

Thermodynamic Simulation and Sensitivity Analysis of the Steam Reforming of Methane Using Gibbs Free Energy Minimisation

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ABSTRACT: Steam reforming of methane (SRM) supplies about half of the world's hydrogen, but a high heat demand and carbon-forming side reactions that deactivate Ni catalysts limit its performance. HSC Chemistry 6 was used to compare the spontaneity of SRM with methane decomposition, water–gas shift, the Boudouard reaction, CO and CO₂ methanation, dry reforming and partial oxidation between 100 and 1000 °C, and to determine by Gibbs free energy minimisation how the CH₄/H₂O feed ratio (1:1, 2:1, 1:2) and pressure (1–5 bar) shift the equilibrium composition. SRM is non-spontaneous at 25 °C and becomes spontaneous above about 620 °C. Methane decomposition becomes spontaneous earlier, at about 545 °C, and is the main thermodynamic carbon threat. A methane-rich feed deposits carbon equal to 47–49% of the methane fed above 640 °C, an equimolar feed forms carbon between about 440 and 840 °C, and a steam-rich feed is carbon-free and reaches 99% conversion at 820 °C. Raising the pressure from 1 to 5 bar lowers methane conversion (76% to 45% at 685 °C) and hydrogen yield, but suppresses carbon formation. The results support steam-rich, low-pressure, high-temperature operation.

KEYWORDS: Steam Reforming of Methane; Gibbs Free Energy Minimisation; HSC Chemistry; Sensitivity Analysis; Carbon Formation; Hydrogen Production.

NOMENCLATURE

Symbol	Definition	Unit	Symbol	Definition	Unit
ΔG	Gibbs free energy change of reaction	kJ/mol	T^*	Temperature at which ΔG changes sign	°C
ΔG°	Standard Gibbs free energy change	kJ/mol	T_{90}	Temperature giving 90% CH ₄ conversion	°C
ΔH	Enthalpy change of reaction	kJ/mol	P	Total pressure	bar
ΔH°_{298}	Standard enthalpy change at 298 K	kJ/mol	p_i	Partial pressure of species i	bar
ΔS	Entropy change of reaction	J/(mol·K)	x_i	Mole fraction of species i	–
K	Equilibrium constant	–	$n_{CH_4,0}, n_{CH_4}$	Initial and equilibrium amounts of CH ₄	kmol
$\log K$	Base-10 logarithm of the equilibrium constant	–	X_{CH_4}	CH ₄ conversion	%
Q	Reaction quotient	–	Δn	Change in moles of gas in a reaction	mol
R	Universal gas constant (8.314)	J/(mol·K)	S/C	Steam-to-carbon ratio	mol/mol
T	Temperature (K in Eqs. 1–3; °C elsewhere)	K or °C			

Abbreviations: SRM, steam reforming of methane; DRM, dry reforming of methane; POM, partial oxidation of methane; MD, methane decomposition; WGS, water–gas shift; BR, Boudouard reaction.

1. INTRODUCTION

Fossil fuels still meet most of the world's energy demand, and their use is the main source of the CH₄ and CO₂ emissions that drive climate change [1]. Hydrogen is attractive as a clean energy carrier because its use in fuel cells or engines produces only water, but it is not available in nature and must be manufactured from other primary energy sources [2,3]. Fossil-based routes dominate: natural gas supplies about 48% of

hydrogen, heavy oils and naphtha 30% and coal 18% [4]. Of the technologies that convert methane into hydrogen and synthesis gas (syngas), steam reforming (SRM), dry reforming (DRM) and partial oxidation (POM), SRM is the most mature and cost-effective and supplies roughly half of the world's hydrogen for oil refining, ammonia and methanol production, metallurgy and other uses [5–7].

In SRM, methane reacts with steam over a Ni-based catalyst to give syngas (R1 in Table I), and the water–gas shift reaction (R2) converts part of the CO into additional H₂. The reforming step is strongly endothermic and increases the number of moles, so it is favoured by high temperature and low pressure; excess steam is normally used to drive the reaction forward and to limit carbon formation [6]. Industrial reformers operate above 700 °C (up to about 980 °C), with steam-to-carbon ratios of roughly 2.5–3.5 and pressures of up to 3.5 MPa [6,8,9].

The main obstacle to more efficient operation is catalyst deactivation. Ni catalysts are active and inexpensive, but they sinter at high temperature and accumulate carbon formed by methane decomposition, the Boudouard reaction and the reduction of CO and CO₂ (R3–R4 in Table I) [10, 11]. Catalyst development has concentrated on improving coke and sintering resistance (Section II), yet the thermodynamic driving force for carbon formation is set by the operating conditions and cannot be removed by the catalyst alone. Knowing where carbon formation is thermodynamically possible, and how feed composition and pressure move those boundaries, is therefore a useful first screen before costly experiments.

Equilibrium analyses have been published for SRM and related reforming routes [6], [12–14], but the link between the spontaneity of each reaction in the SRM network and the response of the equilibrium composition to feed ratio and pressure is less often examined side by side. This work addresses that gap using HSC Chemistry 6. The objectives are (i) to determine the thermodynamics of SRM at standard and elevated temperatures; (ii) to compare the spontaneity of SRM with its competing side reactions and with DRM and POM using the Gibbs free energy change; and (iii) to determine, by Gibbs free energy minimisation, the effect of temperature, CH₄/H₂O feed ratio and pressure on the equilibrium composition and on carbon formation. The study is limited to equilibrium thermodynamics; kinetics, catalyst properties and transport effects are not considered.

The approximate standard enthalpies of the reactions considered are listed in Table I [10, 15].

TABLE I REACTIONS IN THE SRM NETWORK

No.	Reaction	Equation	ΔH°_{298} (kJ/mol)
R1	SRM	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	+206
R2	WGS	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	–41
R3	MD	$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	+75
R4	BR	$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	–173
R5	CO methanation	$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	–206
R6	CO ₂ methanation	$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$	–165
R7	DRM	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	+247
R8	POM	$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2$	–36

SRM: steam reforming; WGS: water–gas shift; MD: methane decomposition; BR: Boudouard reaction; DRM: dry reforming; POM: partial oxidation.

II. BACKGROUND AND LITERATURE REVIEW

A. Reforming Routes and the SRM Process

Hydrogen is produced from fossil fuels mainly by hydrocarbon pyrolysis and reforming [16, 17]. Reforming with oxygen (POM) is exothermic and is the preferred route for heavy feedstocks; the catalytic process runs at about 950 °C with a thermal efficiency of 60–75% from methane [15, 18]. DRM converts two greenhouse gases into syngas but is even more endothermic than SRM and prone to coking [1, 15]. SRM was first applied industrially around 1930 [19] and reaches conversion efficiencies of 74–85% and, after shift and purification, hydrogen of 99.999% purity [8]. Fig. 1 shows a simplified flow scheme: desulphurised natural gas and steam are fed to the reformer, the CO-rich syngas passes to a WGS reactor, and CO₂ is removed in an absorber to give hydrogen. Desulphurisation protects the Ni catalyst from sulphur poisoning [8].

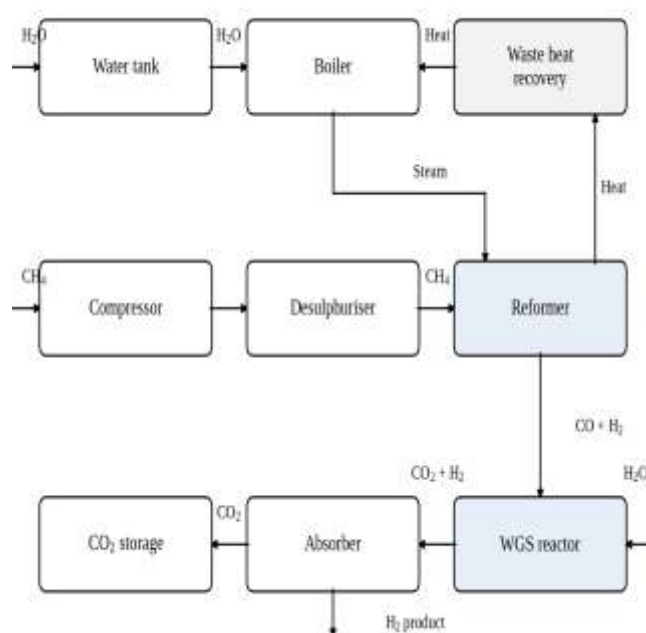


Fig. 1. Simplified flow diagram of the SRM process.

B. Catalyst Deactivation

Two mechanisms limit the life of Ni catalysts. In coking, hydrocarbons dissociate on Ni, and the atomic carbon is either gasified or dissolves in the crystallite, diffuses through it and precipitates as a whisker that can lift the crystallite from the support and fragment it [20]. In sintering, the metal surface area is lost by Ostwald ripening or by crystallite migration and coalescence, accelerated by high temperature and steam atmospheres [11].

C. Strategies for Improving Ni-Based Catalysts

Recent work has therefore targeted coke and sintering resistance [11]. Among promoters, Rh and Ir form alloys with Ni that improve sintering resistance, whereas Ru–Ni was inferior after

ageing at 800 °C [21]; Pd gave 94.6% CH₄ conversion at 650 °C but lowered CO selectivity through Pd-promoted WGS [22]; Au and Ag improve durability but reduce activity by occupying low-coordinated Ni sites [23]; redox oxides such as CeO₂ and Nb₂O₅ reduce carbon deposition and sintering [2, 25]; and boron improves stability although an excess blocks Ni sites [26]. Structural control is equally important: Ni particles of 2–3 nm gave the best activity, whereas whisker carbon was most severe at 4.5 nm [27]; core-shell Ni@SiO₂ reached 85% conversion at 750 °C [28]; and a Ni–MgO solid solution converted CH₄ for 1000 h without deactivation [29]. Non-noble Co and Mo catalysts also show promise but suffer from low reducibility and deactivation [30, 31].

D. Thermodynamic Modelling of Reforming

Thermodynamic analysis complements catalyst research by defining what is possible at equilibrium. A reaction is spontaneous when its Gibbs free energy change is negative, and the standard value is related to the equilibrium constant by $\Delta G^\circ = -RT \ln K$ [32]. In a multi-reaction system, the equilibrium composition is found by minimising the total Gibbs energy subject to element balances, which avoids specifying independent reactions in advance and can include solid carbon [13]. The approach has been used to identify favourable steam-to-carbon ratios and temperatures for steam reforming, partial oxidation and autothermal reforming [14], to relate equilibrium composition to reformer efficiency [12], to run sensitivity studies in Aspen Plus [6], to examine solid carbon in dry reforming [13] and to analyse the sensitivity of CO₂ reforming of methane to operating variables [33]. Its limitation is that it ignores kinetics [34], so predicted compositions are limits that real reactors approach but may not reach.

III. METHODOLOGY

A. Software

Simulations were run in HSC Chemistry 6 (Outokumpu Research Oy), an integrated thermochemical package whose database holds about 28,000 chemical species, and results were post-processed in Microsoft Excel. Two modules were used: the Reaction Equations module, which calculates ΔH , ΔS , ΔG and K of a balanced reaction as a function of temperature, and the Equilibrium Compositions module, which calculates equilibrium amounts of the species in a system by Gibbs energy minimisation with ideal-gas behaviour (activity coefficients of 1).

B. Reaction Thermodynamics

The balanced reactions R1–R8 (Table I) were entered with valid formulae and phase notation. ΔH , ΔS , ΔG , K and $\log K$ were calculated from 100 to 1000 °C in 100 °C steps, and SRM was also evaluated at 25 °C. Results were exported to Excel, ΔG was plotted against temperature, and the temperature T^* at which ΔG changes sign was obtained by linear interpolation between adjacent points. The thermodynamic relations used were

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

$$\Delta G^\circ = -RT \ln K \quad (2)$$

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (3)$$

where Q is the reaction quotient evaluated from the partial pressures in a reacting mixture. Eq. (3) is used in Section IV-B to link the ΔG – T results to the equilibrium calculations.

C. Equilibrium Composition

In the Equilibrium Compositions module the elements C, H and O were selected and six species were defined: CH₄, H₂O, H₂, CO and CO₂ in the gas phase and solid carbon (graphite). Three CH₄/H₂O feed ratios were simulated at 1 bar: 1:1 (50 kmol CH₄ + 50 kmol H₂O), 2:1 (50 + 25 kmol) and 1:2 (25 + 50 kmol). The pressure study used the equimolar feed at 1, 2 and 5 bar. For all cases the temperature was varied from 100 to 1000 °C in 45 °C increments (21 points; plots begin at 200 °C). Equilibrium amounts (kmol) were exported to Excel, from which the CH₄ conversion,

$$X_{\text{CH}_4} = (n_{\text{CH}_4,0} - n_{\text{CH}_4}) / n_{\text{CH}_4,0} \times 100\% \quad (4)$$

the H₂ yield (kmol H₂ per kmol CH₄ fed), the H₂/CO ratio and the amount of solid carbon were derived. Carbon was considered to form when the equilibrium amount exceeded 0.01 kmol. The analysis assumes equilibrium, ideal gases and graphite as the only solid phase.

IV. RESULTS AND DISCUSSION

A. Thermodynamics of SRM

At 25 °C, SRM has $\Delta H^\circ = 206.9$ kJ/mol, $\Delta S^\circ = 214.5$ J/(mol·K) and $\Delta G^\circ = 141.9$ kJ/mol, giving $K = 1.36 \times 10^{-25}$ ($\log K = -24.87$). The reaction is therefore strongly non-spontaneous at room temperature, and the enthalpy is in line with the standard value of about +206 kJ/mol (Table I). Table II shows that ΔH and ΔS increase only slightly with temperature (209 to 226 kJ/mol and 225 to 253 J/(mol·K)), so ΔG falls almost linearly from +125.4 kJ/mol at 100 °C to –95.6 kJ/mol at 1000 °C. It changes sign at about 620 °C (893 K), which agrees with $T^* = \Delta H/\Delta S = 223.1/0.2497 = 893$ K from the 600 °C values. At this temperature $K = 1$; it rises to 11.9 at 700 °C and to 8.4×10^3 at 1000 °C. The positive enthalpy, associated with breaking the stable CH₄ and H₂O molecules, is thus overcome only when the entropy gain from the two extra moles of gas ($\Delta n = +2$) dominates the $-T\Delta S$ term at high temperature. The 620 °C threshold lies below the 700–980 °C range used industrially [6], [8], as expected, because practical conversion requires $K \gg 1$ and an adequate reaction rate, not merely $\Delta G < 0$.

TABLE II. THERMODYNAMICS OF SRM (R1) AT 1 BAR

T (°C)	ΔH (kJ/mol)	ΔS (J/mol·K)	ΔG (kJ/mol)	K	$\log K$
100	209.23	224.53	125.45	2.74×10^{-18}	-17.56
200	213.14	233.85	102.50	4.83×10^{-12}	-11.32
300	216.45	240.20	78.78	6.61×10^{-8}	-7.18
400	219.17	244.59	54.52	5.87×10^{-5}	-4.23
500	221.37	247.65	29.90	9.54×10^{-3}	-2.02
600	223.08	249.74	5.03	0.500	-0.30
700	224.36	251.12	-20.02	11.9	1.08
800	225.22	251.96	-45.18	158	2.20
900	225.70	252.39	-70.40	1.36×10^3	3.14
1000	225.84	252.51	-95.65	8.41×10^3	3.93

B. Spontaneity of SRM Compared with Competing and Alternative Reactions

Fig. 2(a) separates the reactions into two groups. The endothermic reactions with positive entropy change (SRM, MD and, in Fig. 2(b), DRM) become spontaneous as temperature rises, because the $-T\Delta S$ term outweighs the positive ΔH . The exothermic reactions that reduce the number of moles (WGS, BR and the two methanation reactions) are favoured at low temperature and lose spontaneity as it rises (Table III). CO methanation (R5) is simply the reverse of SRM, so its curve is the mirror image of SRM and its crossover is identical (about 620 °C); its loss of spontaneity above this temperature is the same result as SRM becoming favourable, not an independent finding. CO₂ methanation is likewise disfavoured above about 590 °C, which is desirable because it prevents consumption of H₂ and CO in the reformer.

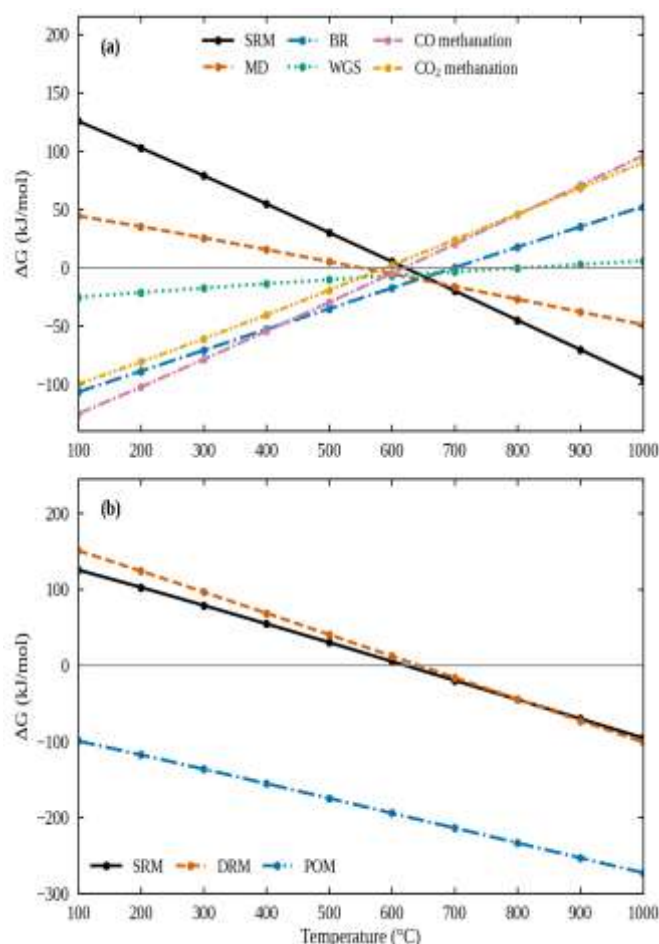


Fig. 2. Gibbs free energy change against temperature at 1 bar: (a) SRM and the competing side reactions; (b) SRM compared with DRM and POM.

TABLE III. $\Delta G - T$ CORRELATIONS AND SPONTANEITY

Reaction	ΔG (kJ/mol), T in °C	T^* (°C)	Spontaneous when
SRM (R1)	$-0.2449T + 150.9$	≈ 620	$T > T^*$
DRM (R7)	$-0.2799T + 179.3$	≈ 640	$T > T^*$
POM (R8)	$-0.1920T - 79.9$	none	all T studied
MD (R3)	$-0.1027T + 55.2$	≈ 545	$T > T^*$
WGS (R2)	$0.0351T - 28.5$	≈ 815	$T < T^*$
BR (R4)	$0.1770T - 124.1$	≈ 700	$T < T^*$
CO meth. (R5)	$0.2446T - 150.9$	≈ 620	$T < T^*$
CO ₂ meth. (R6)	$0.2096T - 122.3$	≈ 590	$T < T^*$

T^* is the temperature at which ΔG changes sign, from interpolation of the simulated values; meth.: methanation. The key difference between the side reactions lies in the order of the crossover temperatures. MD becomes spontaneous at about 545 °C, some 75 °C before SRM (about 620 °C). In this window carbon deposition is favoured while reforming is not, which

identifies the cold end of the catalyst bed, start-up and steam-deficient operation as the most vulnerable conditions. Above 620 °C both reactions are spontaneous, but ΔG is more negative for SRM at every temperature (−95.6 against −49.0 kJ/mol at 1000 °C), so SRM remains thermodynamically dominant while MD cannot be excluded. BR adds a second carbon route up to about 700 °C but is unfavourable above it, and WGS stays favourable up to about 815 °C, helping to convert CO at the lower end of the operating range. MD is therefore the only carbon-forming reaction whose ΔG° remains negative across the whole high-temperature SRM window, and SRM is affected more by MD than by WGS, BR or the methanation reactions.

These ΔG° values refer to pure gases at 1 bar. In a reacting mixture $\Delta G = \Delta G^\circ + RT \ln Q$ (Eq. 3), where for MD $Q = p_{H_2}^2/p_{CH_4}$. Using the equimolar, 1 bar equilibrium composition of Section IV-C, at 595 °C ($x_{H_2} = 0.556$, $x_{CH_4} = 0.153$) $RT \ln Q = +5.1$ kJ/mol cancels $\Delta G^\circ_{MD} = -5.1$ kJ/mol, so $\Delta G \approx 0$, the condition for solid carbon to coexist with the gas. The Boudouard reaction gives the same result ($\Delta G \approx 0$ kJ/mol), because all carbon-forming reactions share one carbon activity at equilibrium. At 1000 °C, $Q = 145$ gives $RT \ln Q = +52.7$ kJ/mol against $\Delta G^\circ_{MD} = -49.0$ kJ/mol, so $\Delta G = +3.8$ kJ/mol and carbon is not stable. Fig. 2 therefore sets the temperature above which carbon *can* form, whereas the composition-dependent equilibrium calculation decides whether it does.

Fig. 2(b) shows that DRM follows SRM closely but is more endothermic (+247 against +206 kJ/mol), so its crossover is about 20 °C higher (about 640 °C) and the two curves nearly coincide above 700 °C (−101 and −96 kJ/mol at 1000 °C). This is consistent with Nikoo and Amin [13], who found that DRM needed temperatures above 1173 K at $CO_2/CH_4 = 1$ to obtain syngas with negligible carbon. POM is spontaneous over the whole range, with ΔG from −100 kJ/mol at 100 °C to −273 kJ/mol at 1000 °C, because it is exothermic and increases the number of moles. The ranking agrees with the Aspen Plus study of Seo et al. [14], in which POX and autothermal reforming required 0.364 and 0.367 mol CH_4 per mol H_2 , against 0.385 for steam reforming. A negative ΔG is, however, a feasibility criterion only: POM needs oxygen, gives $H_2/CO = 2$ instead of 3, and does not by itself make the route preferable.

C. Effect of the CH_4/H_2O Feed Ratio

Fig. 3 shows the equilibrium compositions at 1 bar and Table IV summarises the main metrics. In all three cases H_2 and CO are negligible below about 400 °C and rise steeply between about 450 and 800 °C, in line with the sign change of ΔG at about 620 °C.

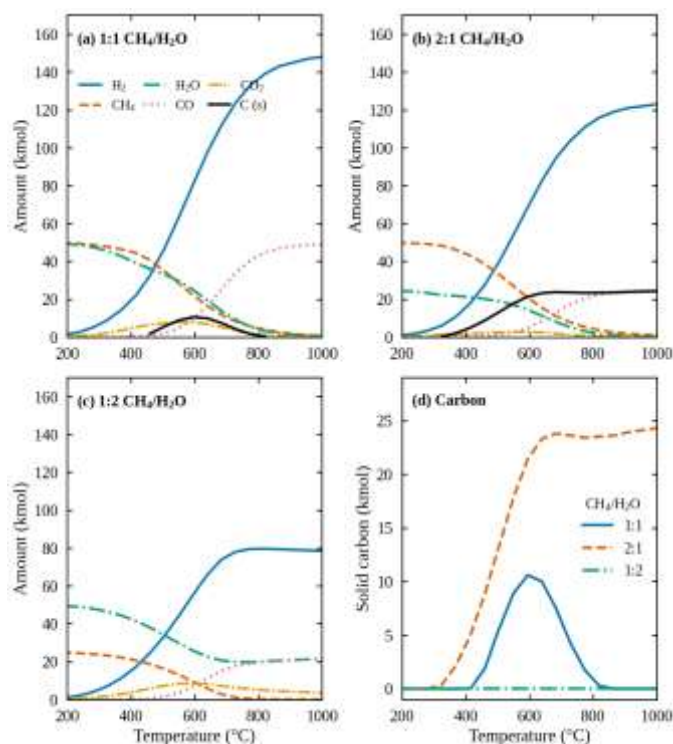


Fig. 3. Effect of the CH_4/H_2O feed ratio on the equilibrium composition at 1 bar: (a) 1:1, (b) 2:1, (c) 1:2 and (d) solid carbon formed in the three cases.

1) Equimolar Feed (1:1): Conversion is 76% at 685 °C and 98.5% at 1000 °C, where $H_2/CO = 3.01$, the stoichiometric value of R1. Solid carbon appears from about 440 °C, peaks at 10.6 kmol (21% of the methane fed) near 600 °C and vanishes above about 840 °C. The peak lies where MD and BR are both spontaneous (Fig. 2(a)) and little methane has yet been reformed; as reforming proceeds the gas becomes H_2 -rich, Q grows and carbon is no longer stable (Section IV-B).

2) Methane-Rich Feed (2:1): Methane in excess of the available steam decomposes: carbon starts at about 300 °C, reaches 23.3 kmol at 640 °C and stays at 23.5–24.3 kmol up to 1000 °C, i.e. 47–49% of the methane fed. Carbon does not disappear at high temperature because there is too little steam to gasify it. H_2/CO rises to about 5 because MD produces H_2 without CO, and although CH_4 conversion (98% at 1000 °C) resembles the equimolar case, H_2 per CH_4 fed is lower (2.46 against 2.96 mol/mol) because carbon acts as a hydrogen sink. This agrees with the experiments of Pashchenko and Makarov [10], who observed the largest decline in methane conversion over a Ni catalyst at a steam-to-methane ratio of 0.5, the ratio for which the present calculations give the most carbon.

3) Steam-Rich Feed (1:2): No solid carbon forms at any temperature. Conversion is 89% at 685 °C and 99.5% or more from 820 °C. H_2 per CH_4 fed peaks at 3.18 mol/mol at about 820 °C because excess steam drives WGS (R2): CO_2 reaches 8.7 kmol at 595 °C and H_2/CO is 3.65–4.0 between 1000 and 820 °C, above the stoichiometric 3, so extra steam raises rather than lowers the H_2/CO ratio. The slight decline in H_2 above 820 °C (79.6 to 78.5 kmol) reflects the reverse WGS reaction and

coincides with the sign change of ΔG_{WGS} at about 815 °C (Table III).

TABLE IV. SUMMARY OF EQUILIBRIUM RESULTS

Case (CH ₄ /H ₂ O, pressure)	X at 685 ° C (%)	T ₉₀ (°C)	H ₂ per CH ₄ fed at 1000 °C	Max. solid C, kmol (at °C)
1:1, 1 bar	76.4	794	2.96	10.6 (595)
2:1, 1 bar	78.0	784	2.46	24.3 (1000)
1:2, 1 bar	89.2	691	3.14	0
1:1, 2 bar	63.6	862	2.92	7.7 (640)
1:1, 5 bar	44.6	954	2.80	3.5 (685)

X: CH₄ conversion; T₉₀: temperature giving X = 90%.

The carbon-free, near-complete conversion at CH₄/H₂O = 1:2 (steam-to-carbon ratio of 2) agrees with Seo et al. [14], who found an optimum steam-to-carbon ratio of 1.9 for steam reforming in Aspen Plus, and with the finding of Li et al. [35] that adding H₂O inhibits carbon deposition in equilibrium calculations for mixed reforming of methane. Industrial plants use steam-to-carbon ratios of about 2.5–3.5 [8], [9]; the extra steam gives a margin against carbon formation under kinetic control, which equilibrium calculations cannot capture [36], at the cost of additional steam generation. The equimolar feed is the stoichiometric minimum for R1 but is not optimal: it is carbon-prone below about 840 °C, a threshold comparable to, and slightly below, the 900 °C reported for carbon-free DRM at CO₂/CH₄ = 1 [13].

D. Effect of Pressure

Raising the pressure from 1 to 5 bar at CH₄/H₂O = 1:1 lowers equilibrium CH₄ conversion at all temperatures below about 950 °C (Fig. 4(a)): at 685 °C conversion falls from 76.4% to 63.6% (2 bar) and 44.6% (5 bar), and at 1000 °C from 98.5% to 97.0% and 93.1%. H₂ falls in parallel (148, 146 and 140 kmol at 1000 °C; Fig. 4(b)) and so does CO (49.1, 48.3 and 46.0 kmol). The temperature needed for 90% conversion rises from about 795 °C at 1 bar to about 860 °C at 2 bar and about 955 °C at 5 bar (Table IV). This is Le Chatelier’s principle: SRM and MD increase the number of moles ($\Delta n = +2$ and $+1$), so higher pressure shifts the equilibrium towards the reactants, whereas WGS ($\Delta n = 0$) is pressure-independent. The result agrees with the statement that reforming is favoured at high temperature and low pressure [6] and with equilibrium studies in which higher pressure reduced syngas yield [13], [35].

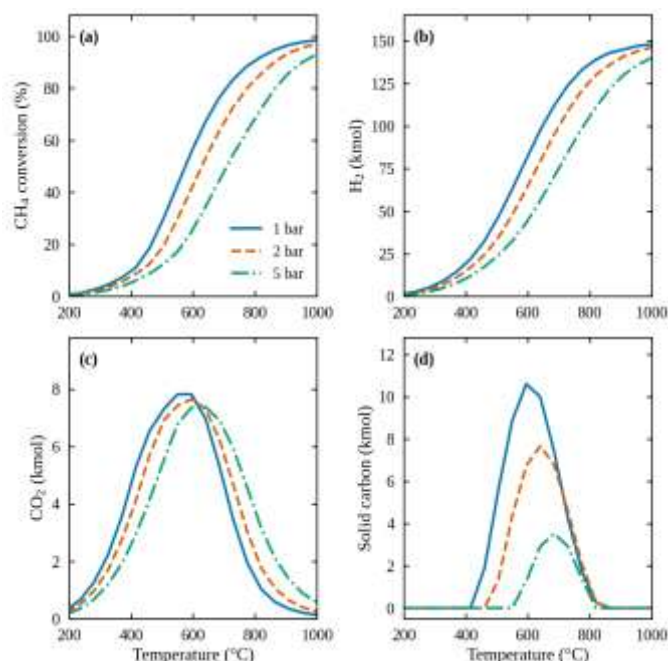


Fig. 4. Effect of pressure on the equilibrium results for an equimolar CH₄/H₂O feed: (a) CH₄ conversion, (b) H₂, (c) CO₂ and (d) solid carbon.

The CO₂ trend is not monotonic (Fig. 4(c)). Below about 600 °C less CO₂ forms at higher pressure, but above about 650 °C more does (0.12, 0.24 and 0.56 kmol at 1000 °C). This mainly reflects the shift of the whole conversion profile to higher temperature: the CO₂ maximum produced by WGS moves from about 550–595 °C at 1 bar to about 640 °C at 5 bar, and at a given high temperature the gas is richer in H₂O and poorer in H₂ and CO, which raises CO₂/CO through the WGS equilibrium.

Pressure also suppresses carbon formation in this range (Fig. 4(d)). The maximum falls from 10.6 kmol (1 bar) to 7.7 kmol (2 bar) and 3.5 kmol (5 bar), and the carbon-forming range narrows from about 440–840 °C to about 570–800 °C. This is consistent with the positive mole change of MD, which pressure disfavors. Nikoo and Amin [13] reported the opposite for DRM, where pressures of 1–25 atm increased carbon deposition through MD and CO disproportionation; the difference probably reflects the CO-rich gas of DRM, in which the Boudouard reaction ($\Delta n = -1$) is favoured by pressure, and the wider pressure range. The suppression of carbon at 1–5 bar should therefore not be extrapolated to industrial pressures of up to 3.5 MPa [8]. Overall, higher pressure buys lower carbon at the price of a much higher temperature requirement (about +160 °C for 90% conversion between 1 and 5 bar), and a steam-rich feed is the more effective carbon control.

E. Practical Implications and Limitations

Taken together, the results point to operation at a steam-to-carbon ratio of at least 2, outlet temperatures above about 820–850 °C (where the equimolar, 1 bar system is carbon-free and WGS-assisted H₂ yield is near its maximum) and the lowest pressure compatible with downstream requirements. The conclusions are limited by the equilibrium assumption. Carbon on Ni is kinetically controlled and its morphology depends on

the catalyst [20], [36], so conditions predicted to be carbon-free are necessary rather than sufficient for stable operation, and conditions predicted to form carbon do not guarantee deposition on an active catalyst. Graphite was the only solid phase considered, and the range 1–5 bar excludes industrial pressures.

V. CONCLUSIONS

The thermodynamics of SRM and its competing reactions were simulated with HSC Chemistry 6, and the effects of temperature, CH₄/H₂O feed ratio and pressure on equilibrium were quantified. The main conclusions are:

1. SRM is non-spontaneous at 25 °C ($\Delta G^\circ = 141.9$ kJ/mol, $\log K = -24.87$). Its Gibbs free energy change becomes negative at about 620 °C ($K = 1$), well below the 700–980 °C used industrially, which is set by conversion and rate requirements.
2. MD becomes spontaneous at about 545 °C, earlier than SRM, and is the only carbon-forming reaction that stays spontaneous across the high-temperature window; BR is favoured only below about 700 °C, and WGS and the methanation reactions below about 815 and 590–620 °C. POM is spontaneous at all temperatures studied, and DRM requires about 640 °C.
3. A methane-rich feed (2:1) deposits carbon equal to 47–49% of the methane fed at all temperatures above 640 °C; an equimolar feed forms carbon between about 440 and 840 °C (maximum 10.6 kmol); a steam-rich feed (1:2) forms no carbon and gives 99.5% or more conversion and the highest H₂ yield (3.18 mol/mol CH₄) from about 820 °C. The equimolar ratio is therefore not optimal.
4. Raising the pressure from 1 to 5 bar lowers CH₄ conversion and H₂ yield (76% to 45% conversion at 685 °C) and raises the temperature required for 90% conversion from about 795 to 955 °C, while suppressing carbon formation (maximum 10.6 to 3.5 kmol) over the range studied.

Future work should add reaction kinetics and catalyst activity to the equilibrium analysis, extend the pressure range to industrial values, test steam-to-carbon ratios of 2–3.5, and validate the predicted carbon boundaries experimentally.

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