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VAPOR—SOLID EQUILIBRIUM FOR THE C—H—O—Ni SYSTEM

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ABSTRACT

The equilibrium states of the C—H—O—Ni system are defined in relation to H_2—CO compositions for temperatures ranging from 300 to 700 K and at atmospheric pressure.

The gaseous species, H_2, H_2O, CO, CH_4 ... C_8H_{18}, C_2H_4 ... C_4H_8 are taken into account to determine the gas phase compositions imposed by the different equilibria between condensed phases (⟨C⟩, ⟨Ni⟩, ⟨NiO⟩, ⟨Ni_3C⟩, ⟨Ni,C⟩ solution).

We have particularly investigated the values of chemical potential of carbon in the gas phase, fixed by equilibria between solid phases involving carbon, at which hydrocarbons higher than CH_4 appear. The method for determining the standard free enthalpy of formation of Ni_3C is discussed.

INTRODUCTION

The thermodynamics of C—H—O—metal (catalyst) systems is one of the fundamental aspects of the study of the catalytic hydrogenation reaction of carbon oxides. In principle, the catalytic synthesis of hydrocarbons from CO and H_2 (i.e. the Fischer—Tropsch reaction) potentially increases the value of any raw material containing carbon: this agrees with the fundamental idea that carbon monoxide constitutes the simplest building element for the construction of hydrocarbon molecules and particularly hydrocarbons larger than CH_4. Determining the C—H—O—metal equilibrium states proves to be extremely complicated due to the great number of reactions that must be taken into account. It requires the development of improved methods and calculation programs based on the use of a computer. To avoid these difficulties, two thermodynamic approaches have been proposed. The first is based on comparisons of the values of the variation of standard Gibbs energy (ΔG^0) of a large number of elementary reactions, complemented by kinetic results [1—4]. The second consists in determining the nature and the composition of the phases in equilibrium in a system including carbon and the principal synthesis gases (CO, CO_2, H_2O, H_2, CH_4) [5,6].

We have adopted this second approach taking into account a greater number of compounds in the C—H—O—Ni system.

THERMODYNAMIC CONSIDERATIONS

The numerical resolution of the equilibrium states is carried out according to a method of minimization of Gibbs energy of the system under consideration, which is computer programmed [7]. It can be carried out taking into account several solid phases and a large number of gaseous species. The number of chemical species considered may be very high. The only constraint arises from the need to know the thermodynamic data of the compounds involved. If a species present at equilibrium is neglected, the results may prove erroneous. Different compounds were selected to define the C—H—O—Ni system, first, the most stable species CO, CO_2, H_2, H_2O, ⟨C⟩ [8] and ⟨Ni⟩ [9], which are detected in large quantities under certain experimental conditions, followed by the less stable species C_2H_6 ... C_8H_{18} ... C_2H_4 ... C_4H_8 [10,11], ⟨NiO⟩ [12], ⟨Ni_3C⟩ [13,14] and the solid solution ⟨Ni,C⟩. The presence of a ⟨Ni,C⟩ phase at the C—H—O—Ni state of equilibrium was considered. Apart from the solid solution ⟨Ni,C⟩, the condensed phases are taken as pure and the gas mixture is assumed ideal. Compositions at equilibrium are determined by considering a closed system of variable volume so as to maintain the constant total pressure at 1 atm. They are calculated for temperatures ranging from 300 to 700 K and for H_2—CO mixtures of different initial compositions. Moreover, the initial quantities of nickel introduced into the system must be sufficient to ensure that nickel will remain present at equilibrium.

C—H—O—Ni

Several cases have been treated. The composition of the gas phase at equilibrium is dependent not only on the temperature and the initial H_2—CO mixture, but also on the condensed phases which may or may not be present. This is the case, for instance, for the carbide Ni_3C which, when it is formed, is metastable with respect to nickel and to carbon. We investigated the variation of the chemical potential of carbon in the gas phase in equilibrium with solid phases involving carbon. The chemical potential of carbon in the gas phase is referenced to graphite. It is shown on the standard Gibbs energy of formation vs. composition diagrams for the solid phases ⟨Ni⟩ ⟨C⟩ ⟨Ni_3C⟩ ⟨Ni,C⟩ [Fig. 1(a)—(c)]. Three distinct cases can be identified.

(1) *The chemical potential of carbon in the gas phase is set by that of graphite [Fig. 1(a)].*

Graphite is present in the system and may be in equilibrium with pure nickel (1) or with a solution ⟨Ni,C⟩ (2). The construction of the tangent from the carbon—graphite to the curve of the Gibbs energy function of the ⟨Ni,C⟩ solutions (which has been expanded for illustration purposes) provides us with the chemical potential of nickel in the ⟨Ni,C⟩ solution. In the two cases mentioned above, the composition of the gas phase, which is dependent on temperature and the initial ratio H_2/CO, is the same. When no graphite is present, the gas phase reaches equilibrium, either independently of the solid phase (pure ⟨Ni⟩ or with a ⟨Ni,C⟩ solution (3). Since we do not know the free enthalpy function of the ⟨Ni,C⟩ solutions which present very little

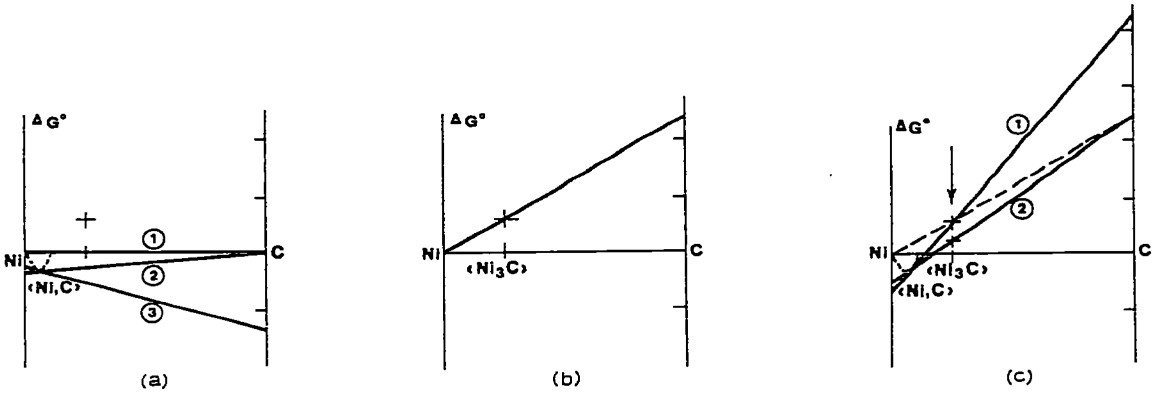

Fig. 1 (a), (b), (c). The standard free enthalpy of formation vs. composition diagrams.

carbon [15,16], we first determined the equilibrium states in the presence of pure ⟨Ni⟩ and ⟨C⟩ phases and that of ⟨NiO⟩.

The results are shown on diagrams of two types: (a) a diagram showing the stability regions of the condensed phases as a function of temperature and the composition of the initial CO—H_2 mixture (Fig. 2) and (b) isothermal diagrams showing the evolution of different gas partial pressures as a function of the composition of the initial CO—H_2 mixture [Fig. 3(a), (b)]. In Fig. 2, we can see that the boundary of the region of stability of the carbon is situated at a composition of the initial H_2/CO mixture equal to 3/1 for all temperatures investigated (300—700 K). (For higher temperatures, this limit depends on the H_2/CO ratio. The boundary of the region of stability of the carbon curve tends towards the initial H_2/CO mixture rich in H_2.) This composition corresponds to that of minimum hydrogen content recommended to avoid poisoning the catalytic synthesis of methane in the presence of nickel by a deposit of carbon [4]. It is also in quite good agree-

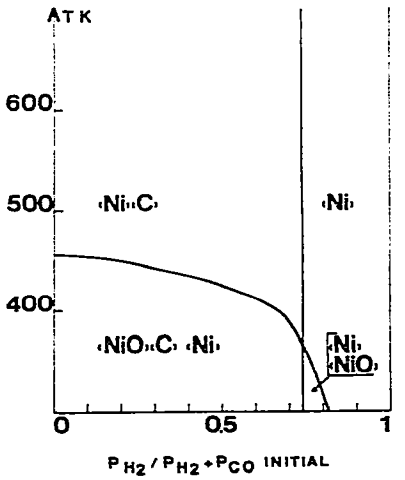

Fig. 2. Stability regions of the condensed phases as a function of temperature and the composition of the initial CO—H_2 mixture.

ment with that determined by Cairns and Tevebaugh [5].

Figure 3(a), (b) shows that hydrocarbons higher than CH_4 are practically absent. (We find a maximum partial pressure of ethane of 3.46×10^{-6} atm at 700 K for a H_2/CO ratio of 7/3.) At the ⟨Ni⟩, ⟨NiO⟩, ⟨C⟩ or ⟨NiO⟩ phase boundaries [Figs. 2 and 3(a)], the variation of partial pressures show angular points. When the gas phase is in equilibrium with the carbon and ⟨Ni⟩, ⟨NiO⟩ phases, the variance is two. Consequently, for fixed P and T, the composition of the gases at equilibrium is not dependent on the initial H_2—CO mixtures. At the ⟨Ni⟩ ⟨C⟩/⟨Ni⟩ phase boundary, the sudden variation in gas partial pressures is due to the disappearance (or appearance) of the ⟨C⟩ phase. Finally, maximum partial pressure of methane is reached for a H_2/CO ratio of 3/1, which in fact corresponds to the ratio required for industrial synthesis of methane [4].

(2) *The chemical potential of carbon in the gas phase is fixed by the equilibrium between the* ⟨Ni⟩ ⟨Ni_3C⟩ *phases [Fig. 1(b)].*

Taking the case of metastable equilibrium between the ⟨Ni⟩ ⟨Ni_3C⟩ phases, we assume that the formation of graphite is voluntarily eliminated, since graphite is the stable form. The stability region of the ⟨Ni⟩ ⟨Ni_3C⟩ phases superimposed on the stability regions of the ⟨Ni⟩, ⟨NiO⟩ ⟨C⟩ phases, is shown in Fig. 4. The gas phase reaches equilibrium with the ⟨Ni⟩ ⟨Ni_3C⟩ phases only for CO-rich mixtures and up to a H_2/Co ratio of 1/1. The gas partial pressures at equilibrium vary linearly with the H_2/CO ratio in the stability region ⟨Ni⟩ ⟨Ni_3C⟩ [Fig. 5(a), (b)]. Here again, hydrocarbons higher than CH_4 are not present at equilibrium.

(3) *The chemical potential of carbon in the gas phase is fixed by an equilibrium between the* ⟨Ni_3C⟩ ⟨Ni,C⟩ *solution phases [Fig. 1(c)].*

There are two possibilities in this case.

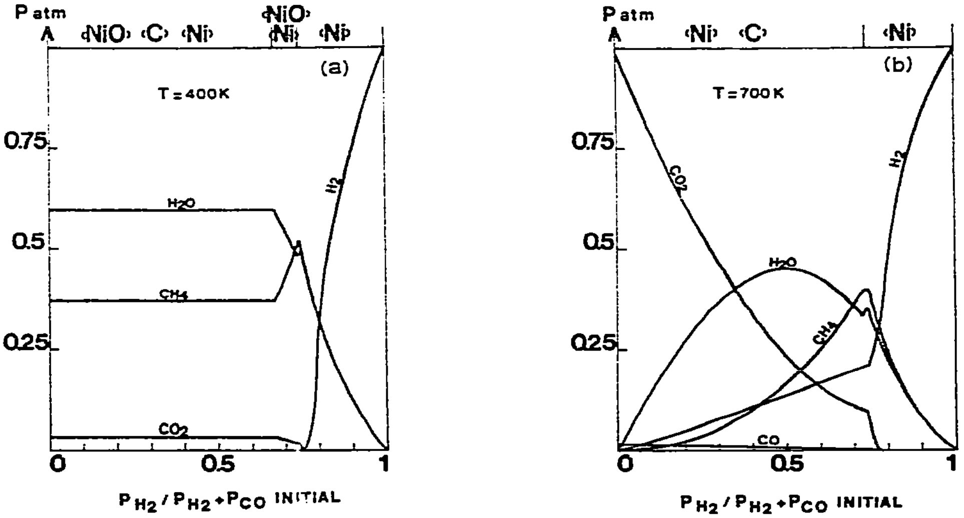

Fig. 3(a), (b). Evolutions of different gas partial pressures as a function of the composition of the initial CO—H_2 mixture.

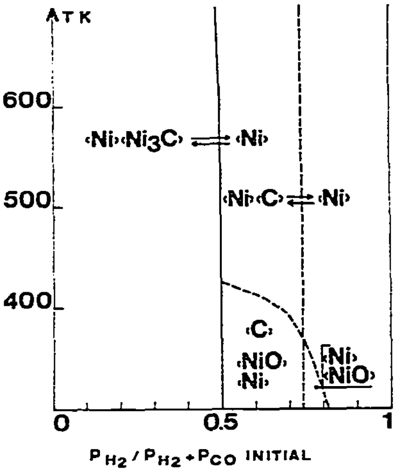

Fig. 4. Stability regions of the ⟨Ni⟩ ⟨Ni_3C⟩ phases (———) superimposed on the stability regions of the ⟨Ni⟩ ⟨NiO⟩ ⟨C⟩ phases (· · · · · ·).

(a) If we use the standard Gibbs energy of ⟨Ni_3C⟩ formation as chosen previously [Fig. 1(c), tangent 1], we find that the chemical potential of carbon in the gas phase, fixed by the equilibrium of the ⟨Ni,C⟩ ⟨Ni_3C⟩ phases, will be higher than that fixed by the ⟨Ni⟩ ⟨Ni_3C⟩ equilibrium. Computation shows that the proportion of hydrocarbons higher than CH_4 increases with the chemical potential of carbon (Fig. 6). In this calculation, different values for the chemical potential of carbon are obtained for given values of the relative

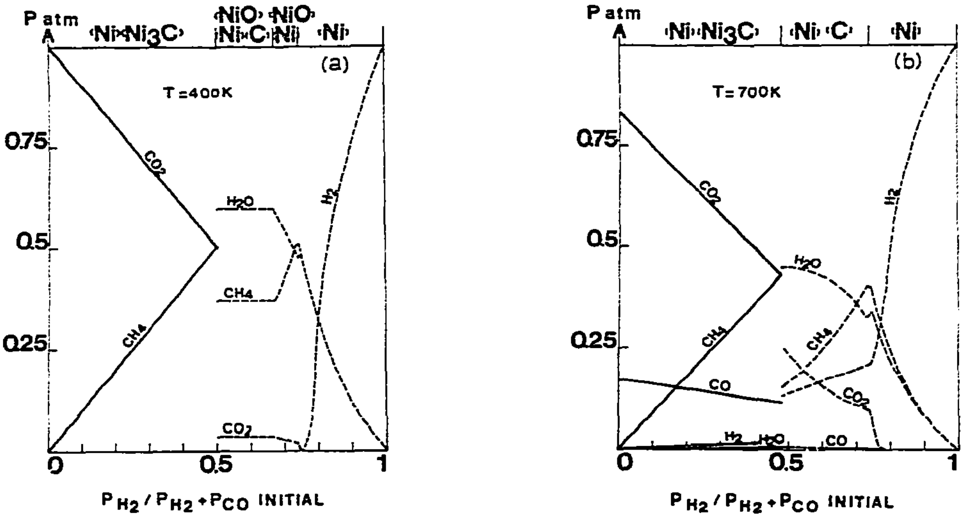

Fig. 5(a), (b). Evolutions of different gas partial pressures as a function of the compositions of the initial CO—H_2 mixture. ———, Without graphite. This is the result of the competition between two complete reactions

$2\ CO + H_2 \rightarrow CO_2 + CH_4$

$2\ CO + \langle Ni \rangle \rightarrow \langle Ni_3C \rangle + CH_4$

- - - - - -, With graphite. The same results as those presented on Fig. 3(a), (b).

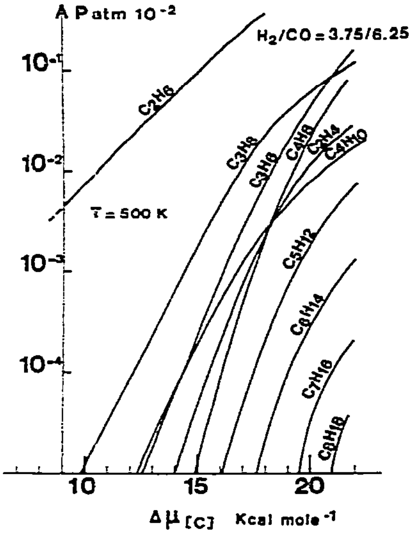

Fig. 6. Evolutions of different hydrocarbon gas partial pressures as a function of the deviation between chemical potential of fixed carbon and chemical potential of graphite.

partial molar Gibbs energy of nickel in the ⟨Ni,C⟩ solution in equilibrium with ⟨Ni_3C⟩.

(b) If we use the chemical potential of carbon defined by the equilibrium between the ⟨Ni⟩ ⟨Ni_3C⟩ phases [Fig. 1(b)] and if we draw a tangent through the corresponding figurative point to the curve of the Gibbs energy function of the ⟨Ni,C⟩ solution, a new value is defined for the standard Gibbs energy of formation of Ni_3C [tangent 2, Fig. 1(c)]. This second possibility illustrates the correct theoretical determination of the Gibbs energy of carbide formation, since it uses basic experimental data: the chemical potential of carbon obtained from the ratio of partial pressures $P_{CH_4}/P_{H_2}^2$, and takes into account the phases present at equilibrium: ⟨Ni,C⟩ solution and ⟨Ni_3C⟩. In practice, Browning and Emmett [17], who did not have the value of the Gibbs energy of formation for the ⟨Ni,C⟩ solution, dealt with equilibrium between pure nickel and nickel carbide. As a result, the compositions of the gas phase at equilibrium are those obtained earlier for case (2).

NOTE ON THE METHOD FOR DETERMINING THE STANDARD FREE ENTHALPY OF FORMATION OF ⟨Ni_3C⟩

The method of determining the standard Gibbs energy of formation of Ni_3C in the presence of the gas pairs H_2—CH_4 or CO—CO_2 has been applied to several carbides [13]. We feel that it has a disadvantage, at least in the case of the iron, cobalt and nickel metals which are known to catalyse the reactions

$$CH_4 \rightleftharpoons 2\,H_2 + \langle C \rangle \qquad (1)$$

$$2\,CO \rightleftharpoons CO_2 + \langle C \rangle \qquad (2)$$

The equilibria

$$CH_4 + 3\,\langle Ni\rangle \rightleftharpoons \langle Ni_3C\rangle + 2\,H_2 \tag{3}$$

$$2\,CO + 3\,\langle Ni\rangle \rightleftharpoons \langle Ni_3C\rangle + CO_2 \tag{4}$$

have been studied at low temperature so that the $\langle Ni_3C\rangle$ decomposition reaction

$$\langle Ni_3C\rangle \rightarrow 3\,\langle Ni\rangle + \langle C\rangle \tag{5}$$

cannot take place [18]. However, reactions (1) and (2), catalysed by the nickel metal [19,20] always occur; this was observed by Browning and Emmett [17] "at the lower temperatures free carbon is reduced or formed very slowly" (sic) and Bromley and Strickland-Constable [21].

So, the systems studied by these authors do not present equilibrium states but pseudo-steady states

$$\begin{tikzcd} 2\,H_2 + \langle Ni_3C\rangle \arrow[r, "v_1"] & CH_4 + 3\,\langle Ni\rangle \arrow[r, "v_2"] & 2\,H_2 + \langle C\rangle + 3\,\langle Ni\rangle \arrow[ll, bend right] \end{tikzcd} \qquad (6)$$

$$\begin{tikzcd} CO_2 + \langle Ni_3C\rangle \arrow[r, "v_1"] & 2\,CO + 3\,\langle Ni\rangle \arrow[r, "v_2"] & CO_2 + \langle C\rangle + 3\,\langle Ni\rangle \arrow[ll, bend left] \end{tikzcd} \qquad (7)$$

defined by $v_1 = v_2$ and very low values of v_1, v_2. The values of the gas partial pressures of these pseudo-steady states are found between those of equilibria (1) and (3) or (2) and (4). Equilibria (3) and (4) cannot therefore be determined because we do not know the velocities v_1 and v_2.

Note that the values of velocities v_1, v_2 may be effectively very low since the experimental temperatures are low and, secondly, the values of the gas partial pressures of states (6) or (7) are close of those of equilibria (1) and (3) or (2) and (4).

Finally, these pseudo-steady states (6) or (7) must evolve slowly towards equilibria (1) or (2). This observation is confirmed when we examine the experimental results of Bromley and Strickland-Constable [21].

Consequently, we feel that this method for determining the standard Gibbs energy of formation of $Ni_3C(\Delta G^0{}_{Ni_3C})$ is an approach that falls short of the $\Delta G^0{}_{Ni_3C}$ value. In other words, the value of $\Delta G^0{}_{Ni_3C}$ that would be obtained if the expressions for velocities v_1, v_2 were taken into account would be necessarily higher than the value determined.

It should be noted that taking v_1, v_2 and the presence of a solid solution $\langle Ni,C\rangle$ into account has opposing effects on the value of $\Delta G^0{}_{Ni_3C}$: taking v_1, v_2 into account increases the value, whereas considering the $\langle Ni,C\rangle$ solid solution decreases it.

DISCUSSION

A more rigorous determination of the C—H—O—Ni equilibrium system should also consider the changes in chemical potential of oxygen and hydrogen in the gas phase, entailed by taking into account the Ni, O, C, H solutions in the equilibria between condensed phases. Under these conditions, we can suppose that the values of the chemical potentials of the O, H, C elements fixed in this way correspond to a gas phase composed partly of hydrocarbons higher than CH_4.

CONCLUSIONS

Our thermodynamic approach shows that, for whatever equilibra of the solid phases (in the Ni—C system) can be reasonably considered [Fig. 1(a)—(c)], the gas phase compositions obtained do not promote the presence of hydrocarbons higher than CH_4, which will only make an appearance for higher chemical potentials of carbon. In the absence of a more rigorous approach, it is reasonable to believe that the explanation of reactions of the Fischer—Tropsch type will rely on kinetic considerations in conjunction with thermodynamic considerations. But taking into account the relatively high temperature which favours thermodynamics, it is also possible to conceive the formation of a ⟨Ni,C⟩ superficial solid solution which could impose a very high carbon chemical potential. In this case, the thermodynamic calculations indicate a very favorable situation for the formation of hydrocarbons.

On the other hand, our results are in relatively good agreement with experimental observations on the catalytic synthesis of methane from CO—H_2 mixtures.

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