WORK RECOVERY EFFICIENCY OF IDEAL GAS THERMOCHEMICAL ENERGY TRANSFER SYSTEMS AND SO_3 SYNTHESIS

ENERGY CONVERSION TECHNICAL REPORT NO 23

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1. Introduction

Work recovery efficiency is a concept introduced by Carden and Williams (1978) which relates the maximum work obtainable from the exothermic terminal of a thermochemical energy transfer loop to the difference in enthalpies of the inflowing and outflowing reactants. The reactant flows are considered to be at the lowest practical temperature at which storage of the reactants may be implemented. This temperature, the storage temperature, is normally at or near ambient temperature.

In defining work recovery efficiency η the convention has been adopted that all processes are thermodynamically reversible except the chemical reaction itself. Thus with a knowledge of how η depends on other parameters, what is usually the most critical process may be designed for optimum performance.

Having worked with Williams to determine the work recovery efficiency of the ammonia system, the author proceeded to study the methane system (Carden, 1980) and then the sulphur trioxide system, these three being probably the most notable of those being researched throughout the world.

These three systems utilise respectively the following reversible reactions.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$CO + aCO_2 + (3 + 4a)H_2 \rightleftharpoons (1 + a)CH_4 + (1 + 2a)H_2$$

$$(a \approx .67)$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

The sulphur trioxide study yielded a surprisingly simple result of a nature that prompted a more general study of systems which we may call ideal gas systems ie. ones in which all the components throughout the operating range of temperature and partial pressure may be considered as ideal gases.

Neither the ammonia system nor the methane system are of course ideal gas systems because of the presence of a condensing component: ammonia and water respectively. The sulphur trioxide system also has condensing components but the proponents of the system, notably Chubb (1975), have always declared that the system should be operated at a storage temperature of approximately 95°C in order to prevent sulphur trioxide condensing into an unmanageably viscous liquid. Perhaps 95°C has been conservatively chosen to be higher than it need be because a second surprising result is that the fugacity coefficients of all the components at 95°C and above, and at the recommended system pressure of 3 atms, are within 0.01 of unity suggesting that the sulphur trioxide system, so operated, is a good example of an ideal gas system.

The present study is designed to give specific results for the sulphur trioxide system but at the same time to demonstrate by the use of generalisations that in fact all ideal gas systems will behave similarly.

2. The Sulphur Trioxide Ideal Gas System

The characteristic of ideal gas mixtures which is drawn upon in our analysis relates to the fugacity coefficient ϕ. For each component of an ideal gas mixture

$$\phi = 1 \qquad (1)$$

The physical and mathematical simplification which follow from this characteristic are well known and explained in detail by Carden (1980). They relate to the fact that each component acts independently obeying the ideal gas law of isothermal compression without interacting with other components. The enthalpy of mixing is therefore zero.

In order to demonstrate that the sulphur trioxide system may be regarded as ideal it is necessary to show that equation (1) is approximately true for each component throughout the range of states of interest. Moreover, to enable quantitative calculations to be made equation (1) should be true over a larger range if necessary, one that includes both the range of states of interest and a set of reference states for which values of the thermodynamic properties are known.

Taking the components one by one we note that oxygen may be regarded as an ideal gas over the system temperature range $368^{\circ}K$ to $1500^{\circ}K$ and partial pressure range 0 to 3 atms. For the components SO_2 and SO_3 the case is not so clear cut. In Table I are listed the critical parameters for each of these components together with the fugacity coefficients corresponding to the lowest reduced temperature to be considered and the highest reduced pressure. In relation to these values, increases in reduced temperature and decreases in reduced pressure will cause ϕ to approach closer to unity. Thus it will be seen that throughout the entire range to be considered

$$0.99 < \phi < 1$$

This suggests that we may safely regard the sulphur trioxide system as being an ideal gas system. Moreover, the range encompasses a set of reference states at 1 atmosphere, eg. as listed in the JANAF tables (1976).

3. The Enthalpy and Free Energy of Ideal Gas Mixtures

Ideal gas mixtures exhibit zero mixing enthalpy ie. the total energy change involved in taking a component isothermally and reversibly from the reference state pressure of one atmosphere to the partial pressure of the component in the mixture is zero.

Hence, for a reaction such as

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3 \qquad (2)$$

which has proceeded to the left to the extent that fraction δ of the original SO_3 has been converted, the enthalpy of the resulting mixture per original SO_3 mole is given by

$$H_{mT} = (1 - \delta)\Delta H_T \qquad (3)$$

where ΔH_T is the heat of formation of SO_3 from the components on the LHS of (2) and H_{mT} is measured relative to the components on the LHS of (2) each at 1 atm.

The free energy G_{mT} of an ideal gas mixture may be obtained in several ways. One way is to proceed in an analogous way to that used above in obtaining equation (3). However, free energy of mixing is non zero so additional quantities must be added representing the free energy change involved in taking each component from the reference pressure to the partial pressure in the mixture.

It is well known that each such quantity is of the form $RTnx_i \ln x_i P$ where n is the total number of moles in the mixture, x_i is the mole fraction of the component of interest and P is the system pressure.

For the particular case of the sulphur trioxide system, taking a total quantity of mixture equal in weight to the weight of 1 mole of SO_3, we find

$$\bar{n} = \tfrac{1}{2}(2 + \delta)$$

$$x_{SO_2} = 2\delta/(2 + \delta)$$

$$x_{SO_3} = 2(1 - \delta)/(2 + \delta)$$

$$x_{O_2} = \delta/(2 + \delta)$$

These values enable us to determine the free energy of the mixture as:

$$G_{mT} = RT\{\delta \ln 2P\delta/(2 + \delta) + (1 - \delta)\ln 2P(1 - \delta)/(2 + \delta) + \delta/2.\ln P\delta/(2 + \delta)\} + (1 - \delta)\Delta G_T \qquad (4)$$

4. Work Recovery Efficiency

As shown by Carden and Williams (1978) work recovery efficiency along any reaction path characterised by a continuous succession of pairs of values of T_F and δ is obtained by integrating along the path $\eta(T_F,\delta)$ with respect to δ where $\eta(T_F,\delta)$ is the 'point' work recovery efficiency given by

$$\eta(T_F,\delta) = \frac{\left.\frac{\partial G}{\partial \delta}\right|_{T_S} - \frac{T_S}{T_F}\left.\frac{\partial G}{\partial \delta}\right|_{T_F}}{\left.\frac{\partial H}{\partial \delta}\right|_{T_S}} \qquad (5)$$

In this equation T_S is the sink temperature for ideal heat engines conventionally taken as being equal to the storage temperature.

A simple explanation of equation (5) is that in an element of the reaction characterised by a small change in reaction extent $d\delta$, free energy dG_{T_F} that would be available as work if the reaction had proceeded reversibly (in the thermodynamic sense) has been instead degraded to heat which appears at the reaction element temperature T_F. Some work is however recovered by passing this heat into a Carnot engine. The net loss in work is then reduced to $T_S/T_F . dG_{T_F}$. This amount is subtracted from the elemental free energy entering the system with the reactant flows at temperature T_S viz dG_{T_S}. Finally, the net elemental work is expressed as a proportion of the relevant enthalpy entering the system dH_{T_S}.

In order to evaluate equation (5) we must differentiate equation (4). Thus we obtain

$$\frac{\partial G_{mT}}{\partial \delta} = RT \ln \left| \frac{p^{\frac{1}{2}} \delta^{3/2}}{(1-\delta)(2+\delta)^{\frac{1}{2}}} \right| - \Delta G_T \qquad (6)$$

which may be generally expressed as

$$\frac{\partial G_{mT}}{\partial \delta} = RT\ F(\delta) - \Delta G_T \qquad (7)$$

By substitution of (7) in (5) we obtain a result independent of $F(\delta)$ viz

$$\eta = \frac{\frac{T_S}{T_F} \Delta G_{T_F} - \Delta G_{T_S}}{-\Delta H_{T_S}} \qquad (8)$$

The reaction equilibrium value of δ at temperature T may be obtained by equating the RHS of (6) to zero.

This method and equation (8) were employed to produce the data shown on Figure 1.

5. Discussion

It will be observed that η is independent of δ ie. contours of equal η on a T,H diagram are a series of horizontal straight lines (ending of course on the equilibrium line). This is to be contrasted to the η contours for the ammonia system which tend to run parallel with the equilibrium line, the equilibrium line being itself a contour of constant η having maximum value. It is also to be contrasted with the result obtained for the methane system (Carden, 1980) for which contours are neither horizontal or parallel to the equilibrium line but which do intersect the equilibrium line.

In order to test the reasonableness of the result (8) let us compare values of η computed for the sulphur trioxide system with the Carnot efficiency $\left(1 - \frac{T_S}{T_F}\right)$. Table II gives values of ΔG_{T_S}, ΔH_{T_S}, ΔG_{T_F} and ΔH_{T_S} derived from data appearing in the JANAF tables. Also shown in Table II are the resulting values of η_{T_F} and $\left(1 - \frac{T_S}{T_F}\right)$.

The correlation is remarkably good suggesting that one might arrive at this result through further analysis. This we will now attempt to do.

The supposed equality

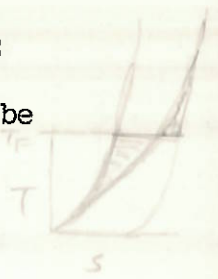
$$\eta_{T_F} = \left(1 - \frac{T_S}{T_F}\right) \tag{9}$$

may be easily shown to imply

$$\Delta G_{T_S} - \Delta G_{T_F} = (T_F - T_S)\Delta S_{T_S} \tag{10}$$

(This result is obtained by combining equations (8) and (9) to eliminate η and then substituting $(\Delta G_{T_S} + T_S \Delta G_{T_S})$ for ΔH_{T_S}.)

Now the free energy of a reaction at temperature T_F is equal to that part of a T-S diagram bounded by $T = T_F$, the equilibrium curve and curves for each side of the reaction. It follows that for (10) to be true, the latter two curves must be of the same shape ie. it is required that ΔS be constant irrespective of temperature. This in turn requires ΔH to be constant.



However, it is clear from Table II that for the sulphur trioxide system there is a 3% variation in ΔH_{T_F} which seems incompatible with the close correlation (to 0.5%) observed for equation (9). The explanation is probably related to the way in which S is derived from H. Characteristically ΔS tends to approach constancy, more so as temperature increases, despite considerable variation in ΔH.

If such an explanation is found to be valid it may be that equation (9) is true enough for a large range of non-ideal gas systems. The work recovery efficiency of all non-separating thermochemical systems may then be reduced to one simple universal equation, the only remaining difference between individual systems being the position of the equilibrium line. The preferred method of operating a gas system to obtain maximum η is obviously with dissociation as complete as possible and synthesis deliberately incomplete. The designer must reach a compromise between work recovery efficiency and reactant flow because increased reactant flows result from less complete synthesis. Apart from the shape and position of the equilibrium line there would seem to be no other theoretical reason to favour one particular system over another. The choice of the best system should therefore depend largely on practical considerations which are related to the nature of the chemicals and the reaction enthalpies.

It must also be observed that an ammonia system may be operated in a non-separating mode by lowering the system pressure sufficiently. Benefits which may come from doing this are increased work recovery efficiency at moderate synthesis temperature, easier dissociation, and advantages which may accrue from working at lower pressure. Against this are the disadvantages of larger pipe sizes due to multiple causes: lower density, higher flow and lower tolerable friction pressure drops. However, whether or not the benefit will outweigh the disadvantages it seems worthwhile comparing a non-separating ammonia system with the sulphur trioxide system.

Finally, some doubt must now be cast on the validity of the values of η at δ above 0.9 previously obtained by Carden and Williams for the ammonia system at 300 ats. In this small region ammonia does not condense out at the storage temperature.

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TABLE I

	$T_c(^oK)$	P_C(atm)	T_S/T_C	P_S/P_C	ϕ min
SO_2	430.2	77.7	0.855	0.039	0.99
SO_3	491.3	83.6	0.749	0.036	0.99

T_S = 368 K (95^oC)

P_S = 3 atm

TABLE II

ΔG_{TS} = -15.37

ΔH_{TS} = -23.68

T_F	G_{TF}	H_{TF}	μ_{TF}	$(1-T_S/T_F)$
600	-10.129	-23.657	.387	.387
800	- 5.639	-23.518	.540	.540
1000	- 1.189	-23.338	.631	.632
1200	3.222	-23.136	.691	.693
1400	7.598	-22.928	.733	.737

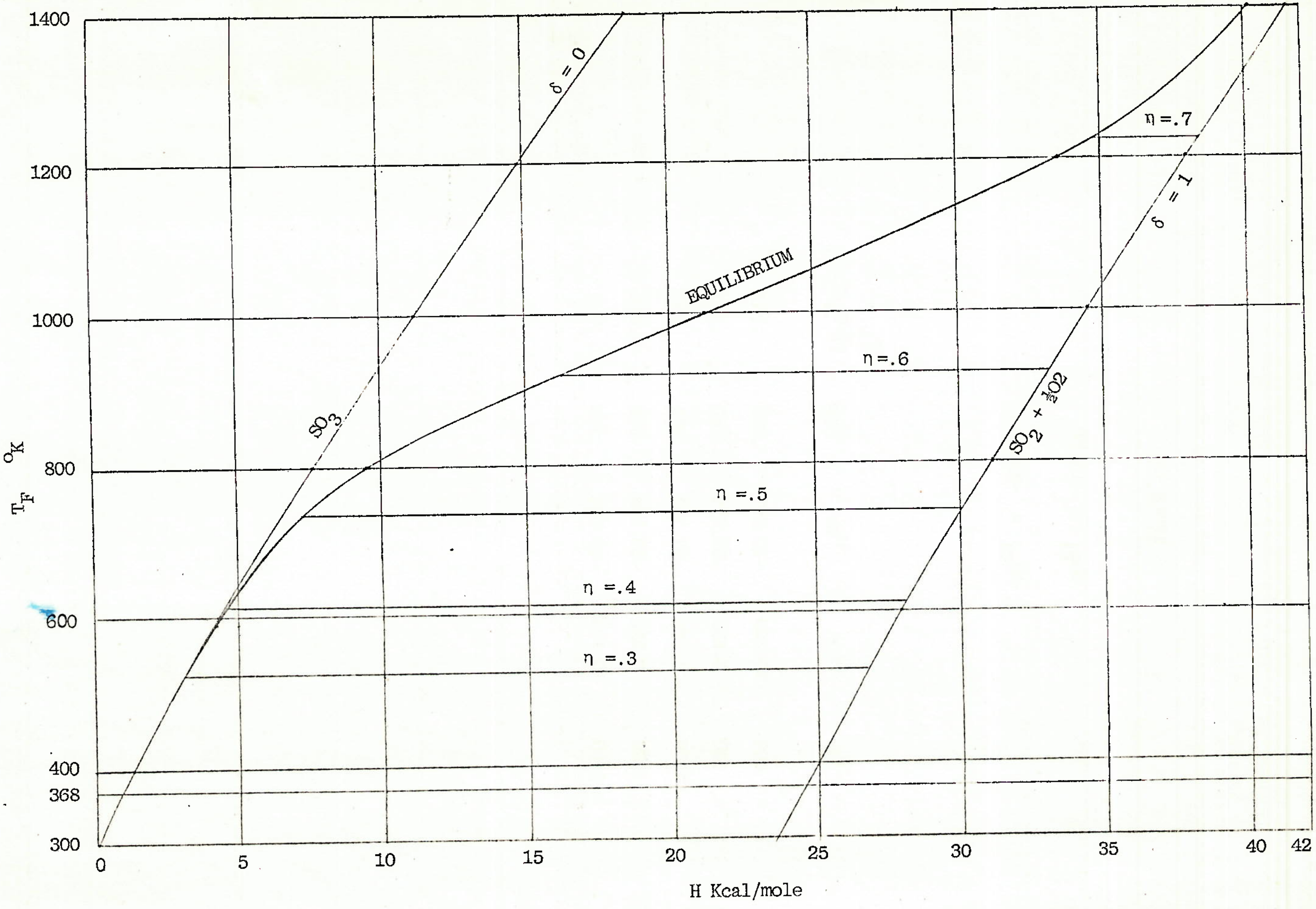

FIGURE 1: Work Recovery Efficiency η for Sulphur Trioxide System P = 3 atm T_S = 368°K (95°C)