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The Le Châtelier Principle: How Much a Principle?

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Abstract: The Principle of Le Châtelier is analyzed for the case of reactions taking place with real gases. The Principle, as usually stated in textbooks, is true only for ideal gas mixtures, and may be violated when the nonideal behavior of a gas is taken into consideration.

The Principle of Le Châtelier is usually introduced by textbooks on thermodynamics and physical chemistry [1–3] when discussing the effect of variables on the position of chemical equilibrium. In its simple expression the Principle, as given by Prigogine and Defay [4], states that any system in chemical equilibrium undergoes, as a result of a variation of one the variables governing the equilibrium, a compensating change in a direction such that had this change occurred alone it would have produced a variation in the factor considered in the *opposite* direction. For example, if a reaction occurs with an increase in the number of moles the Principle states that an increase in pressure will decrease conversion, and so forth. The purpose of this publication is to discuss whether the Principle is valid for every physical possibility, or whether it is restricted in its applications.

A chemical reaction may be considered as a process of rearrangement of the elements from the order present in the reactants to the order present in the products. The process is driven by a negative change in the Gibbs energy function (ΔG) and, as required by the second law of thermodynamics, it will go on until the Gibbs energy function achieves a minimum value, or $\Delta G = 0$. The *initial driving force* (the difference in chemical potential between the initial state and the final equilibrium state) will be the largest and will then decrease to zero when a state of dynamic chemical equilibrium is achieved. Consider the following chemical reaction

$$\mathrm{aA + bB + cC + \ldots \rightleftharpoons mM + nN + oO + \ldots} \tag{1}$$

or in short

$$\sum_i v_i A_i = 0 \tag{2}$$

where A_i represents a particular component and v_i its stoichiometric coefficient, assumed here positive for the products (P) and negative for the reactants (R). Let us first analyze the transient stage of the reaction where the concentration (and activity) of each component is changing with time and the system as a whole is approaching its final chemical equilibrium state. At any stage of the reaction before it reaches equilibrium we can write

$$\Delta G = \sum^{P} v_i \overline{G_i} - \sum^{R} v_i \overline{G_i} \tag{3}$$

where $\overline{G_i}$ represents the value of the partial Gibbs function of component *i*. $\overline{G_i}$ is also called the *chemical potential* μ_i of component *i*, so that eq (3) may be written

$$\Delta G = \sum^{P} v_i \mu_i - \sum^{R} v_i \mu_i \tag{4}$$

The term ΔG will decrease in value as the reaction goes on and eventually will reach the value zero when chemical equilibrium is achieved. The chemical potential μ_i of species *i* may be written [5] as

$$\mu_i = \mu_i^0 + RT \ln \hat{a}_i \tag{5}$$

In eq (5) $\hat{a}_i$ is the activity of component *i* in the reacting mixture, defined as the fugacity ratio $\hat{a}_i = \frac{\hat{f}_i}{f_i^0}$ where $\hat{f}_i$ is the actual fugacity of the component in the mixture and f_i^0 is the fugacity of the pure component in a standard *arbitrary* state (the reference state). The symbol (^) is used to indicate that the property under it *is not* a partial property. For a pure component $\hat{a}_i$ is obviously equal to unity, hence from eq (5) $\mu_i = \mu_i^0$ The latter equality means that μ_i^0 should be interpreted as the chemical potential of *pure* component *i* when in a state where its activity has a value of one. Replacing eq (5) in eq (4) yields after some algebra

$$\Delta G = \left[\sum^{P} v_i \mu_i^0 - \sum^{R} v_i \mu_i^0\right] - RT\left[\ln \frac{\hat{a}_M^m \hat{a}_N^n \hat{a}_O^o \cdots}{\hat{a}_A^a \hat{a}_B^b \hat{a}_C^c \cdots}\right] \tag{6}$$

Defining J_a (extent of the reaction) as

$$J_a = \frac{\hat{a}_M^m \hat{a}_N^n \hat{a}_O^o \cdots}{\hat{a}_A^a \hat{a}_B^b \hat{a}_C^c \cdots} \tag{7}$$

we can write eq (6) as

$$\Delta G = \left[\sum^{P} v_i \mu_i^0 - \sum^{R} v_i \mu_i^0\right] - RT \ln J_a \tag{8}$$

Inspection of the first term on the right hand side of eq (8) shows that it has the same structure as eq (4) where μ_i has been replaced by μ_i^0. Thus eq (8) may be considered the ΔG of the reaction in question (ΔG^0) when conducted at the same pressure and temperature, but under the *forced* conditions of *total* conversion and the reactants and products starting and ending the process with unitary activity. Obviously this is *not a spontaneous reaction,* hence the name *forced*. In spite of its restrictions the term ΔG^0 is extremely valuable because, in general, it can be easily calculated once the pressure, temperature, and standard states f_i^0 are stipulated. Then

$$\Delta G^0 = \sum_i^P v_i \mu_i^0 - \sum_i^R v_i \mu_i^0 \tag{9}$$

equation 8 is now written

$$\Delta G = \Delta G^0 + RT \ln J_a \tag{10}$$

It should be realized that although the value of the terms ΔG and J_a change as the reaction goes on (they are time-dependent) ΔG^0 does not. Equation 10 is usually called the *reaction isotherm* because it describes the evolution of the activities of the different components with time. It may be truly considered the thermodynamic description of the kinetics of the reaction.

The reaction will eventually reach chemical equilibrium, a state for which $\Delta G = 0$ and the activities have attained their final value. For this situation we write

$$\Delta G^0 = -RT \ln J_{a,equil} \tag{11}$$

The value of J_a at the equilibrium state, $J_{a,equil}$, is called the *chemical equilibrium constant* of the reaction, K_a, so that

$$\Delta G^0 = -RT \ln K_a \tag{12}$$

where

$$K_a = \frac{\hat{a}_M^m \hat{a}_N^n \hat{a}_O^o \cdots}{\hat{a}_A^a \hat{a}_B^b \hat{a}_C^c \cdots}_{equil} = \frac{\prod_i^P \hat{a}_i^{v_i}}{\prod_i^R \hat{a}_i^{v_i}} \tag{13}$$

and

$$\Delta G = RT \ln \frac{J_a}{K_a} \tag{14}$$

The second law of thermodynamics teaches us that spontaneous processes occur with a decrease in the Gibbs energy. Thus, eq (14) indicates that the chemical reaction will process *spontaneously* as long as $J_a < K_a$. We see from eq (12) that knowledge of ΔG^0 allows immediate calculation of the equilibrium constant.

When dealing with *phase equilibrium* it is customary to select the standard state f_i^0 for each component as the pure substance at the temperature and pressure of the system. In the case of *chemical equilibrium* it is more convenient to select the standard state of each component at a *fixed* pressure (usually 1 atm). With a standard state so defined, the equilibrium constant becomes *independent* of the pressure of the system.

The greatest value of the equilibrium constant is in the calculation of the equilibrium composition (conversion) of the reacting system under the specified operating conditions. The conversion thus calculated is the *maximum* conversion that can be achieved under the stipulated conditions; it reflects the maximum fraction of the initial chemical energy that is available for obtaining the desired products (final energy of configuration). The observant reader will notice the striking parallel between a chemical reaction and a reversible Carnot engine. Thus the chemical equilibrium constant allows determination of the most favorable conditions of temperature, pressure, composition, and ratio of reactants to obtain the greatest conversion of reactants and the highest yield of products.

Let us now analyze the method for calculating the yield of a given reaction in the gaseous state and the way it is affected by the operating variables. To do so we choose as standard state the ideal gas at 1 atm pressure (as stated above). With this choice $\hat{f}_i^0$ can be considered to have a value of one and the activity of a component in a mixture becomes identical with its fugacity

$$\hat{a}_i = \hat{f}_i \tag{15}$$

and eq (13) becomes

$$K_a = \frac{\hat{a}_M^m \hat{a}_N^n \hat{a}_O^o \cdots}{\hat{a}_A^a \hat{a}_B^b \hat{a}_C^c \cdots} = \frac{\prod_i^P \hat{f}_i^{v_i}}{\prod_i^R \hat{f}_i^{v_i}} \tag{16}$$

Inspection of the right hand side of eq (16) shows that it has the same algebraic structure as K_a (a product divided by a product), hence we can call it $K_{\hat{f}_i}$. In the derivation that follows the algebraic structure of K_a will appear several times with different variables, we will identify the pertinent expression by the appropriate subscript. We now assume that the pressure is moderate and that the fugacity of each component in the mixture may be expressed by the rule of Lewis–Randall [5]

$$\hat{f}_i = y_i f_i \tag{17}$$

where f_i represents the fugacity of the *pure* component at the pressure and temperature of the mixture and $\hat{f}_i$ the fugacity of the same component *in* the mixture of composition y_i. Under this assumption eq (16) becomes

$$K_a = \frac{\hat{a}_M^m \hat{a}_N^n \hat{a}_O^o \cdots}{\hat{a}_A^a \hat{a}_B^b \hat{a}_C^c \cdots} = \frac{\prod_i^P \hat{f}_i^{v_i}}{\prod_i^R \hat{f}_i^{v_i}} = K_{\hat{f}_i} = \left[\frac{\prod_i^P \hat{f}_i^{v_i}}{\prod_i^R \hat{f}_i^{v_i}}\right]\left[\frac{\prod_i^P y_i^{v_i}}{\prod_i^R y_i^{v_i}}\right] = K_f K_y \tag{18}$$

where

$$K_f = \frac{\prod_i^P f_i^{v_i}}{\prod_i^R f_i^{v_i}} \tag{19}$$

and

$$K_y = \frac{\prod_i^P y_i^{v_i}}{\prod_i^R y_i^{v_i}} \tag{20}$$

In eq (22) y_i represents the molar fraction of component i in the equilibrium mixture. Notice, again, the similar algebraic structure of K_a, $K_{\hat{f}_i}$, K_f, and K_y. Defining now the fugacity coefficient of a pure component φ_i as $\varphi_i = \frac{f_i}{P}$ then $f_i = \varphi_i P$ and eq (18) becomes

$$K_a = \frac{\hat{a}_M^m \hat{a}_N^n \hat{a}_O^o \cdots}{\hat{a}_A^a \hat{a}_B^b \hat{a}_C^c \cdots} = \frac{\prod_i^P \hat{f}_i^{v_i}}{\prod_i^R \hat{f}_i^{v_i}} = K_{\hat{f}_i} = \left[\frac{\prod_i^P P^{v_i}}{\prod_i^R P^{v_i}}\right]\left[\frac{\prod_i^P \varphi_i^{v_i}}{\prod_i^R \varphi_i^{v_i}}\right]\left[\frac{\prod_i^P y_i^{v_i}}{\prod_i^R y_i^{v_i}}\right] \tag{21}$$

or, with our shorthand notation

$$K_a = K_\varphi K_y P^{\Delta v} \tag{22}$$

where

$$\Delta v = \sum_i^P v_i - \sum_i^R v_i \tag{23}$$

is the change in the number of moles of the reaction. In eq (22) the terms K_φ and K_y represent the nonideality of the pure gases and the equilibrium composition, respectively.

We will now examine the direction of the shift in the equilibrium position when the pressure or the temperature of the reactive mixture is varied. In order to study the effect of the variables on the conversion we arrange eq (22) as follows

$$K_y = \frac{K_a}{K_\varphi} P^{-\Delta v} \tag{24}$$

Inspection of eq (24) indicates that any change that will increase the value of K_y will increase the conversion.

Effect of Pressure

The pressure of the system affects the terms K_φ and $P^{\Delta v}$ and, in general, the effect on the first factor will be much weaker than that on the second. Although the fugacity coefficient depends exponentially on the pressure [5]

$$\left(\frac{\partial \ln \varphi}{\partial P}\right)_T = \frac{z-1}{P} \tag{25}$$

where z is the compressibility factor $z = \frac{Pv}{RT}$, if the reaction occurs with a change in the number of moles $(\Delta v \neq 0)$ the value of $(z-1)/P$ will be normally smaller than $\Delta v \neq 0$ and, in addition, the algebraic structures of K_φ will tend to damp any significant influence of the pressure. If $\Delta v \neq 0$ the Principle of Le Châtelier will be followed strictly and, for example, for a reaction that goes on with an increase in the number of moles, an increase in pressure will be reflected in a decrease of the conversion. According to the Principle, if the reaction goes on *without* a change in the number of moles, the conversion will not be affected by a change in pressure. A close inspection of eq (22) shows that this is not the case, although the term $P^{-\Delta v}$ has a value of one, the term K_φ may be affected by the pressure in a nonpredictable manner, an increase in pressure may cause it to increase or to decrease, depending on the temperature and pressure levels, as well as the nature of the components. Although the value of K_φ will usually vary with pressure between the limits 0.90–1.10, it will still change the value of the conversion from that predicted by the Principle of Le Châtelier. Only if the gases behave ideally will the reaction mixture behave strictly according to the Principle.

Examples of reactions that proceed without a change in the number of moles are isomerizations and the important water-shift reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ for the production of hydrogen from water.

Effect of Temperature

The temperature of the system affects the terms K_φ and K_a and, in general, the effect on the first factor will be much weaker than that on the second. Both the equilibrium constant and the fugacity coefficients depend exponentially on the temperature [5]

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \tag{26}$$

$$\left(\frac{\partial \ln \varphi}{\partial T}\right)_P = -\frac{H - H^*}{RT^2} \tag{27}$$

where ΔH^0 and $(H - H^*)$ represent the standard heat of reaction and the residual enthalpy of the gas, respectively. The residual enthalpy is the enthalpy of a gas mixture in its actual state (H) and the enthalpy if it was in the ideal state (H^*). In general, the value of the residual enthalpy $(H - H^*)$ will be

Table 1. (a) Conversion of Butane (1) to 2-Methylpropane (2) as a Function of Pressure and Temperature. (b) Fugacity Coefficients of the Pure Components, φ_i, as a Function of Pressure and Temperature

(a) Pressure MPa

T, K	0.1	1	5	10	Ideal[a]
500	0.6408	0.6394	0.6317	0.6216	0.6410
600	0.5475	0.5466	0.5426	0.5380	0.5476
700	0.4787	0.4782	0.4759	0.4734	0.4788
800	0.4266	0.4263	0.4249	0.4234	0.4266
900	0.3892	0.3914	0.3882	0.3873	0.3892
1000	0.3593	0.3591	0.3586	0.3581	0.3593
1500	0.2671	0.2671	0.2671	0.2671	0.2671

(b) Pressure MPa

T, K	0.1		1		5		10	
	φ_1	φ_2	φ_1	φ_2	φ_1	φ_2	φ_1	φ_2
500	0.9939	0.9946	0.9407	0.9471	0.7327	0.7626	0.5529	0.6010
600	0.9968	0.9972	0.9687	0.9725	0.8593	0.8765	0.7584	0.7882
700	0.9983	0.9985	0.9835	0.9858	0.9263	0.9370	0.8738	0.8929
800	0.9992	0.9993	0.9919	0.9933	0.9614	0.9715	0.9416	0.9540
900	0.9997	0.9998	0.9968	0.9878	0.9874	0.9919	0.9827	0.9909
1000	1.0000	1.0000	0.9998	1.0004	1.0014	1.0043	1.0081	1.0134
1500	1.0004	1.0004	1.0042	1.0043	1.0217	1.0218	1.0447	1.0448

[a] Assuming ideal gas behavior.

smaller than that of ΔH^0 so that the controlling variable will be the equilibrium constant [(eq (26)]. Thus the Principle of Le Châtelier will be followed strictly and, for example, an increase in temperature will decrease the conversion of an exothermic reaction and increase the yield of an endothermic reaction. Only for the rare case of a reaction with an extremely small heat of reaction the controlling variable will become K_φ and the Principle will be violated. An additional possibility will be for those reactions where the heat of reaction depends very weakly on the temperature in a particular range of temperature.

We will illustrate these conclusions with the following two examples.

Example 1

Analysis of the effect of the pressure and temperature on the isomerization of butane to 2-methylpropane

$$\text{butane} \rightleftharpoons \text{2-methylpropane}$$

This is a reaction that occurs without change in the number or moles $(\Delta v = C)$. We will determine the conversion of the reaction in the range 400 to 1500 K and 0.01 to 10 MPa, assuming that this is the only reaction that occurs and that because it is an isomerization the rule of Lewis–Randall is valid. The fugacity coefficients will be calculated using the Peng–Robinson equation of state and the value of ΔG^0 with the data available from the Thermodynamics Research Center (TRC) [6].

Assuming that we start with 1 mole of butane and that α is the conversion of the reaction, then at the final equilibrium state we have $(1-\alpha)$ moles of butane and α moles of 2-methyl propane, so that $K_y = \dfrac{\alpha}{1-\alpha}$. Equation 24 becomes

$$\frac{\alpha}{1-\alpha} = \frac{K_a}{K_\varphi} \tag{28}$$

so that

$$\alpha = \frac{K_a}{K_\varphi + K_a} \tag{29}$$

Table 1 describes the results of the calculation for the different pressure and temperature levels. It is clearly seen that although the reaction occurs without a change in the number of moles, the conversion of butane to 2-methylpropane decreases as the pressure is increased isothermally. The pressure effect diminishes as the reaction temperature increases and at 1500 K the theoretical conversion is identical to the ideal one. It is also seen that although the heat of reaction at 0 K is small (-8.41 kJ/mol) [6], it is large enough to offset the possible influence of the temperature on K_φ.

Example 2

Analysis of the effect of the pressure and temperature on the water-shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

This is a reaction that occurs without a change in the number of moles $(\Delta v = C)$. We will determine the conversion of the reaction in the range 400 to 1500 K and 0.01 to 100 MPa for a 1: 1 molar feed. We will use the Peng–Robinson equation of state to calculate the fugacity coefficients and the TRC data [6] for the determination of ΔG^0.

Making a material balance we find that the equilibrium mixture is composed of $(1-\alpha)$ moles of CO, $(1-\alpha)$ moles

Table 2. (a) Conversion of CO (or H_2O) as a Function of Pressure and Temperature. (b) Fugacity Coefficients of the Pure Components, φ_i, as a Function of Pressure and Temperature

(a) Pressure, MPa

T, K	0.1	1	5	10	100	Ideal[a]
700	0.7551	0.7546	0.7521	0.7492	0.7101	0.7552
800	0.6736	0.6731	0.6712	0.6688	0.6382	0.6736
900	0.6038	0.6035	0.6021	0.6003	0.5776	0.6039
1000	0.5462	0.5460	0.5449	0.5437	0.5273	0.5462
1500	0.3841	0.3841	0.3838	0.3836	0.3799	0.3840

(b) Pressure, MPa

T, K	0.1				1				5			
	CO	H_2O	CO_2	H_2	CO	H_2O	CO_2	H_2	CO	H_2O	CO_2	H_2
700	1.0003	0.9987	1.0000	1.0002	1.0035	0.9866	0.9999	1.0025	1.0176	0.9343	1.0002	1.0124
800	1.0003	0.9992	1.0001	1.0002	1.0033	0.9917	1.0012	1.0020	1.0167	0.9594	1.0066	1.0103
900	1.0003	0.9995	1.0002	1.0002	1.0031	0.9949	1.0019	1.0017	1.0157	0.9748	1.0098	1.0087
1000	1.0003	0.9997	1.0002	1.0001	1.0029	0.9969	1.0022	1.0015	1.0146	0.9846	1.0112	1.0075
1500	1.0002	1.0000	1.0002	1.0001	1.0020	1.0004	1.0021	1.0008	1.0100	1.0020	1.0107	1.0040

(b) Pressure, Mpa (continued)

T,K	10				100			
	CO	H_2O	CO_2	H_2	CO	H_2O	CO_2	H_2
700	1.0357	0.8715	1.0019	1.0250	1.4639	0.3438	1.2160	1.2969
800	1.0339	0.9205	1.0141	1.0208	1.4170	0.5404	1.2697	1.2450
900	1.0317	0.9507	1.0201	1.0176	1.3757	0.7027	1.2916	1.2064
1000	1.0294	0.9700	1.0229	1.0151	1.3400	0.8229	1.2957	1.1766
1500	1.0201	1.0041	1.0214	1.0082	1.2208	1.0644	1.2378	1.0950

[a] Assuming ideal gas behavior.

of H_2O, and α moles each of CO_2 and H_2, where α is the conversion. For this case eq (24) becomes

$$K_y = \frac{\alpha^2}{(1-\alpha)^2} \tag{30}$$

and

$$\alpha = \frac{K_a^{0.5}}{K_a^{0.5} + K_\varphi^{0.5}} \tag{31}$$

In this particular example the values of the fugacity coefficients have not been calculated using the Lewis–Randall rule but as present in the actual mixture because of the presence of a quantum gas and the heavy influence of water [5]. Table 2 describes the results of the calculation of the conversion for the different pressure and temperature levels. It is clearly seen that although the reaction occurs without a change in the number or moles, there is a substantial effect of pressure: conversion decreases as the pressure is increased isothermally. The pressure effect diminishes as the reaction temperature increases and at 1500 *K* it approaches the theoretical conversion. The heat of reaction at 0 *K* is large enough (-40.41 kJ/mol) [6], to offset the influence of the temperature on K_φ.

Conclusion

The Principle of Le Châtelier, as usually stated in textbooks, is true only for ideal gas mixtures, and may be violated when the nonideal behavior of a gas is considered.

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