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WORK RECOVERY EFFICIENCY OF THE METHYNATION PROCESS

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by

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1. INTRODUCTION

The work recovery efficiency of thermochemical energy transport and storage systems has been defined by Carden and Williams (1978) as the ratio of maximum work available from the exothermic terminal to the associated change in stored enthalpy. The maximum work is calculated on the assumption that all processes are thermodynamically reversible except for the chemical reaction itself. This assumption allows exploration of real conditions in the reaction vessel characterised by finite reaction rates and significant departures from equilibrium.

Associated with the synthesis processes is a transfer of mass from a "reactant" storage vessel to a "product" storage vessel. The change in stored enthalpy is defined as the formation heat which would be evolved at the storage temperature in producing this mass of stored product from an equal mass of stored reactants.

To date the convention has been adopted that the storage temperature and Carnot engine sink temperature are identical and equal to a specified value approximating ambient temperature e.g. 300K.

Conditions at any point within the reaction vessel may be uniquely defined by the common pressure and by specific values of temperature and composition. A convenient parameter for specifying composition is the reaction extent δ . For the synthesis reaction



in which none of the components of A occur in B, δ for a given mixture is defined as the mass fraction of the mixture that consists of components A. It is important to note that A and B do not necessarily represent the stored reactants and products and that the stored enthalpy is not necessarily related to the heat of formation of equation (1). Rather the stored components are defined by two specific values of δ and these values in turn determine the heat of formation and stored enthalpy per unit mass.

In many important cases we must consider non-isothermal conditions occurring in the reaction vessel. It is important to visualise the vessel as a column having sufficient length to minimise longitudinal heat flow in the catalyst bed and thus enabling conditions to be maintained which are virtually reversible.

The work recovery efficiency, as defined above, will be seen to depend entirely on system pressure P and the T, δ profile in the reaction column. It will also be obvious that if the T, δ profile should coincide with a contour of chemical equilibrium, the work recovery efficiency η will then be

$$\eta = \frac{\Delta G_{T_S}(\delta_1, \delta_2)}{\Delta H_{T_S}(\delta_1, \delta_2)} \quad (2)$$

where the numerator is the free energy change at the sink temperature T_S between the inlet and outlet compositions δ_1, δ_2 respectively and ΔH_{T_S} is the corresponding change in enthalpy.

Carden and Williams (1978) have shown that in general

$$\eta = \frac{\int_{\delta_2}^{\delta_1} n(T, \delta) d\delta}{(\delta_1 - \delta_2)} \quad (3)$$

where (T, δ) is a "point" value of work recovery efficiency.

In this paper we calculate $\eta(T, \delta)$ for the methylation process, a prominent candidate for thermochemical energy transfer being intensively studied by the Atomic Energy Authority of the Federal Republic of Germany (K.F.A.). Resulting values of $\eta(T, \delta)$ for a particular methylation reaction have been displayed as contours on the composite temperature-enthalpy diagram in Fig.1. The value of η for any given reaction column profile drawn on the diagram may then be obtained from (3) by means of simple graphical integration.

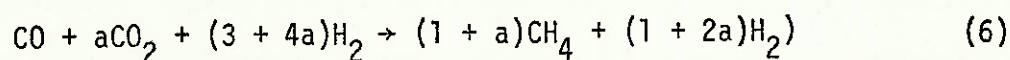
2. METHODOLOGY

2.1 Methane forming reactions

The methylation process is important in relation to thermochemical energy transport involving the endothermic reformation of methane with steam and the subsequent exothermic methylation of the products. Since both CO and CO₂ are produced during steam reformation, two reactions are of importance in describing the methylation process.



The parameter 'a' describes the relative mix of the two reactions. Summing components we obtain



If the heats and free energies of formation for equations (1) and (2) are respectively ΔH_1 , ΔG_1 , $a\Delta H_2$, $a\Delta G_2$ then the values for equation (3) are

$$\Delta H_3 = \Delta H_1 + a\Delta H_2 \quad (7)$$

$$\Delta G_3 = \Delta G_1 + a\Delta G_2 \quad (8)$$

2.2 Fugacity coefficients

In order to obtain both the equilibrium mixture and the point values of work recovery efficiency it is necessary to evaluate $\left. \frac{\partial G_{TF}}{\partial \delta} \right|_{TF}$ where G_{TF} is the free energy of the mixture at the temperature T_f and δ is the extent of reaction defined in this instance as the fraction by weight of the products CO + aCO₂ + (3 + 4a)H₂ in the mixture.

The partial free energy of a species in a mixture is rigorously defined in terms of the fugacity \hat{f}_i in the mixture of species i (Chem Eng Handbook, a).

$$dG = RTd\ln f_i \quad (9)$$

$$\lim_{P \rightarrow 0} \frac{\hat{f}_i}{x_i P} = 1 \quad (10)$$

where x_i is the mole fraction of species i and P is the system pressure.

The integration of (6) is greatly simplified if it can be shown that \hat{f}_i can be replaced by $x_i P$ while retaining acceptable precision. In order to demonstrate this it is necessary to show that the approximation is acceptable for the pure components and that, in the mixture, interactions do not deleteriously effect this. The second proviso follows from the thermodynamic relation (Chem Eng Handbook, b).

$$\ln \frac{f}{P} = \sum (x_i \ln \frac{\hat{f}_i}{x_i P})$$

Clearly as \hat{f}_i approaches the partial pressure $x_i P$ for each component, $f \rightarrow P$ proving that interactions must be negligible.

The first condition will be demonstrated to be satisfied by showing that the fugacity coefficient $f_i/x_i P = \phi$ for each component, over the range of integration, is close to unity.

The proportions of the products entering the methylation process are taken from Harth et al (1978) viz:

CO	11.3 vol%
CO ₂	7.6 vol%
H ₂	64.2 vol%
CH ₄	16.9 vol%

System pressure, also following Harth et al, is assumed to be 44 bar.

Table 1
RANGE OF FUGACITY COEFFICIENTS IN GASEOUS MIXTURE

i	P_C atm	T_C °K	xP/P_C	T_S/T_C	T_F/T_C	ϕ_{T_S}	ϕ_{T_F}
CO	35	139	.142	2.16	10.80	.99	1.002
CO ₂	73	304	.046	.99	4.93	.99	1.001
H ₂	12.8	33	2.207	9.09	45.45	1.02	1.005
CH ₄	45.8	190.5	.96	1.57	7.85	.95	1.015
H ₂ O	217.7	647	0(l), .118(g)	.46	2.30	0 *	.99*

$$P = 44 \text{ atm}, T_S = 300, T_{Fmax} = 1500$$

$$* .97 \text{ for } T_F = 600 \text{ K}, 0.99 \text{ for } T_F \geq 900 \text{ K}$$

Table 1 lists the components, their critical parameters and reduced pressures and temperatures at the upper limit of partial pressure and at the extremes of temperature for the range of interest. The coefficients of fugacity were read from the charts appearing in the Chemical Engineers' Handbook. For reduced temperatures greater than 5, ϕ has been estimated from

$$\phi = e^{\alpha P_r}$$

where P_r is the reduced pressure and α is the slope of the compressibility vs P_r line.

It will be noted that the range of reduced pressures in Table 1 embrace 1 atm for which tables of standard thermodynamic properties are available.

The results of Table 1 lead us to assume that ϕ is sufficiently close to unity for all components except water between 300 K and 600 K. At 300 K it is assumed water appears only as a liquid. These assumptions allow us to replace \hat{f}_i in equation (9) by $x_i P$ where x_i is the mole fraction of species i in the gaseous mixture appropriate for the temperature i.e. including or excluding water as the case may be.

2.3 Free Energy

We are now able to integrate from the standard state to other partial states of interest using straightforward mathematical procedures. Under these circumstances free energy of a mixture is given by:

$$G(T, \delta) = RT \sum n_i \ln P x_i + (1 - \delta) \Delta G_{3T} \quad (11)$$

where n_i is the number of moles of component i , P the system pressure in atm and ΔG_{3T} is the free energy of the combined reaction at 1 atm and at temperature T .

G is measured with respect to the components on the left side of equation (6) at 1 atm pressure.

2.4 Equilibrium

Differentiation of (11) gives

$$\left. \frac{\partial G}{\partial \delta} \right|_T = RT \left[\sum \frac{n_i}{x_i} \cdot \frac{dx}{d\delta} + \sum \frac{dn}{d\delta} \cdot \ln px \right] - \Delta G_{3T}$$

Since $n_i = x_i N$, where N is the total number of moles, the first summation equals zero and the second summation simplifies to give:

$$\frac{\partial G}{\partial \delta} = RT \ln \left[\left(\frac{P}{N} \right)^{dN/d\delta} \left\{ n_1 (dn/d\delta)_1 \times n_2 (dn/d\delta)_2 \times \dots \right\} \right] - \Delta G_{3T} \quad (12)$$

Equilibrium may then be determined from the condition:

$$\frac{\partial G}{\partial \delta} = 0 \quad (13)$$

Within the limits of our assumption equilibria may be determined within the temperature range 600 K to 1500 K.

2.5 Work Recovery Efficiency

Point values of work recovery efficiency $\eta(T, \delta)$ are determined from (Carden and Williams)

$$\eta(T, \delta) = \frac{\left. \frac{\partial G_T}{\partial \delta} \right|_{T_S} - \frac{T_S}{T_F} \left. \frac{\partial G_T}{\partial \delta} \right|_{T_F}}{\frac{\partial H_{T_S}}{\partial \delta} T_S} \quad \delta \geq \delta_e \quad (14)$$

The G and H in this equation refer to mixtures of the components of the combined reactions. In order to evaluate the denominator of equation (14) it is necessary to know the enthalpy of the mixture of components. Since for ideal mixtures there is no enthalpy of mixing we obtain simply

$$H = (1 - \delta)\Delta H_3 \quad (15)$$

where H is referred to the components on the left side of equation (6) at 1 atm. Therefore

$$\left. \frac{\partial H_{T_S}}{\partial \delta} \right|_{T_S} = -\delta \Delta H_{3T_S} \quad (16)$$

3. HEATS AND FREE ENERGIES OF FORMATION

3.1 Data Sources

The JANAF thermochemical tables were used to evaluate the required heats and free energies of formation. These tables give standard values of ΔH_i , ΔG_i for a range of compounds i formed from standard states of the elements taken as references. Hence, $\Delta H_1, \Delta H_2, \Delta G_1, \Delta G_2$ may be directly calculated and from these values ΔH_3 and ΔG_3 obtained from (7) and (8) given a value for a .

A slight complication arises at 300 K (T_S) because we require water in the liquid state whereas the table values are for the gaseous state.

Accordingly additional components were added to the table values for ΔH_{H_2O} and ΔG_{H_2O} in order to obtain the correct values.

Starting from the interpolated table value for ΔH_{H_2O} for 373°K the additional components were:

correction due to latent heat	-9.712 Kcal/mole
correction due to heating $H_2 + \frac{1}{2}O_2$ from 300 K	
to 373 K and cooling water from 373 K to 300 K	-0.548
correction due to pressurising liquid to 44 atm	+0.018
corrected value $\Delta H_{H_2O} T_S$	-68.220

Starting from the table values for G_{H_2O} for 300 K the additional components were:

correction for condensation	0
correction for pressurising liquid to 44 atm	+0.018
corrected value $G_{H_2O T_S}$	-54.599

3.2 Values

Table 2 lists the values used in the computations.

Table 2

$$T_S = 300 \text{ K} \quad P = 44 \text{ atm}$$

$$\Delta G_{IT_S} = -33.886 \text{ Kcal/mole}$$

$$\Delta G_{2T_S} = -27.041$$

$$\Delta H_{IT_S} = -59.715$$

$$\Delta H_{2T_S} = -60.294$$

$$T_F = 600^\circ\text{K to } 1500^\circ\text{K}$$

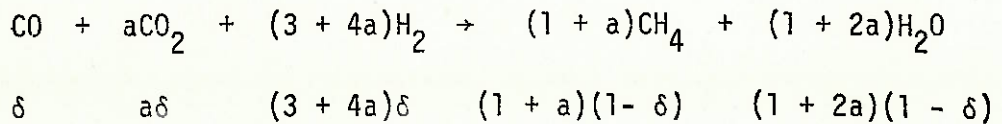
T_F	600	700	800	900	1000	1100	1200	1300	1400	1500
G_{1T_F}	-17.338	-11.493	-5.567	.421	6.444	12.492	18.565	24.639	30.721	36.803
G_{2T_F}	-13.347	-8.366	-3.269	1.921	7.173	12.471	17.826	23.192	28.585	33.993

4. EVALUATION OF EQUILIBRIUM AND WORK RECOVERY EFFICIENCY

4.1 Formulation

Equation (9) is the principle equation for computing both equilibria and η . In this equation N is the total number of moles and n_i the number of moles of component i . The mass is kept constant and equal to the mass of either side of equation (3).

Clearly the mole values n_i of components in a mixture of reacted and unreacted components are the quantities written under the formulae in the following repetition of equation (6)



If water is a gas, then

$$\begin{aligned} N_{TF} &= \delta + a\delta + (3 + 4a)\delta + (1 + a)(1 - \delta) + (1 + 2a)(1 - \delta) \\ &= 2\delta(1 + a) + 2 + 3a \end{aligned}$$

and if water is a liquid,

$$\begin{aligned} N_{TS} &= \delta + a\delta + (3 + 4a)\delta + (1 + a)(1 - \delta) \\ &= \delta(3 + 4a) + 1 + a \end{aligned}$$

Values for $dN/d\delta$ and $dn_i/d\delta$ are therefore as follows in Table 3.

Table 3

$$dN_{TF}/d\delta = 2a + 2$$

$$dN_{TS}/d\delta = 3 + 4a$$

i	CO	CO ₂	H ₂	CH ₄	H ₂ O
n_i	δ	$a\delta$	$(3 + 4a)\delta$	$(1 + a)(1 - \delta)$	$(1 + 2a)(1 - \delta)$
$\frac{dn_i}{d\delta}$	1	a	$(3 + 4a)$	$-(1 + a)$	$-(1 + 2a)$

4.2 Computed results

Values were computed for the case described by Harth et al. For this case $a = 0.67$, $P = 44$ atm and T_S is taken as 300 K.

The computed data has been set out on the T-H diagram Figure 1. In this diagram the extreme mixtures, $\delta = 0$, $\delta = 1$ were plotted for equation (6) using the JANAF data for $H^0 - H_{298}^0$. A constant has been added to the left hand side values so as to make the differences in enthalpy between the two mixture extremes equal to the heat of formation ΔH_3 . Enthalpies for intermediate values of δ were obtained by linear interpolation using equation (15).

5. DISCUSSION AND CONCLUSION

The $\eta(T, \delta)$ contours are significantly different from those of the NH_3 thermochemical system. Whereas for the latter, the equilibrium line is a contour of maximum η , in the present instance this is not the case because η on the equilibrium line increases with temperature. In the present case the η contours are almost horizontal whereas for NH_3 they tend to run parallel with the equilibrium line.

The reason for the difference in characteristics is that for NH_3 the product of synthesis is a liquid at T_S whereas for CH_4 only part of the product of synthesis is liquid. This in turn means that the free energy of the mixture at T_S is not a linear function of δ as it is for NH_3 .

It will be shown elsewhere (Carden 1980) that contours for ideal gas thermochemical systems containing no condensing components are horizontal. The characteristics of the CH_4 contours can therefore be regarded as intermediate between those of an ideal gas system and the NH_3 system.

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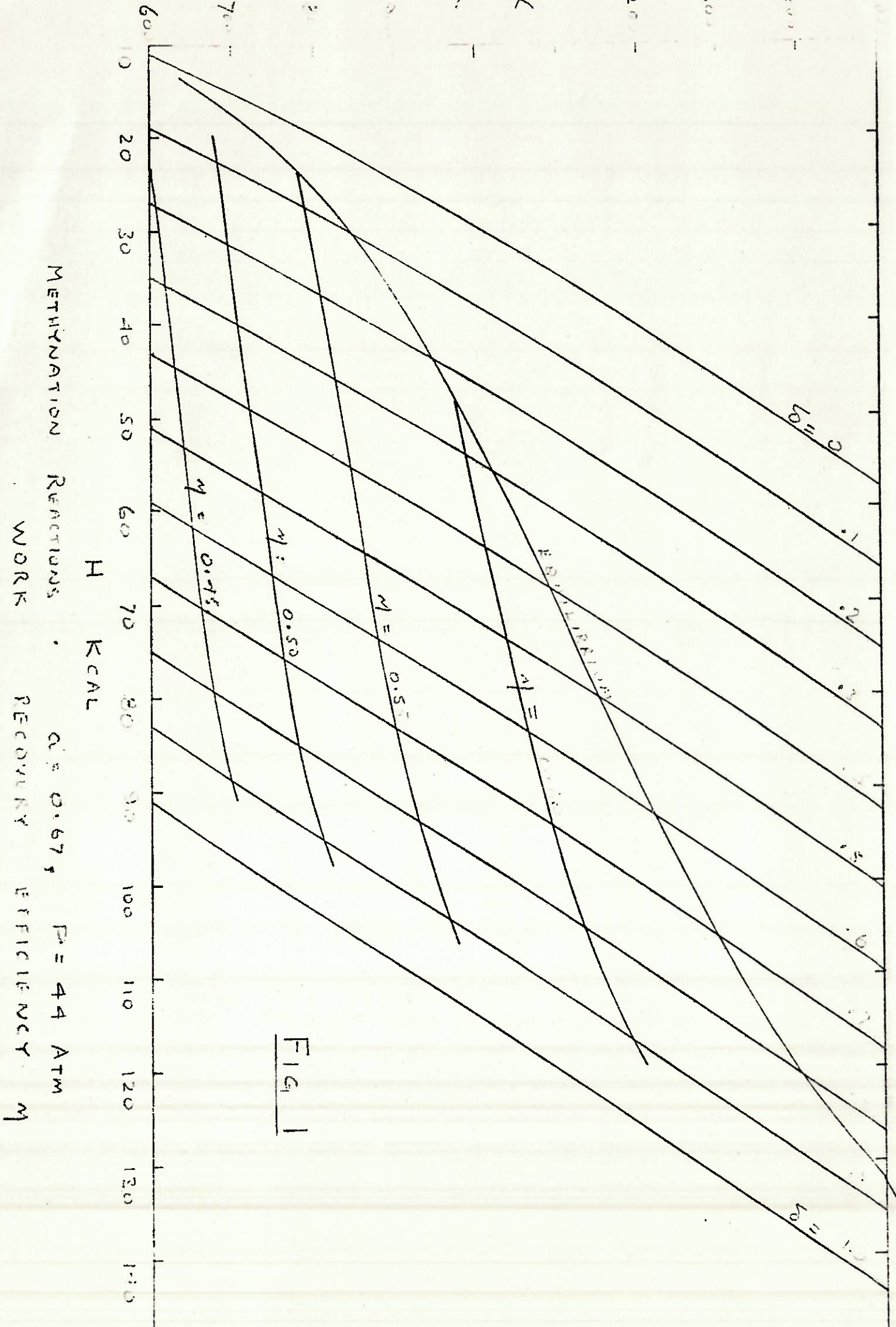


FIG 1

$\alpha = 0.67, P = 44 \text{ ATM}$

