)
1180 FORMAT (I2,I2,T6,F5.3,3X,4(F5.2,3X),F5.4)
STOP
END

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Appendix III: Equilibrium Constant for the Boudovard Disproportionation
Reaction at 250°C

The disproportionation reaction can be written as



Assuming ideal gas behavior and that the deposited carbon exists in a elemental form (graphite) one can calculate the equilibrium constant using tabulated equilibrium constants (113). These constants are based on formation reactions of the given components from their corresponding elements (reference states). The equilibrium constants ($\ln K_p$) given below are interpolated values based on tabulated values (113).

<u>component</u>	<u>$\log_{10} K_p$ (250°C)</u>
CO ₂	39.7
CO	15.8
C	0.0

The equilibrium constant is now given as

$$\frac{[\text{CO}_2] [\text{C}]}{[\text{CO}]^2} = \frac{10^{39.7} 10^{0.0}}{(10^{15.8})^2} = 1.25 \times 10^8$$

Appendix IV: The Amount of H_2O and CH_3OH Produced Under Typical
Reaction Conditions

At 2% CO conversion the amount of water produced, P_w , (neglecting the shift reaction) is given by the following equation

$$P_w = \frac{(Q) (P) (X_{CO}) (\%conv/100) (t)}{RT} \quad \text{VI-1}$$

where Q is the volumetric flow rate (l/min)

R is the gas constant

P is the pressure at which the flow is measured (atm.)

T is the temperature at which the flow is measured ($^{\circ}K$)

X_{CO} is the CO mole fraction in feed

$\%CONV$ is the amount of CO converted

t is the time on stream (min)

Typical values employed under reaction conditions are as follows

$$Q = 50\text{cc/min} \quad \text{where } P = 1\text{atm}, T = 298^{\circ}K \text{ and } R = 0.82 \frac{1\text{-atm}}{\text{mole}^{\circ}K}$$

$$X_{CO} = 0.5$$

$$\%CONV = 2\%$$

$$t = 120 \text{ mins}$$

Using the above values one finds that 2.45×10^{-2} moles of water are produced. Assume that the surface area of an adsorbed water molecule is twice the geometric area based on the H-OH bond angle (104.45°) and o-H bond length (0.958\AA) (26). This surface area is roughly 2\AA^2 . The amount of water molecules produced corresponds to

1.5×10^{22} molecules which translates to a monolayer coverage of $3 \times 10^{22} \text{ \AA}^2$. This area is comparable to the silica surface area available for adsorption. Typically the silica surface area of the catalyst is 1.5×10^{22} . (Typically catalyst samples are 0.5 gms and the silica has a surface area of $285 \text{ m}^2/\text{gm}$).