

# MULTIPLE REACTION EQUILIBRIA— WITH PENCIL AND PAPER

## A Class Problem on Coal Methanation

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**E**QUILIBRIA OF MULTIPLE and heterogeneous chemical reactions are accorded only a rather cursory treatment in most textbooks on thermodynamics and reaction engineering. Yet problems of this kind are frequent in practice. Moreover, the textbook methods involve extensive calculations that require a computer if three or more reactions are involved.

The purpose of this article is to point out a different and much simpler approach that can be taken in many practical situations. The problem is especially suited for the undergraduate classroom in that it acquaints the student not only with the topic immediately at hand, but also introduces him to a widely applicable technique of problem solving in chemical engineering practice which is largely unrealized in undergraduate textbooks.

In my experience, the message is delivered most effectively in a setting where the class plays the role of a development group in a fictional major industrial company. The description that follows is along such lines.

### THE PROBLEM

The Vice President of Research and Development explains that the company has acquired major coal

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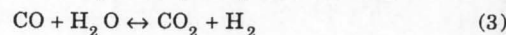
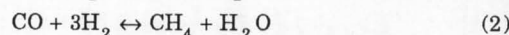
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TABLE 1  
Standard Free Energies and Enthalpies of  
Formation of Gaseous Participants  
from Elements at 298.15 K, in kcal/mol  
(from Hill [1], Appendix A)

	$\Delta G_f^\circ$	$\Delta H_f^\circ$
H <sub>2</sub> O	- 54.6351	- 57.7979
CO	- 32.8077	- 26.4157
CO <sub>2</sub>	- 94.2598	- 94.0518
CH <sub>4</sub>	- 12.140	- 17.889

leaves as a hedge against the day when oil and gas reserves will dwindle. However, to serve a technology that has been nursed on fluid fuels, much of that coal will have to be liquefied or gasified. In the context of a preliminary feasibility study, our group receives an assignment to evaluate the thermodynamics of coal methanation. Specifically, the question of whether and under what conditions 90% of the coal can be converted to methane (as opposed to oxides of carbon) should be answered.

For the classroom the problem is simplified and dressed up as follows. Coal is regarded as elementary carbon. Only the three main reactions are to be considered:



The starting materials are carbon, water, and, if needed, hydrogen. All potential catalysts catalyze all three reactions, so they cannot be conducted in separate reactors. All reactants except coal should be gaseous. A minimum temperature of 550 K is required for reasonable catalyst activity. High temperatures and pressures, as well as the presence of liquid water, are undesirable because of cost and corrosion prob-

lems. For the purpose at hand, calculations which are based on ideal gas behavior and temperature-independent standard enthalpy changes are acceptable. A strict and short deadline is set for the presentation of conclusions to management.

### FIRST TRY

To obtain an idea of the system, an obvious first step is to calculate and plot the equilibrium constants of the three reactions as a function of temperature. This calls for the  $\Delta G^\circ$  and  $\Delta H^\circ$  values of the reactions, readily calculated from tabulated thermochemical data (see Table 1) by the standard procedure [1] (formation values of products minus those of reactants). The resulting values as well as the changes  $\Delta n_g$  in gas mole number are shown in Table 2. The equilibrium constants

$$K_1 \geq p_{\text{CO}} p_{\text{H}_2} / p_{\text{H}_2\text{O}} \quad (4)$$

$$K_2 = p_{\text{CH}_4} p_{\text{H}_2\text{O}} / p_{\text{CO}} p_{\text{H}_2}^3 \quad (5)$$

$$K_3 = p_{\text{CO}_2} p_{\text{H}_2} / p_{\text{CO}} p_{\text{H}_2\text{O}} \quad (6)$$

at any temperature  $T$  can now be obtained from the Van't Hoff equation

$$\ln K_i(T) = -\Delta G^\circ/R * 298 + (\Delta H^\circ/R)(1/298 - 1/T) \quad (7)$$

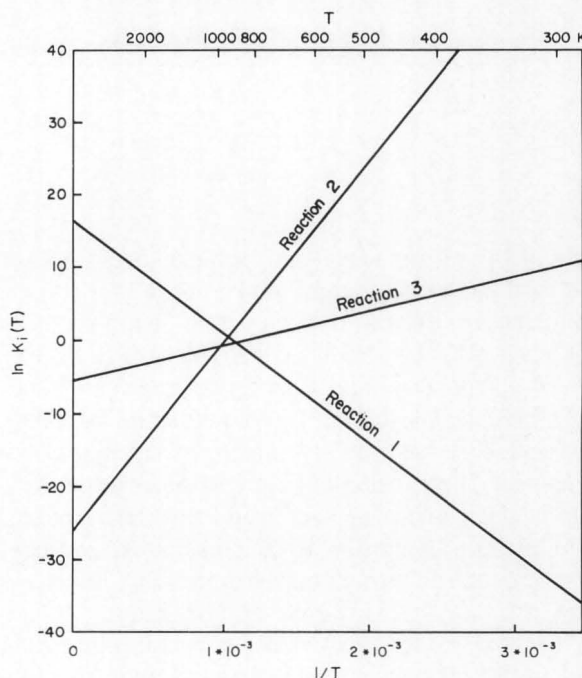
Plots of  $\ln K_i(T)$  versus reciprocal temperature are shown in Figure 1. In the absence of solid carbon, the inequality in Eq. (4) may apply.

The data reveal conflicting demands with respect to temperature and pressure. Both reactions 1 and 2 are necessary for methane formation from coal, but reaction 1 is seen to be favored by high temperature (positive  $\Delta H^\circ$ ) and low pressure (increase in gas mole number), while for reaction 2 the opposite holds. Intuitively, we may wish to seek conditions giving not too low an equilibrium constant of either reaction, and thus be led to a temperature "window" of, say, 600 to 1200 K. If this line of reasoning were correct, we

**TABLE 2**  
Changes in Standard Free Energy, Standard Enthalpy, and Gas Mole Number for Reactions 1, 2, and 3  
( $\Delta G^\circ$  and  $\Delta H^\circ$  in kcal/mol, calculated from data in Table 1)

	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta n_g$
Reaction 1	+ 21.83	+ 31.38	+ 1
Reaction 2	- 33.97	- 49.27	- 2
Reaction 3	- 6.83	- 9.84	0

The task at hand now is to find what sets, if any, of operating variables . . . will produce the desired 90% equilibrium yield to methane, basis carbon reacted (i.e., 0.9 moles of methane produced per mole of carbon reacted).



**FIGURE 1.** Van't Hoff plot for equilibrium constants of reactions 1 to 3.

would seek low pressure at low temperature and high pressure at high temperature, in order to have pressure favor the reaction discouraged by temperature. Obviously, we prefer low to high temperature and pressure, and so we might start our search for conditions with temperatures in the vicinity of 600 to 700 K and pressures of perhaps a few atmospheres. This, however, is no more than a working hypothesis, to be carried on our fingertips so it can be blown away by the slightest breeze of better insight (as indeed it will).

The task at hand now is to find what sets, if any, of operating variables—temperature  $T$ , pressure  $P$ , and  $\text{H}_2:\text{H}_2\text{O}$  mole ratio  $R$  in the reactor feed—will produce the desired 90% equilibrium yield to methane, basis carbon reacted (i.e., 0.9 moles of methane produced per mole of carbon reacted). The most common procedure [1-5] is to establish the relations between the mole fractions  $y_i$  of the gaseous participants at equilibrium and the extents  $x$ ,  $y$ , and  $z$  of the three

reactions, as shown in Table 3, and then to rewrite the equilibrium expressions (4) to (6) in terms of the extents of reaction and mole fractions  $y_i = p_i/P$ . With the mole fraction in Table 3, Eqs. (4) to (6) in terms of extents of reaction become

$$K_1 P^{-1} \geq \frac{y_{H_2} y_{CO}}{y_{H_2O}} = \frac{(R+x-3y+z)(x-y-z)}{(1-x+y-z)(1+R+x-2y)} \quad (8)$$

$$K_2 P^2 = \frac{y_{CH_4} y_{H_2O}}{y_{CO} y_{H_2}^3} = \frac{y(1-x+y-z)(1+R+x-2y)^2}{(x-y-z)(R+x-3y+z)^3} \quad (9)$$

$$K_3 = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = \frac{z(R+x-3y+z)}{(x-y-z)(1-x+y-z)} \quad (10)$$

Sets of operating variables—temperature, pressure, and feed mole ratio—can then be chosen for screening (temperature determining the equilibrium constants). For each set, the simultaneous Eqs. (8) to (10) must be solved for  $x$ ,  $y$ , and  $z$ , and the gas mole fractions must be calculated from the expressions for the  $y_i$  in Table 3. This task involves a lot of calculation since ranges of three independent variables must be covered, but it can be performed without trouble on a mainframe computer with a packaged routine for solving simultaneous algebraic equations. For the purpose at hand, this is the method of choice.

Two other methods could be considered here. The first is the relaxation method (also called the series-reactor technique [3, 4, 6]; this is an iteration over a large number of reactors in series, in each of which only one of the three reactions occurs. The other is the method of minimization of Gibbs energy (also called Lagrangian multiplier technique [3, 4]), which operates with equilibrium equations (one for each species) and material balances (one for each element),

to establish the minimum of free energy. Both methods involve extensive calculation and would require more computer programming, although the Gibbs method has advantages if systems are more complex and a packaged routine is available.

### MISFORTUNE STRIKES

Unfortunately for our group, we are informed that the mainframe must be shut down to repair water damage from Hurricane Fidel and that all stand-by computing facilities have been reserved for tasks of higher priority. We are reduced to using our hand-held, programmable calculators. To meet the deadline we shall have to streamline the problem.

Indeed, our approach as originally envisaged is inefficient in that many chosen sets of variables will produce results that are useless because the methane yield falls short of our goal. Instead, we can choose that yield as one of our "design options," that is, as one of the three variables we can specify. Desired is

$$y_{CH_4} / (y_{CO} + y_{CO_2} + y_{CH_4}) = 0.9$$

which amounts to

$$y_{CH_4} / (y_{CO} + y_{CO_2}) = 9 \quad (11)$$

With the expressions for the mole fractions in Table 3 this reduces to

$$y = 0.9x \quad (12)$$

a result so simple as to be suspect. It makes sense, however: Carbon appears only in reaction 1, as reactant; and methane, only in reaction 2, as product. Therefore,  $y/x = 0.9$  translates into 0.9 moles of methane formed per mole of carbon reacted. With Eq. (12),  $y$  can be eliminated from Eqs. (8) to (10), greatly reducing our calculation load. We still have three simultaneous equations to solve, but we can solve for  $x$ ,  $z$  and  $R$  and have only ranges of two variables,  $P$  and  $T$ , to screen instead of three. Moreover, every successful calculation (*i.e.*, giving a physically realizable answer) will now produce a useful result as the demanded methane yield is guaranteed. A possible approach is to fix temperature and pressure within our window, select pairs of values of  $x$  and  $z$ , solve the three equations for  $R$ , and adjust the choice of  $x$  and  $z$  until all three equations give the same value of  $R$ . This will take time and our time is short, but with, say, ten or twelve good programmable calculators in our groups we might just be able to come up with at least a few sets of conditions giving the desired result.

TABLE 3  
Initial Mole Numbers  $n_i^0$ , Equilibrium Mole Numbers  $n_i$ , and Equilibrium Gas Mole Fractions  $y_i$  of Gaseous Participants in Dependence on Extents  $x, y$ , and  $z$  of Reactions 1 to 3  
(procedure as in Hill [1])

	$n_i^0$	$n_i$	$y_i$
CH <sub>4</sub>	0	$y$	$y/(1+R+x-2y)$
CO	0	$x-y-z$	$(x+y-z)/(1+R+x-2y)$
CO <sub>2</sub>	0	$z$	$z/(1+R+x-2y)$
H <sub>2</sub> O	1	$1-x+y-z$	$(1-x+y-z)/(1+R+x-2y)$
H <sub>2</sub>	$R$	$R+x-3y+z$	$(R+x-3y+z)/(1+R+x-2y)$
TOTAL		$1+R+x-2y$	



. . . in our days of easy access to computers and the temptation to use [them] on every occasion, it will be educational for a student to see that the human brain still has a place in our world: That, in fact, a problem properly thought through might possibly be solved long-hand in a shorter time than it would take to be fed to a computer.

## BACK TO THE STONE AGE

Now the time has come to let misfortune strike again. Fate (personified by the instructor), decrees that we are running out of batteries and have no replacements. Can our problem be solved in the few hours left with just pencil and paper alone?

On closer inspection we might realize that we have not derived full benefit from our idea to start the calculation with the desired result. There is no longer any need to translate the simple, partial-pressure equilibrium Eqs. (4) to (6) into the more complex extent-of-reaction Eqs. (8) to (10). It is true that total pressure does not appear explicitly in Eqs. (4) to (6) and so can no longer be chosen as a design option. However, we are not held to calculate results for specified total pressures and so can let ourselves be surprised by what that pressure will turn out to be.

Following up on this idea, we find that if we fix temperature, and thus the three equilibrium constants, we have five unknowns (the five partial pressures), three equations (if for the time being we accept the equality in condition (4)), and one constraint (the selectivity requirement (11)). Accordingly, we can choose one partial pressure and calculate all others. For instance the four other partial pressures can be expressed as functions of only  $p_{\text{CH}_4}$  and the equilibrium constants and can be calculated once a value of  $p_{\text{CH}_4}$  (and of temperature) has been chosen.

Proceeding in this fashion we can obtain explicit equations for our partial pressures, but at least one is a quadratic equation. Because the deadline is so close, we might want to streamline the problem even further. Experience with other projects and the very large decrease in  $\Delta G^\circ$  from CO to  $\text{CO}_2$  (see Table 1) tells us that at all reasonable temperatures and pressures the amount of CO at equilibrium will be small compared with that of  $\text{CO}_2$ . We should thus be fairly safe if we set

$$p_{\text{CH}_4} / p_{\text{CO}_2} = 10 \quad (13)$$

instead of

$$p_{\text{CH}_4} / (p_{\text{CO}} + p_{\text{CO}_2}) = 9$$

This still leaves some margin for CO and should bring us quite close to the desired result.

By simple algebraic manipulation, Eqs. (4) to (6) are easily solved for  $p_{\text{H}_2}$  and  $p_{\text{CO}}$  in terms of  $p_{\text{CH}_4}$  and  $p_{\text{CO}_2}$ :

$$p_{\text{CO}} = (K_1 p_{\text{CO}_2} / K_3)^{1/2} \quad (14)$$

$$p_{\text{H}_2} = (p_{\text{CH}_4} / K_1 K_2)^{1/2} \quad (15)$$

$p_{\text{H}_2\text{O}}$  is then obtained from Eq. (4)

$$p_{\text{H}_2\text{O}} = p_{\text{H}_2} p_{\text{CO}} / K_1 \quad (16)$$

Eq. (13) allows us to choose a partial pressure of methane and one of  $\text{CO}_2$  one-tenth as large and calculate the other three. In each case, we shall have to check whether the stipulated methane yield is indeed attained or exceeded; if not, the calculation must be repeated with a slightly lower partial pressure of  $\text{CO}_2$ . Time permitting, if the yield turns out to be significantly better than needed, the calculation should also be repeated, with a slightly higher partial pressure of  $\text{CO}_2$ , for better comparison of conditions giving the desired result.\*

We still have to deal with the possible inequality in the equilibrium condition (4) for reaction 1 and with the possibility that water may condense at equilibrium. It becomes immediately apparent that an inequality in condition (4), as would be produced by continued reaction after all coal is consumed, leads to a higher water content of the product gas and thus is undesirable. As to water condensing, at temperatures below 647 K (critical temperature of water) the calculated partial pressure of water must be checked against the vapor pressure at that temperature. If it exceeds the vapor pressure, the calculation is invalid and would have to be repeated with  $p_{\text{H}_2\text{O}}$  set equal to the vapor

### Note Added in Proof:

As pointed out to me by J.-M. Chern, the approximation (13) and the recalculations it may necessitate can be avoided as follows: select a value of  $p_{\text{CO}}$ ; then calculate  $p_{\text{CO}_2} = K_3 p_{\text{CO}}^2 / K_1$  [from Eqs. (6) and (4)],  $p_{\text{CH}_4} = 9(p_{\text{CO}_2} + p_{\text{CO}})$  [from Eq. (9)],  $p_{\text{H}_2} = (p_{\text{CH}_4} / K_1 K_2)^{1/2}$  [from Eqs. (4) and (5)], and  $p_{\text{H}_2\text{O}} = p_{\text{CO}} p_{\text{H}_2} / K_1$  [from Eq. (4)]. The only disadvantage of this more direct procedure is that it is harder to anticipate what the total pressure will turn out to be when starting with CO, in most cases a very minor component, instead of  $\text{CH}_4$ , the main component.

pressure. Only one other partial pressure can now be freely chosen, and the desired methane yield might not be attained. However we were instructed to avoid such conditions because they would invite corrosion problems, and so should rather discard the case.

As to information on the three operating variables: Temperature was fixed to calculate the equilibrium constants; total pressure is immediately obtained as the sum of the partial pressures; the H<sub>2</sub>:H<sub>2</sub>O feed mole ratio still remains to be determined. This requires material balances. Since water is the only source of oxygen, the oxygen balance is

$$\text{moles H}_2\text{O in} = (\text{moles H}_2\text{O} + \text{CO} + 2^* \text{CO}_2) \text{ out}$$

and the hydrogen balance is

$$(\text{moles H}_2 + \text{H}_2\text{O}) \text{ in} = (\text{moles H}_2 + \text{H}_2\text{O} + 2^* \text{CH}_4) \text{ out}$$

giving

$$R = \frac{\text{moles H}_2 \text{ in}}{\text{moles H}_2\text{O in}} = \frac{P_{\text{H}_2\text{O}} + P_{\text{H}_2} + 2P_{\text{CH}_4}}{P_{\text{H}_2\text{O}} + P_{\text{CO}} + 2P_{\text{CO}_2}} - 1 \quad (17)$$

This completes the information needed.

With each member of the group calculating, say, four or five cases in assigned ranges of temperature

and partial pressure of methane, a rather broad and thorough coverage of conditions giving the desired methane yield can be achieved, with just pencil and paper, in time for presentation to an impressed management. (Slide rules would come in handy but are hard to find short of raiding the local science museum—and rare is now the student who has learned to use one.)

## RESULTS AND CONCLUSIONS

Results of nine calculated cases in the range of 600 to 1000 K and 2 to 85 atm and with methane yield (based on carbon converted) tuned to fall between 0.900 and 0.902 have been collected in Table 4. The table also includes the ratio of H<sub>2</sub> fed to CH<sub>4</sub> formed, a measure of the economically highly important hydrogen utilization.

It turns out that, contrary to our initial intuitive idea, the desired methane yield is easily attained at almost any temperature and pressure. Indeed, the yield is relatively insensitive to these operating variables and can be tuned at will by changes in the H<sub>2</sub>:H<sub>2</sub>O feed ratio; the required feed changes are minor except at high temperature and low pressure, where much hydrogen is needed to force methane formation. This serves to demonstrate that, in multiple reaction equilibria, one reaction can fairly effectively

**TABLE 4**  
Calculated Equilibrium Partial Pressures, Selectivities to Methane (Basis Carbon Reacted),  
H<sub>2</sub>:H<sub>2</sub>O Mole Ratios in Feed, and Mole Ratios H<sub>2</sub> Fed to CH<sub>4</sub> Formed, in Range 600 to 1000 K and 2 to 85 atm  
(Courtesy of L. C. Eagleton)

temperature, K	600			800			1000		
total pressure, atm	1.97	9.68	95.7*	2.05	9.16	85.2	2.65	9.74	82.3
H <sub>2</sub> :H <sub>2</sub> O in, m/m	1.83	1.79	1.77	3.40	2.77	2.46	14.74	7.59	3.99
P <sub>CH<sub>4</sub></sub> , atm	1.00	5.00	50.0	1.00	5.00	50.0	1.00	5.00	50.0
P <sub>CO<sub>2</sub></sub>	0.109	0.546	5.47	0.0836	0.490	5.24	0.0068	0.116	3.27
P <sub>H<sub>2</sub>O</sub>	0.793	3.971	39.73	0.473	2.56	26.50	0.107	0.991	16.62
P <sub>H<sub>2</sub></sub>	0.071	0.159	0.504	0.465	1.04	3.29	1.43	3.20	10.13
P <sub>CO</sub>	0.0004	0.0009	0.0029	0.0272	0.0659	0.216	0.104	0.429	2.28
(CH <sub>4</sub> out):(C in), m/m	0.9014	0.9014	0.9014	0.9002	0.9000	0.9016	0.9003	0.9017	0.9002
(H <sub>2</sub> in):(CH <sub>4</sub> out), m/m	1.85	1.81	1.79	2.27	2.00	1.85	3.31	2.51	2.02

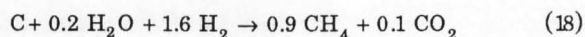
\* Invalid case: Calculated partial pressure of water exceeds vapor pressure.

drive another, even if the latter's equilibrium constant is quite unfavorable. It scuttles the hypothesis we started out with.

In the broader context of the project, we might say that we have worked ourselves out of a job. Our analysis has shown that thermodynamics does not impose serious limitations and that optimum operating conditions will be dictated mostly by other considerations, such as catalyst chemistry, rates, corrosion and materials of construction, solids handling, *etc.*

### HINDSIGHT

Had we been more clever, we might have anticipated these conclusions. We could have written an overall stoichiometric equation approximately reflecting our desired conversion:



The mere fact that we *can* write such an equation should have made us realize that the methane yield depends on the relative amounts of  $\text{H}_2$  and  $\text{H}_2\text{O}$  reacted, while temperature and pressure play only an indirect role by affecting the extent of CO formation and the relative amounts of  $\text{H}_2$  and  $\text{H}_2\text{O}$  leaving unreacted with the product gas.

For reaction (18) we find

$$\begin{aligned} \Delta G^\circ &= -943 \text{ kcal/mol} \\ \Delta H^\circ &= -13.95 \text{ kcal/mol} \\ \Delta n_g &= -0.8 \end{aligned}$$

We see that the reaction, constrained to roughly the desired methane yield, is somewhat favored by low temperature (small negative  $\Delta H^\circ$ ) and high pressure (small negative  $\Delta n_g$ ) and has a reasonable favorable equilibrium (negative  $\Delta G^\circ_{298}$ );  $K_i(T)$  by Eq. (7) turns out to be larger than unity up to  $T = 920 \text{ K}$ . The gist of the conclusions from our calculations could thus have been foreseen on the basis of an even simpler, if crude, reasoning.

### QUI BONO?

Apart from having been placed in the atmosphere of an industrial development project and having gained some insight (even if superficial), into coal methanation equilibria, the student should have derived other benefits from this exercise.

Regarding reaction equilibria, the student will have learned a much simpler approach that can often be used in practice. More importantly, he or she will

take home the message that many practical problems in chemical engineering are more easily solved not by stipulating conditions and calculating results, but by starting from the desired result and finding conditions that will produce it—just as, say, an equation such as  $x^3 + x \ln x = a$  requires a root finder to calculate  $x$  (the result) for given  $a$  (conditions) but is solved directly in seconds for  $a$  if  $x$  is given. As our exercise has shown, this approach is most effective if the relevant equations are written in their simplest form and the “design options” (that is, the variables that can be chosen) are selected from the variables appearing in these equations (in our case, the partial pressures).

This “cart-before-the-horse” approach is rarely found in elementary texts. However, there is one well-established precedent in chemical engineering education: the McCabe-Thiele construction for binary fractionation columns. Here, the desired purities of the tops and bottoms are specified, and reflux ratios and numbers of trays to attain them are determined. I recommend to my students that they fill an hour of boredom with an attempt to use the construction to find the tops and bottoms purities for a given tray number and reflux ratio, just to see how much more complicated and difficult the procedure becomes.

Lastly, in our days of easy access to computers and the great temptation to use these wonderful machines on every occasion, it will be educational for a student to see that the human brain still has a place in our world, that in fact a problem properly thought through might possibly be solved long-hand in a shorter time than it would take to be fed to a computer.

### ACKNOWLEDGMENT

I am indebted to R. L. Kabel for his suggestion to use coal methanation as a class problem.

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