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THERMODYNAMICS AND KINETICS OF THE CARBONYL PROCESS FOR THE REFINING OF NICKEL

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The discovery by Langer and Mond in 1889 of the reaction of carbon monoxide at atmospheric pressure with active nickel at 315-353K to form gaseous $Ni(CO)_4$ and its ready reversibility at higher temperatures paved the way for the development of the carbonyl refining process for nickel. Subsequently, to improve the kinetics, a high pressure process was developed for the carbonyl refining of Ni at somewhat higher temperatures. The carbonyl process makes it possible to produce nickel of very high purity and extremely fine size. This paper describes the thermodynamics and kinetics of the formation of nickel carbonyl from pure nickel and its alloys, its vapour phase transport and its decomposition. The thermodynamic analysis includes construction of Ellingham diagrams, pressure-temperature relationships, partial pressure-temperature relationships and productivity function-temperature-pressure relationships for the various carbonyls. The kinetics of $Ni(CO)_4$ formation and decomposition has been analyzed based on the information available in the literature.

INTRODUCTION

A knowledge of the thermodynamics and kinetics of formation and decomposition of the carbonyls of nickel and its associated impurities is necessary to optimise the process conditions during the carbonyl refining of nickel. Schafer[1] first analysed the thermodynamics of vapour phase transport in a temperature gradient for reactions involving a solid phase with a gas phase to yield a gaseous product and outlined the conditions for efficient vapour transport. However, Schafer's rules are fully applicable only to reactions whose multiplicity (ratio of number of moles of the gas in the product to the reactant) is unity. Subsequently, Alcock and Jeffes[2] have analyzed the thermodynamics of all types of vapour transport reactions based on the Ellingham diagram. They have elucidated thermodynamic conditions for efficient vapour transport for various types of reactions. Alcock and Jeffes have introduced a productivity function $(PF_1=p_i\{dp_i/dK\})$, which is a measure of the amount of metal transported per unit increment of the equilibrium constant(K). More recently, Rao [3] has analyzed diffusion and equilibrium in the refining of Ni by the carbonyl route in a three zone horizontal glass reactor.

Goldberger and Othmer[4] studied the effect of temperature, total pressure and gas velocities on the rates of formation of nickel carbonyl. The effect of crystal orientation on the formation of $Ni(CO)_4$ was investigated by Liang et al[5] and Gland and coworkers[6]. It is reported that S, Se, Te and NH_3 enhances the carbonyl formation rate[7] while trace amounts of oxygen inhibit the reaction rate[8]. Presence of small amounts of carbon also appears to enhance the reaction rate[9]. Crabtree and Moll[10] have shown that the rate of carbonyl decomposition have been studied by Chan and Mc Intosh[11] in a static system and by Carlton and Oxley[12] in a dynamic system.

THERMODYNAMICS OF CARBONYL PROCESS

Variation of Free Energy of Formation with Temperature and Pressure

The variation of the free energies of formation of Ni, Fe and Cr carbonyls per mole of the carbonyl from the element and CO as a function of T at 1 atm pressure[13] is shown in Fig. 1. Gibbs' energy data for the various sub-carbonyls of iron [$Fe_2(CO)_9$ and $Fe_3(CO)_{12}$] and of cobalt carbonyls[$Co_2(CO)_8$, $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$] are not available in literature. It is seen that $Cr(CO)_6$ is most stable followed by $Ni(CO)_4$ and then $Fe(CO)_5$. Because of large negative volume and consequently, entropy changes associated with the carbonylation reaction, the free energies of formation of the carbonyls shows a steep variation with temperature. At 1 atm pressure, the decomposition temperatures of Fe, Ni and Cr carbonyls are 315, 390 and 480 K respectively. The variation of free energy of formation (ΔG^{for}) with pressure can be estimated from the volume changes associated with the carbonylation reaction. If the vapour phase is assumed to behave ideally, it can be shown that:

$$d\Delta G^{for}/d\ln P = \Delta nRT$$

where P is the total pressure, Δn is the number of moles of the carbonyl minus the number of moles of carbon monoxide, R is the gas constant and T, absolute temperature. As Δn is negative (-3, -4 and -5 for Ni, Fe and Cr carbonyl respectively), the carbonyls will be increasingly stabilised over a larger temperature range with application of pressure; $Cr(CO)_6$ being stabilised the most followed by $Fe(CO)_5$ and then $Ni(CO)_4$. At higher pressures, the process can be operated at higher T where the kinetics is favourable.

Pressure-Temperature Relationship for the Carbonyls

The variation of temperature with total pressure(P) for the s→l, s→v and l→v equilibria can be computed from the Clausius-Clapeyron equation($dP/dT=\Delta H/T\Delta V$). The P-T diagrams for $Ni(CO)_4$, $Fe(CO)_5$ and $Cr(CO)_6$ constructed from thermodynamic data[13] is given in Fig.2. The volumes of the solid and liquid carbonyls were from density data reported in the literature and the vapour was assumed to behave ideally. The condensed to gas phase transition of Fe, Ni and Cr carbonyls at 1 atm pressure are 376, 315 and 425K respectively. Therefore, at 1 atm pressure and temperatures favourable for the formation of gaseous $Ni(CO)_4$ (315-390K), $Fe(CO)_5$ is unstable and $Cr(CO)_6$ exists as a solid enabling easy separation of Ni. At high P, the condensed→gas phase equilibrium is shifted to higher temperatures and therefore in the high pressure process for the refining of Ni, the carbonyls will exist as a liquid mixture which can then be separated by fractional distillation.

Vapour pressure data on Ni, Fe, Cr and Co carbonyls are available in the literature[13,14]. At the boiling point of $Ni(CO)_4$ (315K), the vapour pressure of $Fe(CO)_5$ is 10^4 Pa and that of $Cr(CO)_6$ is 10^2 Pa. The total pressure of all the Co-based effusing species at 270 K is ~0.3 Pa[14]. It would therefore in principle be possible to produce pure $Ni(CO)_4$ by the atmospheric pressure refining route at lower temperatures. The Ni carbonyl formation can be represented by the reaction:

$$Ni(s) + 4CO(g) = Ni(CO)_4(g)$$

$$\Delta G^0 = -163681-12.5T\ln T+490.1T \text{ J} = -RT\ln[p_{Ni(CO)4}/a_{Ni}\cdot p_{CO}^4] \qquad (1)$$

In addition,

$$p_{CO}+p_{Ni(CO)4}=P \qquad (2)$$

where a_{Ni} is the activity of nickel, p_{CO} and $p_{Ni(CO)4}$ are the partial pressures of CO and $Ni(CO)_4$ respectively and P is the total pressure. If pure nickel is used, Eqs. (1) and (2) can be solved simultaneously at different total pressures to determine the partial pressures of $Ni(CO)_4$ and CO as a function of temperature. The calculated conversions of $Ni(CO)_4$ from partial pressure data as a function of T for total pressures of 1, 5 and 10 atm are given in Fig. 3. At a fixed pressure, thermodynamically, highest conversions are achieved at the lowest temperatures and at a fixed temperature, higher conversions are achieved at higher pressures. Nickel obtained from the reduction process is in general present as an alloy containing mostly Fe as impurity and small amounts of Cr and Co and not at unit activity. As a first approximation, the presence of Cr and Co in the alloy can be neglected and the binary Fe-Ni system can be considered. The carbonylation reaction for Fe can be given as:

$$Fe(s) + 5CO(g) = Fe(CO)_5(g)$$
$$\Delta G^0 = -178539-15.7T\ln T+677.0T = -RT\ln\{p_{Fe(CO)5}/a_{Fe}\cdot p_{CO}^5\} \qquad (3)$$

In addition, the total pressure equation (Eq.2) will include $Fe(CO)_5$. Partial pressures of CO, $Fe(CO)_5$ and $Ni(CO)_4$ at 373K and at the phase boundaries calculated by simultaneously solving Eqs. (1) to (3) for total pressures of 1 and 10 atm is given in Table I. Activities of Fe and Ni were taken from the recent evaluation of Swartzendruber et al[15]. It is seen that up to a total pressure of 10 atm, the partial pressures of $Fe(CO)_5$ is negligible in comparison to $Ni(CO)_4$. For dilute multi-component alloys, one can assume that the solvent Ni to obey Raoult's law and $p_{Ni(CO)4}$ and p_{CO} can be calculated by substituting the mole fraction of Ni in Eq. (1). At 373 K, the partial pressures of iron, chromium and cobalt carbonyls can be assumed to be negligible in comparison to that of nickel carbonyl.

Table I.Partial Pressures at 373 K for Carbonylation of an Fe-Ni Alloy.

X_{Ni}	1 atm total pressure			10 atm total pressure		
	p_{CO}	$p_{Ni(CO)4}$	$p_{Fe(CO)5}$	p_{CO}	$p_{Ni(CO)4}$	$p_{Fe(CO)5}$
0.001	0.940	0.0601	2.3×10^{-6}	5.037	4.962	10.1×10^{-4}
0.01	0.753	0.2474	0.7×10^{-6}	3.078	6.9216	0.86×10^{-4}
0.72	0.753	0.2474	0.7×10^{-6}	3.078	6.9216	0.86×10^{-4}
0.90	0.443	0.5571	0.03×10^{-6}	1.554	8.4459	0.0
0.96	0.443	0.5571	0.03×10^{-6}	1.554	8.4459	0.0
1.00	0.400	0.5997	0.0	0.143	9.8567	0.0

Conditions for Efficient Vapour Transport for the Nickel Carbonyl Process

Alcock and Jeffes[2] suggest that efficient vapour phase transport can be achieved by varying the equilibrium constant(K). Lines of constant K are shown on the Ellingham diagram in Fig. 1. In order to vary the values of K, one has to vary the temperature of reaction according to van't Hoff equation. For example, varying the reaction temperature from 320 to 350 K, the equilibrium constant for $Ni(CO)_4$ formation varies from 10^{10} to 10^5. Larger the value of the enthalpy of reaction, greater will be the variation in K for a given difference in T. Carrying out an analysis similar to that proposed by Alcock and Jeffes [2], it can be shown that for $Ni(CO)_4$ formation, 72% of the theoretical possible transport takes place in varying K from 10^{10} to 1 i.e., from 268 to 394 K and about 69% by varying K from 10^6 to 1. (307 to 394 K). Therefore, according to this analysis, the optimum temperature for carrying out the carbonylation reaction for nickel would be 307 K, corresponding to a K value of 10^6. The kinetics of the reaction will be very slow at this temperature. For the analysis of vapour transport reactions, Alcock and Jeffes define a productivity function which for the case of nickel carbonyl formation can be derived as:

$$PF_1 = p_{Ni(CO)_4} \cdot \frac{dp_{Ni(CO)_4}}{dK} = p_{Ni(CO)_4} \cdot \frac{P - p_{Ni(CO)_4}}{P + 3\,p_{Ni(CO)_4}} \qquad (4)$$

This function is plotted as a function of log K(temperature) in Fig. 4 for a range of total pressures. Maximum in these plots corresponds to conditions of maximum efficiency. The main conclusion is that low temperatures and high total pressures thermodynamically favour the transport of nickel by carbon monoxide. However, the kinetics of the reaction and the requirement of $Ni(CO)_4$ to exist as a gas phase necessitates the use of higher temperatures.

KINETICS OF NICKEL CARBONYL PROCESS

Kinetics of the process discussed in this paper is based on information available in the literature. It is reported that nickel carbonyl formation is a topochemical reaction and is a function of temperature, gradient in partial pressure of CO, surface activity and crystal orientation. The rate equation for the formation of nickel carbonyl can be given as[4,16]:

$$\ln(a_s^0/a_s^0 - f) = k.(p_{COi} - p_{COeq}).t \qquad (5)$$

where f is the fraction converted, a_s^0 is the surface activity, k is the rate constant, p_{COi} and p_{COeq} are the partial pressures of CO at the reaction interface and equilibrium value respectively and t is the time. Goldberger and Othmer[4] have studied the variation of rates of formation of $Ni(CO)_4$ at atmospheric pressure with temperature in the range 323-388 K as well as with gas velocities of CO at 348K . They observed maximum rates of formation at 348 K and the rates were independent of flow in the range 1.17 to 1.92 cm/sec. Goldberger and Othmer also studied the effect of total pressure on the nickel carbonyl formation rate and found that the surface activity and consequently the formation rate increases markedly with pressure. NH3, S, Se, Te and C were found to have a catalytic effect[7,10,17] whereas, traces of oxygen on the surface inhibits nickel carbonyl formation.

Several studies have been reported in the literature on the decomposition of nickel carbonyl[12,18-20]. They report that the decomposition reaction is chemically controlled below 448 K and is controlled by the diffusion of the reactants to the deposition surface above these temperatures. They also propose that at temperatures below 521 K, the decomposition reaction occurs through heterogeneous nucleation and in the temperature range of 521 to 578 K, it occurs by homogeneous nucleation. The homogeneous part of the decomposition of $Ni(CO)_4$ follows the rate for a typical surface chemical reaction:

$$r_w = k_0 p_a / 1 + k_r p_r \qquad (6)$$

where k_0 is the rate constant, p_a and p_r are the partial pressures of $Ni(CO)_4$ and CO respectively and $k_{r,}$ the adsorption constant of CO on metal. For the heterogeneous decomposition of $Ni(CO)_4$, the rate equation conformed to a diffusion controlled reaction:

$$r_w = k_0 k_a p_a / 1 + k_a p_a + k_r p_r \qquad (7)$$

Here, k_a is the adsorption constant of carbonyl on metal. In the temperature range where the decomposition occurs through heterogeneous nucleation and where surface chemical reaction is the rate controlling step (<448 K), the rate equation can be given as [20]:

$$r_w = \frac{k_0 k_a^2 \exp[-E_0 / RT] \exp[2 E_a / RT].[p_{ai}^2 - (p_{ri}^4 / K)^2]}{[1 + k_a \exp[E_a / RT] p_{ai} + k_r.\exp[E_r / RT].p_{ri}]^2} \qquad (8)$$

where, E_0 is the activation energy, E_a is the adsorption energy for $Ni(CO)_4$, E_r is the adsorption constant for CO, p_{ai} and p_{ri} are the partial pressures at the interface and K is the equilibrium constant for the decomposition reaction. Below 448 K, where the reaction is controlled by surface chemical reaction, the rate increases exponentially with temperature; above 448 K, in the diffusion controlled region, rate is independent of temperature and in the range 521 to 578 K, homogeneous decomposition occurs. The total pressure has little effect on the decomposition of $Ni(CO)_4$. Carlton and Oxley[12] have observed that all the diluents decrease the effective concentration of $Ni(CO)_4$ to a degree roughly proportional to the amount of diluent present. Clements et al[20] found that at lower temperatures (423-450K), deposition rates are less dependent on flow rate and at higher temperatures, the deposition rate is a strong function of flow rate. Nickel carbonyl can also be photochemically decomposed by light of wavelength shorter than 3900 A[21].

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