

Metal carbonyl clusters: thermodynamics of their formation and stability. Some novel results on cobalt, rhodium, ruthenium, and mixed clusters

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Abstract: A series of reversible cluster formation and degradation reactions with neutral metal carbonyls and carbonyl hydrides was studied by high-pressure IR-spectroscopy, under CO and/or H₂ pressure, in alkane solutions. Fundamental reversible reactions were analyzed for cobalt, rhodium, ruthenium, and mixed Co-Fe, Co-Ru and Co-Rh carbonyl systems. Log K_p vs 1/T equations, their graphical illustrations and thermodynamic parameters are given for the homometallic Co, Rh and Ru systems.

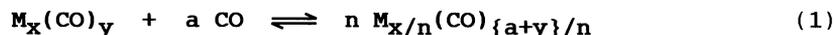
In the combined system of Co and Ru carbonyls and hydridocarbonyls proper conditions were found where mixed hydridocarbonyl clusters are obtained in stable equilibria with the homonuclear compounds. Of the Co_x(HRu)_{4-x}(CO)₁₂ species the one with x=3 is strongly favored thermodynamically. - In the mixed Co-Fe system no thermodynamically stable compound could be found: HCo₃Fe(CO)₁₂ decomposes irreversibly, under CO as well as H₂ or N₂, to homometallic species.

Of particular interest is the coordinatively unsaturated mixed species CoRh(CO)₇, which represents a key link between the homo- and hetero-metallic equilibria of these metals.

The connection of our data with thermochemical results from other laboratories, and their application to bond enthalpy calculations is presented.

INTRODUCTION

The chemistry of transition metal carbonyl clusters has attracted considerable interest since the mid-1960's. There is a growing amount of scientific knowledge on the formation and degradation reactions of the cluster carbonyls, however, mainly in terms of preparative routes. In contrast to the dramatic increase of efforts on this field, only a few studies are known which treat in a quantitative way the reversible reactions of type (1) or (2) with the aim of obtaining thermodynamical data for them.



Besides the per se importance of the knowledge of the reaction enthalpies and entropies for such processes the direct determination of these thermodynamic parameters via measurements of the temperature variation of the equilibrium constants, represents a complementary source of thermochemical data, which adds to the direct calorimetric results.

I wish to emphasize two important advantages of our method:

(1) the uncertainties of the equilibrium measurements are generally small since the reaction enthalpies themselves are much smaller than the enthalpies of formation of the carbonyls. These relationships are illustrated for the system of the cobalt carbonyls in Fig. 1.

(2) With the method of quantitative equilibrium measurements we can obtain the enthalpies of formation even for compounds which cannot be prepared in pure form. We present the corresponding values obtained in this way for $\text{Rh}_2(\text{CO})_8$ and $\text{Ru}(\text{CO})_5$ further on.

At the time of starting our studies in this field (1975) only a few papers existed on metal carbonyl equilibria: those of Ercoli et al. on the dicobalt octacarbonyl vs. tetracobalt dodecacarbonyl equilibrium (Eq.6 in Table 1.), determined with pure molten phases (i.e. without solvent) of the carbonyls [1], and in a toluene-heptane mixture, respectively [2], and the publication of Ungváry on the dicobalt octacarbonyl vs. cobalt carbonyl hydride equilibrium (Eq.5 in Table 1.) in heptane solution [3].

On this last mentioned equilibrium another study has been published meanwhile by Alemdaroğlu et al. [4]. We have found this data, however, to be in error, and could essentially confirm the data of Ungváry as it will be shown further on.

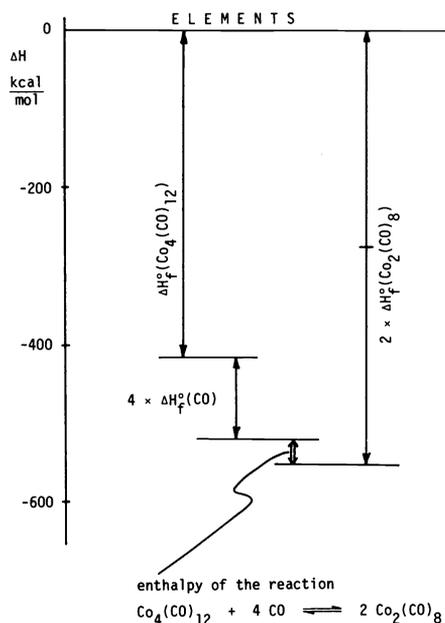


Fig. 1. Relationship between enthalpies of formation and enthalpy of reaction

The main obstacle for investigations of this kind seems to be the difficulty related to the gaseous state of the free form of the entering reactants CO and/or H_2 . The development of high-pressure infrared cells should have brought a rapid development on this field. As reflected by the publications in this field the primary aim of the application of high-pressure IR spectroscopy appears to be the desire to gain insight into the mechanism of the reactions in which metal carbonyls are used as homogeneous catalysts, or catalyst precursors.

The application of high-pressure IR spectroscopy for the study of the fundamental reactions of metal carbonyls is much more limited and authors with interesting new observations in this field frequently limit themselves to qualitative characterization of

such reactions, or indicating only the extreme limiting conditions for the forward and backward reactions to render them complete.

The application of this method in a way to obtain results which are valuable even in quantitative terms is not an easy task. The following principle rules must be kept thoroughly:

- IR spectra must be obtained with expanded wavenumber scale to permit the observation of the exact band positions;
- high optical resolution (ca. 1 cm^{-1} or better) is needed not only for good separation of closely occurring bands but also for having a good linearity in the absorbance vs. concentration relationship;
- solvents are to be chosen to minimize their solvent effect exerted on the band forms and for background absorption;
- concentration of the solvents should lie in regions that allow a reliable determination of the concentrations from band intensities (absorbance values higher than 1.5 are to be avoided even with microprocessorized or FT instruments);
- the analytical bands should be very carefully selected to minimize overlap;

- (f) the limits of elimination of background absorptions by compensation (solvents, dissolved carbon monoxide) should be carefully checked, since "black against black" cannot yield useful spectral information.

Keeping in mind these criteria necessary for obtaining reliable results, a programme was started to collect quantitative data for the most important fundamental reversible metal carbonyl reactions. Our primary aim was to furnish good data for the chemists and engineers who work with metal carbonyls as catalyst precursors, to enable them to predict or at least to estimate the equilibrium concentrations in different systems. On this level of the presentation of our results we use easily applicable practical equations of the type

$$\log K_p = A - B/T \quad (3)$$

where K_p is a practical value of the equilibrium constants, obtained for the reactions of type (1) according to:

$$K_p = \frac{[M_{x/n}(CO)_{(a+y)/n}]^n}{[M_x(CO)_y] \times p_{CO}^a} \quad (4)$$

i.e. the partial pressure of carbon monoxide (or hydrogen, in the equilibria involving hydrides) is used rather than the concentration of the dissolved gas. The total pressure observed in the experiments is corrected, at this level, only by the subtraction of the vapor tension of the solvent n-hexane. It is clear that the degree of completion of these reactions depends on the concentration of the gaseous reactants (CO, H₂) dissolved in the liquid phase. Thus these equations are valid only for the particular solvent used. In our studies we used throughout n-hexane as the solvent to allow the comparison and combination, respectively, of the equations obtained for the different systems.

On this point a critical comment seems appropriate concerning the choice of the solvent by some authors. In some papers dealing with the results of high-pressure IR spectroscopic results involving carbon monoxide the solvents were chosen according to the criterion that carbon monoxide should have a low solubility, to reduce the disturbing effect of dissolved CO in the IR spectra. This argument is scientifically invalid, since low solubility gives rise to low conversion values, and for making the reactions more complete, higher pressures are needed. This in turn increases the intensity of the broad absorption band of carbon monoxide.

Keeping in mind the observation that, for alkanes, the solubility of carbon monoxide or hydrogen is roughly constant if it is expressed in molar fractions, i.e. ca. 1.8×10^{-3} mol/mol [5], a ca. 2.63-times higher pressure is needed to obtain the same concentration in the liquid phase if e.g. hexadecane is used as solvent instead of hexane.

With the use of high-MW solvents also reaction rates are often reduced owing to the higher viscosity of these solvents and consequently to the lower diffusion rate of the gases.

HOMOMETALLIC CARBONYL CLUSTERS

The four homometallic systems for which very accurate equations of type (3) were obtained are shown in Table 1. (For the discussion of the thermodynamic parameters vide infra).

TABLE 1. Some $\log K_p$ vs $1/T$ equations for carbonyl fragmentation reactions in n-hexane solution

$\text{Co}_2(\text{CO})_8 + \text{H}_2 \rightleftharpoons 2 \text{HCo}(\text{CO})_4$	$\log K_p = -0.696 - 877/T$	(5)
$\text{Co}_4(\text{CO})_{12} + 4 \text{CO} \rightleftharpoons 2 \text{Co}_2(\text{CO})_8$	$\log K_p = -21.84 + 6455/T$	(6)
$\text{Rh}_4(\text{CO})_{12} + 4 \text{CO} \rightleftharpoons 2 \text{Rh}_2(\text{CO})_8$	$\log K_p = -21.61 + 2377/T$	(7)
$\text{Ru}_3(\text{CO})_{12} + 3 \text{CO} \rightleftharpoons 3 \text{Ru}(\text{CO})_5$	$\log K_p = -10.70 + 1111/T$	(8)

We developed a computer plot-programme to present these equilibrium systems in graphical form. These plots (c.f. Fig. 2-5) are the usual complex equilibrium representations, similarly to e.g. titration curves;

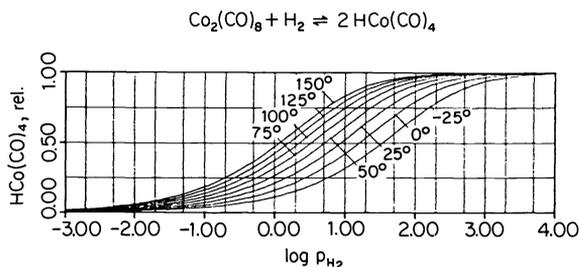


Fig. 2.

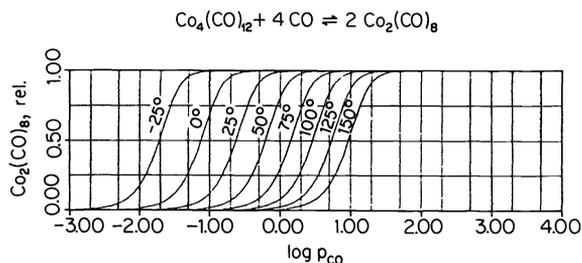


Fig. 3.

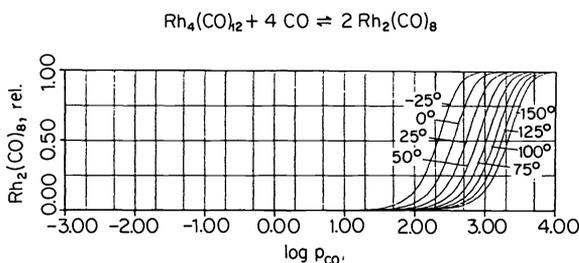


Fig. 4.

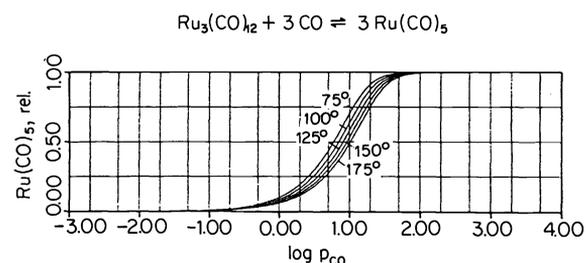


Fig. 5.

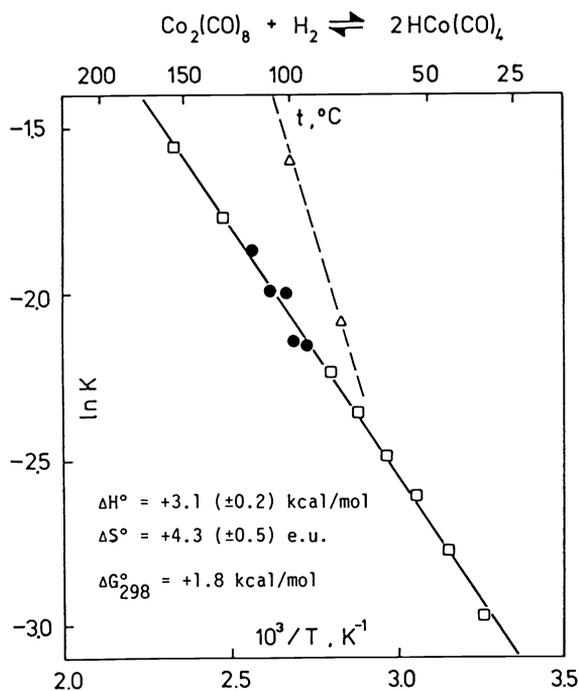
Fig. 2-5. Rel. concentration vs $\log p(\text{H}_2)$ or $\log p(\text{CO})$ curves for the reactions indicated. The absolute concentration is throughout 10^{-3} molar, with respect to the higher nuclearity component.

the curves are in these case isotherms, and they reflect the relative fraction (normalized to: sum of moles of both carbonyls involved = 1) of the lower nuclearity carbonyl species versus logarithm of $p(\text{CO})$ or $p(\text{H}_2)$. To our knowledge these are the first graphical representations of this kind in metal carbonyl chemistry. Of course these plots are valid only for n-hexane as solvent. For other solvents the curves are to be shifted by the logarithm of the ratio of the gas-solubility in the solvent relative to the solubility in n-hexane. The value of this ratio is not necessarily constant for different temperatures, although for a limited temperature range great variations are not to be expected.

Fig. 3 and 4, and the corresponding equations were already published [6,7]. Equation (5) of Table 1, (and Fig. 2 obtained therefrom) concerning the equilibrium between $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ under hydrogen pressure, is based on our hitherto unpublished results [8]. In Fig. 6 our data points are shown together with those based on the work of Ungváry [3], and also with those taken from the work of Alemdaroğlu et al.[4]. A very satisfactory common best fit line can be obtained based on the points of ourselves and of Ungváry, whereas the $\ln K$ vs $1/T$ values of the other authors show a considerable deviation from this fit. Since Ungváry applied completely different analytical method, the agreement between the results of our both laboratories seem very convincing.

It is very educative to compare the form of these titration-like equilibrium curves.

In the $\text{HCo}(\text{CO})_4$ vs $\text{Co}_2(\text{CO})_8$ (we show here this Figure for the first time) reaction H_2 acts on the first power: this is reflected by the flatness of the curves which extend over 6(!) orders of magnitude of $p(\text{H}_2)$. The narrow spacing of the curves is a consequence of the very low temperature-dependence of K_p , i.e. of the low $|\Delta H_r^\circ|$ value (vide infra).



□ UNGVÁRY (1972) Δ ALEMDAROĞLU ET.AL.(1976)
 ● TANNENBAUM, DIETLER, BOR (1980)

Fig. 6. Graphical comparison of the $\ln K$ vs $1/T$ values obtained for the given reaction by different authors.

In the $\text{Co}_4(\text{CO})_{12}$ vs $\text{Co}_2(\text{CO})_8$ reaction CO figures on the fourth power and this causes the isotherms to have the steep slope shown. The wide spacing reflects the relative high $|\Delta H_r^\circ|$ value of this reaction.

This last feature contrast with the $\text{Rh}_4(\text{CO})_{12}$ vs $\text{Rh}_2(\text{CO})_8$ equilibrium (Fig. 4) where although the isotherms are steep similarly to the plot of the analogous cobalt carbonyl reaction, but the spacing of the curves (drawn for the same temperatures) is rather narrow pointing to the considerably lower $|\Delta H_r^\circ|$ value of this reaction.

Our results on the $\text{Ru}_3(\text{CO})_{12}$ vs $\text{Ru}(\text{CO})_5$ reaction are very recent ones [9]. The plot of this equilibrium (Fig. 5) combines a somewhat less steepness of the curves, corresponding to the third power of the entering CO ligand, and the very narrow spacing connected with the extreme low $|\Delta H_r^\circ|$ value of this reaction.

The single equilibria couple with each other, of course, in systems with three or more carbonylic components. The rate in reaching the stable overall equilibrium situation is governed by the kinetics of the

slowest reaction. An illustration is shown in Fig.7 . In this experiment, first a stable equilibrium between $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ was achieved at 108°C , with $p_{\text{CO}}=5.8$ bar (status left from the line of time=0). This system was then pressurized with additional hydrogen ($p(\text{H}_2)=100$ bar), on the same temperature. As the curves of the relative concentrations of the three species show, the equilibrium between $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ is reached in ca. 15 minutes. The ratio $\text{Co}_2(\text{CO})_8/\text{Co}_4(\text{CO})_{12}$ is, however , thus shifted

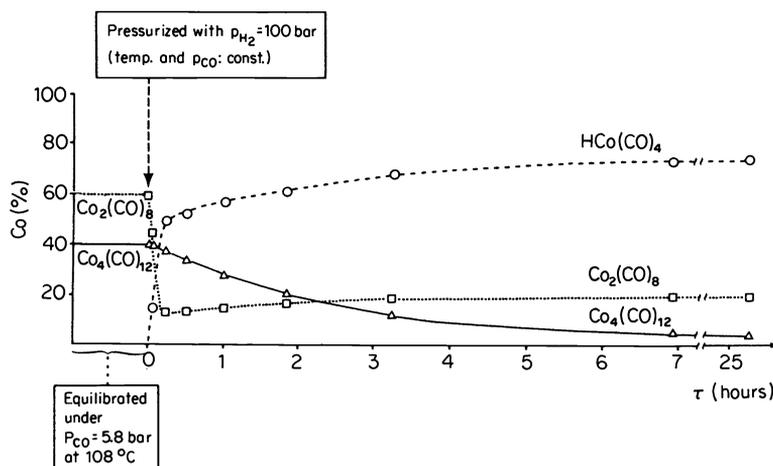


Fig. 7. Concentration vs time curves in a cobalt carbonyl system under the conditions indicated.

far from the equilibrium concentration. The rate of the reaction $\text{Co}_4(\text{CO})_{12} + 4 \text{CO} \rightarrow 2 \text{Co}_2(\text{CO})_8$ is quite low under these conditions [10], but within ca. 25 hours the stable overall equilibrium between all three components (plus H_2 and CO) is reached.

The second level in our studies is the determination of the thermodynamic parameters of these reactions, ΔH° , ΔS° , and ΔG° . Keeping in mind the fundamental thermodynamical relationship

$$\ln K = (\Delta S/R) - (\Delta H/R)/T \quad (9)$$

by comparison of Eq.(9) with (3) one could expect that by performing the transformation from K_p to K (i.e. an equilibrium constant expressed in terms of activities for all components rather than in pressure of the gases) would establish a direct relationship between the constants A and B of Eq.(3) and ΔS° and ΔH° , respectively. However, this is only a rough approximation, applicable only for an orienting estimation of these parameters. The deviation from a direct, linear, and general connection between ΔS° and A, and ΔH° and B is caused by the temperature dependence of the solubility of CO or H_2 , i.e. their enthalpy of dissolution, by the deviation of the gases from ideality, by the variation of the volume of the liquid phase under pressure, etc. Hence for the evaluation of the thermodynamic parameters, the corrections are introduced separately for each experiment (for various T and p values). The results obtained for are shown in Table 2.

TABLE 2. Thermodynamic parameters of some homometallic carbonyl reactions as determined by high-pressure IR spectroscopy

Reaction (solvent: n-hexane)	ΔH°	ΔS°	ΔG_{298}°	ref.
(6) $\text{Co}_4(\text{CO})_{12} + 4 \text{CO} \rightleftharpoons 2 \text{Co}_2(\text{CO})_8$	-29.5(± 0.5) -123.5(± 2.1)	-64.7(± 1.3) -270.9(± 5.4)	-10.2 -42.7	[6]
(7) $\text{Rh}_4(\text{CO})_{12} + 4 \text{CO} \rightleftharpoons 2 \text{Rh}_2(\text{CO})_8$	-14.0(± 2.5) -58.6(± 10.0)	-73.0(± 6.0) -305.0(± 25)	+7.7 +32.3	[7]
(5) $\text{Co}_2(\text{CO})_8 + \text{H}_2 \rightleftharpoons 2 \text{HCo}(\text{CO})_4$	+3.1(± 0.2) +13.0(± 0.9)	+4.4(± 0.5) +18.4(± 2.1)	+1.8 +7.5	[8]
(8) $\text{Ru}_3(\text{CO})_{12} + 3 \text{CO} \rightleftharpoons 3 \text{Ru}(\text{CO})_5$	-6.5(± 0.5) -27.1(± 1.9)	-27.0(± 2.0) -114.0(± 5.0)	+1.6 +6.7	[9]

N.B.: Upper values in kcal.mol⁻¹ and cal.mol⁻¹.K⁻¹ units, respectively; lower values in kJ.mol⁻¹ and J.mol⁻¹.K⁻¹ units, respectively.

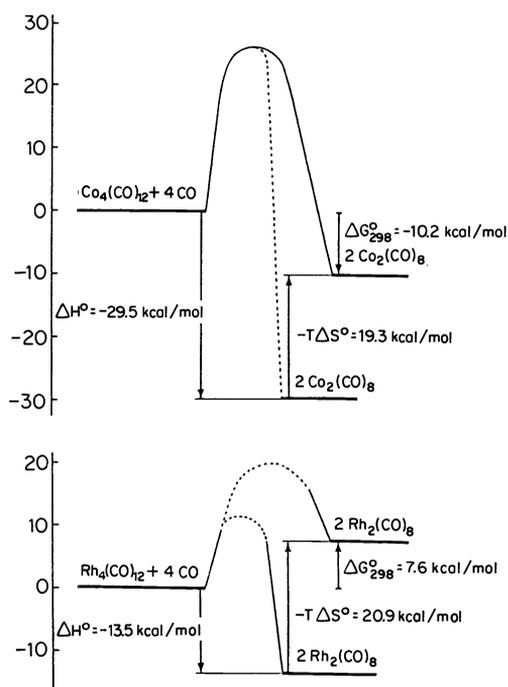
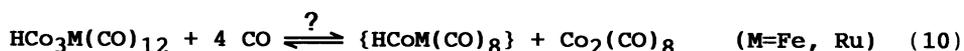


Fig. 8. Graphical comparison of the enthalpies of reaction and free enthalpies of reaction for reactions (6) and (7).

Because of the special importance of the quantitative data obtained for the first time for the concentrations of $\text{Rh}_2(\text{CO})_8$ at high pressure of CO and at low temperature we show, in Fig. 8, a graphical comparison of the thermodynamical parameters of the analogous reactions of the cobalt and rhodium carbonyls. Although the sign of ΔH° is equal for both reactions, this is not true for the ΔG° values which are directly related to the chemical potential of these reactions. Fig. 7, illustrates that for cobalt carbonyls $\text{Co}_2(\text{CO})_8$ is the thermodynamically stable form under standard conditions at 25°C, whereas in the rhodium case the system $\{\text{Rh}_4(\text{CO})_{12} + 4 \text{CO}\}$ is more stable.

MIXED METAL CARBONYL CLUSTERS

The cluster compounds $\text{HCo}_3\text{M}(\text{CO})_{12}$ (M=Fe or Ru) are usually prepared through acidification of the corresponding anions which, in turn, are obtained in various yields, in Lewis-base solvents, from different homometallic precursors [11]. We were interested to learn if the neutral dodecacarbonyl hydrides form stable equilibria, starting from homometallic carbonyls and/or carbonyl hydrides in alkane solutions, under CO and/or H_2 pressure. Or, vice versa, we wondered if fragmentation according Eq. (10) gives rise to



binuclear mixed hydrides, $\{HCoM(CO)_8\}$. A corresponding compound with $M=Fe$ has been prepared [12] and the structure of the anion $[FeCo(CO)_8]^-$ has been characterized by X-ray diffraction [13].

$HCo_3Fe(CO)_{12}$ turned out to be thermodynamically unstable. It is not formed thermally from any of the iron carbonyls and cobalt carbonyl hydride. In turn, if it is prepared via its anion, it invariably and irreversibly decomposes to $Fe(CO)_5$ and $Co_2(CO)_8/HCo(CO)_4$ (or $Co_4(CO)_{12} + H_2$) under any CO/H_2 mixture [14].

In contrast, for $HCo_3Ru(CO)_{12}$ conditions could be found where this mixed cluster forms stable equilibrium mixtures with various monometallic cobalt and ruthenium carbonyls and (small amounts of) other $(HRu)_{4-x}Co_x(CO)_{12}$, ($x=0,1,2,4$) clusters [14]. Fig. 9 shows that this equilibrium can be reached from both sides, with $p(H_2)=100$ bar and $p(CO)=0.6$ bar, at $T=70^\circ C$. Among the mixed $(HRu)_{4-x}Co_x(CO)_{12}$, ($x=1,2,3$) clusters the title compound ($x=3$) is thermodynamically favoured relative to the di- and tri-hydro species ($x=1,2$). Since the equilibrium mixture contains seven soluble carbonylic components as shown by Scheme 1 the quantitative evaluation of the thermodynamic parameters for the formation or fragmentation of $HCo_3Ru(CO)_{12}$ is difficult.

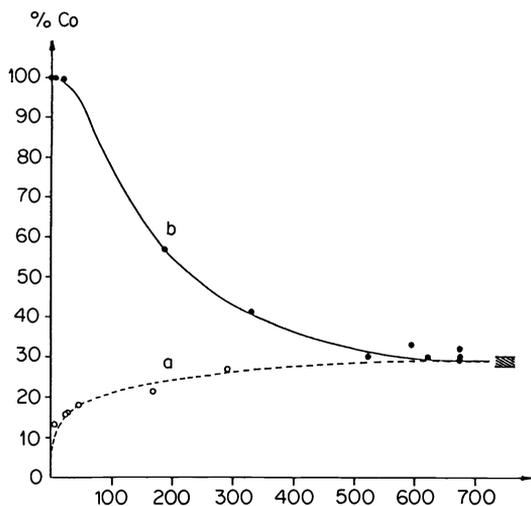
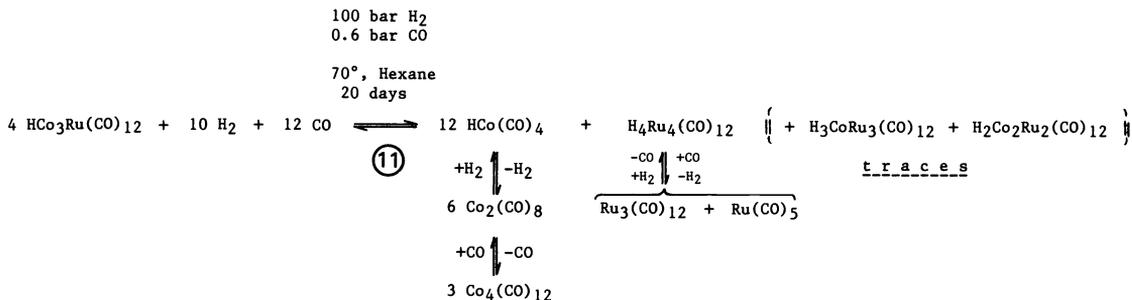


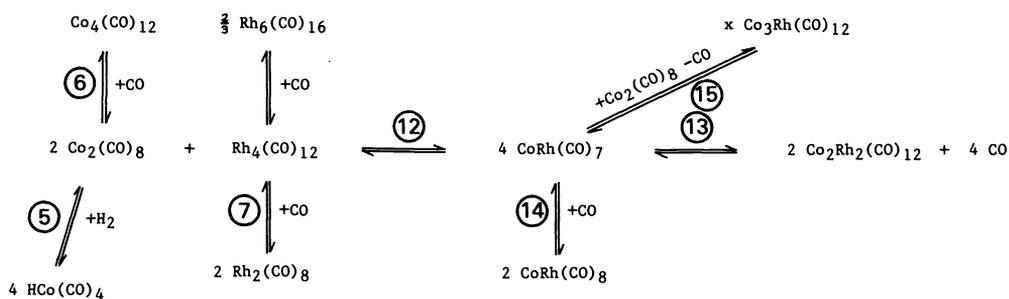
Fig. 9. Concentration(Co%) vs time (hr) curves for the equilibrium reaction (11) in Scheme 1, at $T=70^\circ C$, $p(CO)=0.6$ bar, $p(H_2)=100$ bar, in hexane.
a, Formation of $HCo_3Ru(CO)_{12}$;
b, Partial fragmentation of $HCo_3Ru(CO)_{12}$ into homometallic species.

Scheme 1



A much more interesting reversible mixed-metal carbonyl system is the cobalt-rhodium one. The previously [15] tentatively formulated $CoRh(CO)_7$, observed first in reaction 12 (Scheme 2), was now obtained in pure form,

Scheme 2



by reaction 13 (Scheme 2) [16], (for details c.f. paper #336 of this Conference, by I.T.Horváth et al.).

Very high CO pressure (>130 bar) at ca. 0°C gives rise to the formation of a hitherto unknown compound, which, on the basis of its IR spectrum, is formulated as $\text{CoRh}(\text{CO})_8$. Approximate preliminary equilibrium curves are shown for equilibria 13 and 14 (Scheme 2) at 10°C in Fig. 10. The shaded zones should reduce to single curves, after refinement (in progress), and other isotherms will be added when the temperature dependence of the K_p values will be known.

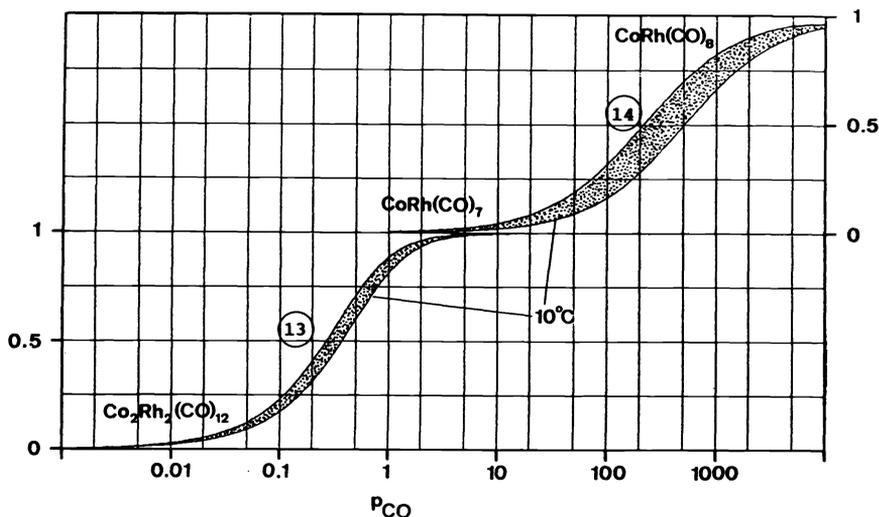


Fig. 10. Approximate concentration vs $p(\text{CO})$ plots for reactions (13) and (14) (Scheme 2) at 10°C; for details see text.

New enthalpies of formation

From the new values of the reaction enthalpies for reactions 5, 7 and 8 the ΔH_f values as shown in Table 3 can be calculated for $\text{HCo}(\text{CO})_4$, $\text{Rh}_2(\text{CO})_8$ and $\text{Ru}(\text{CO})_5$ (relative to the ΔH_f values of $\text{Co}_2(\text{CO})_8$, $\text{Rh}_4(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$, respectively, obtained by microcalorimetric method [17]).

TABLE 3. New enthalpies of formation

Compound	ΔH_f kcal.mol ⁻¹ /kJ.mol ⁻¹
Rh ₂ (CO) ₈ , (g)	-265.1 (±7.5)/ -1109 (±30)
CoRh(CO) ₇ , (g)	-243.1 (±15) / -1017 (±50)
Ru(CO) ₅ , (g)	-172.0 (±7) / -719 (±30)

Based on these enthalpies of formation the following modified bond enthalpy contribution values could be calculated (all values in kcal/mol): M(Co-Co)...23.7; M(Rh-Rh)...32.5; M(Ru-Ru)...36.5; D(Co-CO)...31.1; D(Rh-CO)...36.0; D(Ru-CO)...38.5; D(H-Co(CO)₄)...62.9 .

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