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GASEOUS EQUILIBRIA: SOME OVERLOOKED ASPECTS

ABSTRACT: For some gaseous equilibria, with particular stoichiometric characteristics, the addition of some reactant or products, as large as it may be, when operated under constant temperature and pressure, cannot cause a (practically) complete shift of the equilibrium to the right, or to the left. The effect of the addition is counteracted by the increase of volume that the system undergoes to keep constant the pressure. [*Chem. Educ. Res. Pract. Eur.*: 2000, *1*, 145-149]

INTRODUCTION

It is well known that there are circumstances such that, for a perfect-gas system in chemical equilibrium, the addition of a reactant (or product), under constant temperature and pressure, will shift the equilibrium so as to produce more of the added species (Levine,1988). In the present paper, we describe another apparently surprising effect of the addition of a species participating in a gaseous equilibrium, when its stoichiometric coefficient is equal to the difference of the coefficients of the products and reactants.

THEORY

Let us consider a perfect gas system under constant pressure P and temperature T, at equilibrium with respect to a reaction represented, in the most general way, by the equation

$$0 = \Sigma v_i X_i \qquad (\Sigma v_i = \sigma) \qquad (1)$$

where X's represent the various chemical species taking part in the reaction, v's are the corresponding stoichiometric coefficients, to be considered as preceded by a minus sign if belonging to a reactant, and σ is the sum of all the stoichiometric coefficients (in the usual speech, σ would have been designated as the difference between the sum of the coefficients of the products and that of the reactants).

In this paper, we discuss the effect of adding a species X_k, whose stoichiometric coefficient v_k is equal to σ, to the above system, while keeping constant both the temperature and the pressure:

"if X_k is a reactant, an addition of X_k, as large as it may be, cannot force the reaction to proceed forwards until the (practically) complete consumption of the limiting reactant; if X_k is a product, an addition of X_k as above cannot force the reaction backwards up to a (practically) complete regeneration of the initial amount of the limiting, or the only, reactant."

To illustrate the above statements, let us consider a gas-phase reaction equilibrium such as

$$2\, NOCl \quad \rightleftarrows \quad 2\, NO + Cl_2 \tag{2}$$

where the stoichiometric coefficient of Cl_2 is equal to the sum $(2+1) + (-2)$ of the coefficients of the products and reactants. To simplify the discussion, let the initial amounts (in mol) of $NOCl$, NO, and Cl_2 be a_o, 0, and b_o, respectively, with $a_o > 0$ and $b_o \geq 0$. The system is at a temperature T and under a pressure P, and these values will be kept constant throughout the various transformation the system is supposed to undergo. From the initial state, the system will move towards equilibrium through a partial dissociation of $NOCl$, taking place according to a certain degree α, until all the three species will be present in the system in such amounts as to satisfy the equilibrium constant:

$$\frac{K_p}{P} = \frac{\alpha^2}{(1-\alpha)^2} \cdot \frac{\frac{1}{2}\alpha \cdot a_o + b_o}{a_o \cdot \left(1 + \frac{1}{2}\alpha\right) + b_o} = \frac{\alpha^2}{(1-\alpha)^2} \cdot y_{Cl_2} \tag{3}$$

where K_p is the equilibrium constant of reaction (2) in terms of partial pressures and y_{Cl_2} is the mole fraction of Cl_2. Obviously (see also Appendix), α will attain its maximum value when $b_o = 0$ and will decrease as b_o is increased, but, unlike what could be naïvely thought, if this increase is made larger and larger, α will not tend to 0 for $b_o \to \infty$, i.e., for $y_{Cl_2} \to 1$, but will tend asymptotically to a non-zero minimum value $\alpha*$. From equation (3), by setting y_{Cl_2} equal to 1,

$$\alpha* = \sqrt{K_p/P} \Big/ \left(\sqrt{K_p/P} + 1\right) \tag{4}$$

From a physical standpoint, this means that the effect of adding increasing amounts of Cl_2, that should shift the equilibrium to left, is counteracted by the increase undergone by the volume of the system to keep the pressure constant, that tends to shift the equilibrium to right, and the two effects are of the same magnitude.

Similar considerations could apply to a reaction equilibrium such as $2\,CO + O_2 \rightleftarrows 2\,CO_2$: under constant pressure and at a constant (suitably high) temperature, an addition of O_2, as large as it may be, cannot cause the (practically) complete transformation of CO into CO_2. So, by going back to reaction (2), at equilibrium, all the values of α lower than $\alpha*$ are to be excluded as chemically impossible, and the only

chemically-significant root of equation (3), of third-degree with respect to unknown α, has to lie in the interval between $\alpha*$ and 1, whichever the value of b_o.

But, with a small further effort, the interval where this root has to lie can be further restricted, if a_o and b_o are known. By recalling that

$$y_{Cl_2} = \frac{\frac{1}{2}\alpha \cdot a_o + b_o}{a_o \cdot \left(1 + \frac{1}{2}\alpha\right) + b_o} \tag{5}$$

if we take the derivative of y_{Cl_2} with respect to α (keeping b_o constant), we obtain

$$\left(\frac{\partial y_{Cl_2}}{\partial \alpha}\right)_{b_o} = \frac{2a_o^2}{(a_o \cdot \alpha + 2a_o + 2b_o)^2} > 0 \tag{6}$$

which means that y_{Cl_2} will increase as α increases, as, for instance, when the system moves from the initial state towards equilibrium. But, since at equilibrium the degree of dissociation α has to be greater than $\alpha*$, it will follow that

$$y_{Cl_2} = \frac{\frac{1}{2}\alpha \cdot a_o + b_o}{a_o \cdot \left(1 + \frac{1}{2}\alpha\right) + b_o} > \frac{\frac{1}{2}\alpha* \cdot a_o + b_o}{a_o \cdot \left(1 + \frac{1}{2}\alpha*\right) + b_o} \tag{7}$$

So, with reference to equation (3), if we assume the right-hand member of inequality (7), to be designated as $\left(y_{Cl_2}\right)_{def}$, as an approximation by defect of y_{Cl_2}:

$$\left(y_{Cl_2}\right)_{def} = \frac{\frac{1}{2}\alpha* \cdot a_o + b_o}{a_o \cdot \left(1 + \frac{1}{2}\alpha*\right) + b_o} \tag{8}$$

it will represent the lowest value that y_{Cl_2} can take at equilibrium. If we insert it into equation (3) and solve for α, the value of α thus obtained, to be designated as $(\alpha)_{exc}$ will certainly be approximated by excess, and represents an upper bound for the values that α can take at equilibrium:

$$(\alpha)_{exc} = \frac{\sqrt{\dfrac{(K_p/P)}{(y_{Cl_2})_{def}}}}{1 + \sqrt{\dfrac{(K_p/P)}{(y_{Cl_2})_{def}}}} \tag{9}$$

Therefore, at equilibrium, $\alpha* < \alpha < (\alpha)_{exc}$, and not, *tout court*, $0 < \alpha < 1$.

TABLE. *For equilibrium (2) at 377 °C ($K_p = 1.19$), under a pressure of $0.13\overline{2}$ atm, the values of α and $(\alpha)_{exc}$, plus the constant value of α^* , as a function of various initial amounts, (in mol) of the participants in the reaction.*

a_o	n_{NO}^o	b_o	α^*	α	$(\alpha)_{exc}$
1	0	0	0.750	0.846	0.852
1	0	0.5	0.750	0.813	0.814
1	0	1	0.750	0.797	0.798
1	0	2	0.750	0.781	0.781
1	0	10	0.750	0.759	0.759
1	0	100	0.750	0.751	0.751
1	0	1000	0.750	0.750	0.750

A NUMERICAL APPLICATION

Here is a numerical application of the above considerations to equilibrium (2), for which, at 377 °C, $K_p = 1.19$. If, for instance, $P = 0.13\overline{2}$ atm, $a_o = b_o = 1$ mol, $n_{NO}^o = 0$ mol, where n_{NO}^o is the initial amount of *NO*, then, from formulae (4), (8), and (9), we obtain $\alpha^* = 0.750$, $(y_{Cl_2})_{def} = 0.579$, $(\alpha)_{exc} = 0.798$, respectively.

The Table reports the values of $(\alpha)_{exc}$ and α at equilibrium (plus the constant value of α^*) as a function of various ratios for the initial amounts of *NOCl* and Cl_2 . The initial amount of *NO* is kept equal to 0 in order to grant that the system, when moving from the initial state towards equilibrium, shifts to the right.

MAIN FINDINGS AND SOME IMPLICATIONS

In a gaseous chemical equilibrium showing stoichiometric features as previously specified, the addition (under constant *T* and *P*, and however large it may be) of a species whose stoichiometric coefficient is equal to the difference of the coefficients of products and reactants cannot cause the reaction to proceed up to a (practically) complete exhaustion of the limiting reactant, unlike what happens when the same addition is operated under constant temperature and volume. This behaviour seems to contradict Le Châtelier's principle, but the contradiction is only apparent. Actually, the effect of adding increasing amounts of this species is counteracted by the increase undergone by the volume of the system to keep the pressure constant, and the two effects, which are of the same magnitude and tend to shift the equilibrium in opposite directions, cancel each other.

Knowing the boundaries of the "permitted" interval for α may be helpful when trying to solve 3rd-degree equation (3) for α by means of the interval-bisection method (Mukesh, 1988), or by an iterative method (Eberhart, 1986), choosing from the same interval the first-guess value α_1, needed to start the iterative calculations. By employing either method, we found the α values at equilibrium reported in the 5th column of the Table.

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APPENDIX

Equation (3) may be rewritten as

$$F(b_o,\alpha)=(K_p/P)\cdot[(a_o\cdot\alpha+2a_o+2b_o)/(a_o\cdot\alpha+2b_o)]-[\alpha^2/(1-\alpha)^2]=0 \quad (10)$$

By taking the derivative of α with respect to b_o, keeping P and a_o constant, we obtain, according to the rules for the derivation of implicit functions

$$\left(\frac{\partial\alpha}{\partial b}\right)_{P,a_o}=-\frac{4a_o\cdot(K_p/P)/(a_o\cdot\alpha+2b_o)^2}{[2a_o^2\cdot(K_p/P)/(a_o\cdot\alpha+2b_o)^2]+[2\alpha/(1-\alpha)^3]}<0 \qquad (11)$$

which shows, in accordance with what could be intuitively expected, that the equilibrium value of α must decrease upon increase of b_o. On the other hand, we know that, at equilibrium, α can never be 0, so that, for $b_o\to\infty$, derivative (11) must tend to 0. This means that, for $b_o\to\infty$, α must tend asymptotically to a limiting value, as actually given by formula (4).

REFERENCES

Eberhart, J.G. (1986). Solving equations by successive substitution. The problems of divergence and slow convergence. *Journal of Chemical Education, 63,* 576-578.

Levine, I. N.(1988). *Physical chemistry,* (3rd edition), p.186, McGraw – Hill International Editions (Chemistry Series).

Mukesh, D. (1988). Successive substitution. *Journal of Chemical Education*, 65**,** 838.