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Fugacity Examples 2: The fugacity of a "hard-sphere" semi-ideal gas and the van der Waals gas

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The fugacity of the vander Waals gas is obtained after a review of the concept itself.

I. INTRODUCTION

The fugacity is a strange concept which is introduced into Physical Chemistry with the intent of preserving the notational convenience of formulas which apply to ideal gases when one is studying real ones. This paper is a return to the subject handled earlier [1], but with an emphasis this time on the derivation of the fugacity function for the van der Waals gas. In addition, the fugacity of a fictitious hard-sphere type gas is also obtained.

II. PAST TREATMENTS

Students complain bitterly that studying two years of calculus and one year of physics based calculus is a waste of time for chemists. Perhaps they are right. But since all chemists will study Physical Chemistry and since the curriculum traditionally consists of trying to convince students that the formulas they use are valid, an emphasis on calculus in the Physical Chemistry curriculum seems warranted.

Here, we re-discuss the fugacity [1], a concept introduced once one starts studying thermodynamics (in chemistry). It is a strange concept indeed.

An example of an early treatment can be found in the venerable Prutton and Lando [3], who write that, per mole, the free energy (Gibbs) would be

$$G = RT\ell n f + B$$

where B is a temperature dependent constant, and

$$G^o = RT\ell n f^o + B$$

is the Gibbs' free energy in the "standard state". Then

$$G - G^o = RT\ell n \frac{f}{f^o}$$

Moore [4] *defines* the fugacity as

$$dG = RT d\ell n f$$

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so that integrating "between the given state and some freely chosen standard state, we obtain"

$$\mu = \mu^o + RT\ell n \frac{f}{f^o}$$

For an ideal gas, $\mu_{ig} = \mu_{ig}^o + RT\ell n p$ is our starting point; this equation has units inside the logarithm, something which is totally inappropriate. There exist texts which write $\mu_{ig} = \mu_{ig}^o + RT\ell n \frac{p}{1\ atm}$ showing that the argument of the logarithm is atm/atm (or bar/bar), i.e., unitless where the 1 in the denominator is assumed to be in (or define) the same units as the numerator.

III. DEFINITIONS AND PRECURSOR MATERIALS

We start with the primitive definition

$$\left(\frac{\partial \bar{G}}{\partial p}\right)_T = \bar{V}$$

i.e.,

$$\int d\bar{G} = \int \bar{V} dp$$

We will here define a dimensionless variable, z, defined as

$$z \equiv \frac{p}{p_{std}} \tag{3.1}$$

so

$$\int d\bar{G} = \int \bar{V} p_{std} dz$$

$\bar{V} = \frac{nRT}{p}$ with $n = 1$, i.e., $\bar{V} = \frac{RT}{p} = \frac{RT p_{std}}{z}$. Then

$$\int d\bar{G} = \int \bar{V} p_{std} dz = \int \frac{RT}{z p_{std}}(p_{std} dz) = \int \frac{RT}{z} dz$$

It is customary to now employ indefinite integration to introduce two constants of integration, one on the left and the other on the right, i.e.,

$$\bar{G} + C_1 = RT\ell n z + C_2$$

Back-substituting, we have the traditional (possibly defective) form

$$\bar{G} + C_1 = RT\ell n \frac{p}{p_{std}} + C_2$$

where the traditional form can be achieved by declaring p_{std} to be 1 ("atm in the older literature, "bar in the newer texts), i.e.,

$$\bar{G} + C_1 = RT\ell n p + C_2$$

(The form of the equation $\bar{G} + C_1 = RT\ell n p + C_2$ i.e., the natural occurrence of the natural logarithm of p, is what motives the subsequent *definition/invention* of the fugacity as a "fudged" pressure. By employing the fugacity instead of the pressure, we can treat both ideal and non-ideal gases using the *same* functional form.)

For the ideal gas, one has that the constant of integration is fixed by a choice of standard state, i.e., $p = 1bar$,

so that

$$\bar{G}_{ideal}[T,p] + C_1 = RT\ell n p + C_2$$

(there is a unit problem here, with the natural logarithm of a pressure showing) where $C_2 = -RT\ell n 1$ and $C_1 \rightarrow -\bar{G}_{ideal}[T, p = 1] \equiv \bar{G}_{ideal}^o[T]$, so that one can write (using square brackets to indicate functionality)

$$\bar{G}_{ideal}[T,p] - \bar{G}_{ideal}^o[T] = RT\ell n \frac{p}{1}$$
$$\bar{G}_{ideal}[T,p] = \bar{G}_{ideal}^o[T] + RT\ell n \frac{p}{p^0} \qquad (3.2)$$

The first form is the form that would have been obtained had we done a definite integral between $p = 1bar$ and $p = pbars$. It is noteworthy that the letter "p" appears in these formulii several times with different meanings depending on where it is placed.

$$\int d\bar{G} = \int \frac{RT}{x} dx = RT \int d\ell n x = RT\ell n x +' a\ constant\ of\ integration' \qquad (3.3)$$

conforms better to the notation used in introductory calculus courses. This means that choosing the standard state to be that of an equivalent amount of an ideal gas at 1 bar leads to lots of not-so-fortuitous cancellations and simplifications.

IV. A FICTITIOUS HARD SPHERE KIND OF GAS [2]

Consider the non-ideal (wholly fictional) gas whose configurational partition function is

$$Z = \frac{(V - N\sigma)^N}{N!} \Lambda^{\frac{3N}{2}} \lambda^N$$

where Λ is the standard translational partition function, and λ is the internal atom/molecule partition function which includes electronic, vibrational, rotational, etc., energy terms. It is known that the Helmholtz Free Energy for this gas is

$$\frac{A}{kT} = -N\ell n(V - N\sigma) - \frac{3N}{2}\ell n\Lambda - N\ell n\lambda + \ell n N!$$

since $A = -kT\ell n Z$. The pressure of this gas (given by the expression $\left(\frac{\partial A}{\partial V}\right)_T = -p$) is

$$pV = NkT + Np\sigma$$

and the Gibbs Free Energy (which is given by G = A + pV) is

$$\frac{G}{kT} = -N\ell n \frac{NkT}{p} - \frac{3N}{2}\ell n\Lambda - N\ell n\lambda + N\ell n N + \frac{p}{kT}N\sigma$$

Therefore, the partial molar Free Energy, the chemical potential (per molecule), is

$$\frac{1}{kT}\left(\frac{\partial G}{\partial N}\right)_{T,p} = \frac{\mu}{kT} = -\ell n\left(\frac{kT}{p}\right) - \frac{3}{2}\ell n\Lambda - \ell n\lambda + \frac{p\sigma}{kT}$$

i.e.,

$$\mu = kT\ell n\left(\frac{p}{kT}\Lambda^{-\frac{3}{2}}\lambda^{-1}e^{+p\sigma/kT}\right)$$

and, multiplying appropriately by $N_{Avogadro}$, we obtain the "per mole" value

$$\bar{\mu} = RT\ell n\left(\frac{p}{kT}\Lambda^{-\frac{3}{2}}\lambda^{-1}e^{+p\Sigma/RT}\right)$$

As $p \rightarrow p_o$ we expect to pass to the "standard state", i.e.,

$$\bar{\mu}^o = \bar{\mu}(p \rightarrow p_o) = RT\ell n\left(\frac{p_o}{RT}\Lambda^{-\frac{3}{2}}\lambda^{-1}e^{+p_o\Sigma/RT}\right)$$

where Σ is $N_{Avogadro} \times \sigma$.

Rewriting, we have

$$\bar{\mu} - \bar{\mu}^o = RT\ell n\left(\frac{p}{RT}\Lambda^{-\frac{3}{2}}\lambda^{-1}e^{+p\Sigma/RT}\right) - RT\ell n\left(\frac{p_o}{RT}\Lambda^{-\frac{3}{2}}\lambda^{-1}e^{+p_o\Sigma/RT}\right) \qquad (4.1)$$

which we wish to write in something like the form:

$$\bar{\mu} = \bar{\mu}^o + RT\ell n f$$

Clearly, we have from Equation 4.1:

$$\bar{\mu} - \bar{\mu}^o = RT\ell n\left(\frac{p}{RT}e^{+p\Sigma/RT}\right) - RT\ell n\left(\frac{p_o}{RT}e^{+p_o\Sigma/RT}\right) = RT\ell n\left(\frac{p}{p_o}e^{+(p-p_o)\Sigma/RT}\right)$$

This suggests using (for real, i.e., non-ideal gases, in analogy with Equation 3.2)

$$\bar{G}_{real}[T,p] - \bar{G}^o_{real}[T] = RT\ell n\frac{f}{f^o} \qquad (4.2)$$

where f^o is the fugacity in the standard state (of the non-ideal gas).

We therefore seem to have a definition of the fugacity, i.e.,

$$f = \frac{p}{RT}\Lambda^{-\frac{3}{2}}\lambda^{-1}e^{+p\Sigma/RT}$$

and

$$f^o = \frac{p_o}{RT}\Lambda^{-\frac{3}{2}}\lambda^{-1}e^{+p_o\Sigma/RT}$$

so that

$$\bar{G}_{real}[T,p] - \bar{G}^o_{real}[T] = RT\ell n\frac{f}{f^o} = RT\ell n\left(\frac{p}{p_o}e^{+(p-p_o)\Sigma/RT}\right)$$
$$(4.3)$$

where p_o is the pressure at the standard state.

This would enable us to write, subtracting Equation 3.2 from Equation 4.2,

$$(\bar{G}_{real}[T,p] - \bar{G}^o_{real}[T, p = 1\ bar]) - (\bar{G}_{ideal}[T,p] - \bar{G}^o_{ideal}[T]) = RT\ell n\frac{f}{f^o} - RT\ell n\frac{p}{1}$$

If the standard state of the real (non-ideal) gas is <u>chosen</u> to be the standard state of an ideal gas at p_o=1 bar, (i.e., choosing $\bar{G}^o_{real}[T] = \bar{G}^o_{ideal}[T]$) one obtains

$$\bar{G}_{real}[T,p] - \bar{G}_{ideal}[T,p] - \left(\bar{G}^o_{real}[T] - \bar{G}^o_{ideal}[T]\right) = RT\ell n\frac{\frac{f}{p}}{\frac{f^o}{1}}$$

and since $\bar{G}_{ideal}[T,p] - \bar{G}^o_{ideal}[T] = 0$

$$\bar{G}_{real}[T,p] - \bar{G}_{ideal}[T,p] = RT\ell n\frac{f/p}{f^o/1} = RT\ell n\frac{f/f^o}{p/1}$$
$$(4.4)$$

Further

$$\lim_{p\to 0}\frac{f}{p} = 1$$

where the fugacity shares the same units as the pressure. As the pressure approaches zero, all gases become ideal, and therefore the fugacity approaches the pressure and their ratio approaches unity.

V.   CONVENTIONAL DETERMINATION OF FUGACITY

For a real gas

$$d\bar{G} = \bar{V}dp$$

and for an ideal gas

$$d\bar{G}_{ideal} = \bar{V}_{ideal}dp$$

the difference between the two can be integrated from some low pressure P_{lo} to the pressure desired (This is the standard argument based on Equation 4.4.) (as the Gibbs Free Energy of the non-ideal gas approaches that of the ideal gas at low pressure, and therefore their difference vanishes at this lower limit):

$$\int_{P_{lo}}^{P_{desired}} d(\bar{G} - \bar{G}_{ideal}) = \int d\left(RT\ell n\frac{f/f^o}{p/1}\right)$$

$$\int_{P_{lo}}^{P_{desired}} d(\bar{G} - \bar{G}_{ideal}) = \int_{P_{lo}}^{P_{desired}} (\bar{V} - \bar{V}_{ideal})dp$$

which is

$$(\bar{G} - \bar{G}_{ideal})\big|_{P_{lo}}^{P_{desired}} = \int_{P_{lo}}^{P_{desired}} (\bar{V} - \frac{RT}{p})dp$$

$$(\bar{G}[P_{desired}] - \bar{G}[P_{desired}]_{ideal}) - (\bar{G}[P_{lo}] - \bar{G}_{ideal}[P_{lo}]) = \int_{P_{lo}}^{P_{desired}} (\bar{V} - \frac{RT}{p})dp$$

so that, in the limit $P_{lo} \to 0$ we have

$$\lim_{p \to 0}(\bar{G}[P_{lo}] - \bar{G}_{ideal}[P_{lo}]) \to 0$$

and thus we finally obtain

$$(\bar{G}[P_{desired}] - \bar{G}_{ideal}[P_{desired}]) = \int_{0}^{P_{desired}} (\bar{V}[T, p_{desired}] - \frac{RT}{p})dp$$
$$(5.1)$$

where we are emphasizing the functional dependence of $\bar{V}$ on T and $p_{desired}$.

We re-write this equation as

$$(\bar{G}[T, P_{desired}] - \bar{G}_{ideal}[T, P_{desired}]) = \int_{0}^{P_{desired}} \left(\bar{V}[T, x] - \frac{RT}{x} \right) dx = RT\ell n \frac{f_{desired}}{p_{desired}} \qquad (5.2)$$

to emphasize that the p inside the integral is a dummy variable.

VI. THE VAN DER WAALS FUGACITY; DOING THE INTEGRATION EXPLICITLY

The van der Waals [1] in obtained by explicit integration and requires some attention to limits and other

aspects of calculus which are worthy of review in this context.

Since the integration by parts required here can be confusing, it is included here in some detail. We had (in Equation 5.2):

$$(\bar{G}[p_{desired}, T] - \bar{G}[p_{desired}, T]_{ideal}) = \int_{0}^{p_{desired}} \left(\bar{V}[x, T] - \frac{RT}{x} \right) dx$$

but now, we use the van der Waals equation of state

$$\left(p + \frac{a}{\bar{V}^2} \right)(\bar{V} - b) = RT$$

(admittedly, with p = x when we do the substitution,

so as to reduce the numbers of confusing pressures being discussed) which can not be solved for $\bar{V}$ in order to do the integration classically. Instead, we attempt integration by parts (knowing that we will eventually go to the limit $p_{lo} \to 0$), i.e.,

$$\int_{p_{lo}}^{p_{desired}} \left(\bar{V}[x, T] - \frac{RT}{x} \right) dx = x\bar{V}[x, T]\big|_{p_{lo}}^{p_{desired}} - \int_{\bar{V}[p_{lo}, T]}^{i\bar{V}[p_{desired}, T]} x d\bar{V} - \int_{p_{lo}}^{p_{desired}} \left(\frac{RT}{x} \right) dx$$

or, suppressing the functionality of $\bar{V}$,

$$(\bar{G}[p_{desired},T] - \bar{G}_{ideal}[p_{desired},T]) = \left(\frac{RT\bar{V}}{\bar{V}-b} - \frac{a\bar{V}}{\bar{V}^2}\right)\Bigg|_{p_{lo}}^{p_{desired}} - \int_{p_{lo}}^{p_{desired}}\left(\frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}\right)d\bar{V} - \int_{p_{lo}}^{p_{desired}}\left(\frac{RT}{x}\right)dx$$

or, again using p_{lo} rather than zero, and knowing that we will pass to the limit $p_{lo} \to 0$ later, we have

$$= \left(\frac{RT\bar{V}}{\bar{V}-b} - \frac{a\bar{V}}{\bar{V}^2}\right)\Bigg|_{p_{lo}}^{p_{desired}} - RT\;\ell n(\bar{V}-b)\Big|_{\bar{V}[p_{lo}]}^{\bar{V}[p_{desired}]} - \frac{a}{\bar{V}}\Big|_{\bar{V}[p_{lo}]}^{\bar{V}[p_{desired}]} - RT\;\ell nx\Big|_{p_{lo}}^{p_{desired}}$$

which is

$$= \frac{RT\bar{V}[p_{desired}]}{\bar{V}[p_{desired}]-b} - \frac{a}{\bar{V}[p_{desired}]} - \cancel{\frac{RT\bar{V}[p_{lo}]}{\bar{V}[p_{lo}]-b}}^{\;RT} + \cancel{\frac{a}{\bar{V}[p_{lo}]}}^{\;0}$$
$$-RT\ell n(\bar{V}[p_{desired}]-b) + RT\ell n(\bar{V}[p_{lo}]-b)$$
$$-\frac{a}{\bar{V}[p_{desired}]} + \cancel{\frac{a}{\bar{V}[p_{lo}]}}^{\;0}$$
$$-RT\ell np_{desired} + RT\ell np_{lo} \tag{6.1}$$

since $\bar{V}[p_{lo}] > b$, as $\bar{V}[p_{lo}] \to \infty$ i.e., $\bar{V}[p_{lo}] - b \to \bar{V}[p_{lo}]$, we have

and, passing to the limit $p_{lo} \to 0$, we have

$$\lim_{\bar{V}[p_{lo}]\to\infty} \frac{RT\bar{V}[p_{lo}]}{\bar{V}[p_{lo}]-b} = RT$$

and

$$\lim_{\bar{V}[p_{lo}]\to\infty} \frac{a}{\bar{V}[p_{lo}]} = 0$$

we have

$$\frac{RT\bar{V}[p_{desired}]}{\bar{V}[p_{desired}]-b} - \frac{2a}{\bar{V}[p_{desired}]} - RT$$
$$-RT\ell n\left(\frac{\bar{V}[p_{desired}]-b}{\bar{V}[p_{lo}]-b}\right)$$
$$-RT\ell n\left(\frac{p_{desired}}{p_{lo}}\right) \tag{6.2}$$

$$= \frac{RT\bar{V}[p_{desired}]}{\bar{V}[p_{desired}]-b} - \frac{2a}{\bar{V}[p_{desired}]} - RT - RT\ell n\left(\frac{(p_{desired}(\bar{V}[p_{desired}]-b))}{(p_{lo}(\bar{V}[p_{lo}]-b))}\right) \tag{6.3}$$

But

so

$$p\bar{V}-b)+\frac{a}{\bar{V}^2} = RT \to (p(\bar{V}-b) = RT - \frac{a(\bar{V}-b)}{\bar{V}^2}$$

$$= \frac{RT\bar{V}[p_{desired}]}{\bar{V}[p_{desired}]-b} - \frac{2a}{\bar{V}[p_{desired}]} - RT - RT\ell n\left(\frac{\left(RT - \frac{a(\bar{V}[p_{desired}]-b)}{\bar{V}[p_{desired}]^2}\right)}{\left(RT - \frac{a(\bar{V}[p_{lo}]-b)}{\bar{V}[p_{lo}]^2}\right)}\right) \tag{6.4}$$

dividing through by RT inside the logarithm, we have

$$= \frac{RT\bar{V}[p_{desired}]}{\bar{V}[p_{desired}] - b} - \frac{2a}{\bar{V}[p_{desired}]} - RT - RT\ell n\left(\frac{\left(1 - \frac{a(\bar{V}[p_{desired}] - b)}{RT\bar{V}[p_{desired}]^2}\right)}{\left(1 - \frac{a(\bar{V}[p_{lo}] - b)}{RT\bar{V}[p_{lo}]^2}\right)^0}\right) \tag{6.5}$$

or, in the limit $\bar{V}[p_{lo}, T] \to \infty$ we have

$$= \frac{RT\bar{V}[p_{desired}]}{\bar{V}[p_{desired}] - b} - \frac{2a}{\bar{V}[p_{desired}]} - RT - RT\ell n\left(1 - \frac{a(\bar{V}[p_{desired}] - b)}{RT\bar{V}[p_{desired}]^2}\right) \tag{6.6}$$

or,

$$= \frac{RT(\bar{V}[p_{desired}] - b + b)}{\bar{V}[p_{desired}] - b} - \frac{2a}{\bar{V}[p_{desired}]} - RT\frac{RT(\bar{V}[p_{desired}] - b)}{\bar{V}[p_{desired}] - b} - RT\ell n\left(1 - \frac{a(\bar{V}[p_{desired}] - b)}{RT\bar{V}[p_{desired}]^2}\right) \tag{6.7}$$

and multiplying RT by 1 (the third term disguised as $\frac{RT(\bar{V}[p_{desired}] - b)}{\bar{V}[p_{desired}] - b} = 1$)

$$= \frac{RT(\bar{V}[p_{desired}] - b + b)}{\bar{V}[p_{desired}] - b} - \frac{2a}{\bar{V}[p_{desired}]} - RT\frac{RT(\bar{V}[p_{desired}] - b)}{\bar{V}[p_{desired}] - b} - RT\ell n\left(1 - \frac{a(\bar{V}[p_{desired}] - b)}{RT\bar{V}[p_{desired}]^2}\right) \tag{6.8}$$

After some further algebraic manipulations, what finally emerges is the result quoted [5], i.e.,

$$RT\ell n\frac{f}{p_{desired}} = \frac{RTb}{\bar{V}[p_{desired}] - b} - \frac{2a}{\bar{V}[p_{desired}]} - RT\ell n\left(1 - \frac{a(\bar{V}[p_{desired}] - b)}{RT\bar{V}[p_{desired}]^2}\right) \tag{6.9}$$

A. Is there a reduced form for the van der Waals fugacity?

Assuming

$$p_c = \frac{a}{27b^2} \to a = 27b^2 p_c$$

and

$$v_c = 3b$$

(we have changed to lower case v for the molar volume) we obtain

$$RT\ell n\frac{f}{p_{desired}} = \frac{RT\frac{v_c}{3}}{v[p_{desired}] - \frac{v_c}{3}} - \frac{2(27b^2 p_c)}{v[p_{desired}]} - RT\ell n\left(1 - \frac{(27b^2 p_c)\left(v[p_{desired}] - \frac{v_c}{3}\right)}{RTv[p_{desired}]^2}\right) \tag{6.10}$$

which becomes, changing to reduced molar volumes (v_r is the new dependent variable)

$$RT\ell n\frac{f}{p_{desired}} = \frac{RT\frac{v_c}{3}}{v_r v_c - \frac{v_c}{3}} - \frac{2(27\left(\frac{v_c}{3}\right)^2 p_c)}{v_r v_c} - RT\ell n\left(1 - \frac{(27\left(\frac{v_c}{3}\right)^2 p_c)\left(v_r v_c - \frac{v_c}{3}\right)}{RT(v_r v_c)^2}\right) \tag{6.11}$$

or

$$RT\ell n\frac{f}{p_{desired}} = \frac{RT}{3(v_r - 1)} - \frac{6v_c p_c}{v_r} - RT\ell n\left(1 - \frac{v_c p_c(v_r - 1)}{RTv_r^2}\right) \tag{6.12}$$

The inelegance of these formulas is a powerful antidote to pursuing the issue further.

VII. CONCLUSIONS

The are no gases such as the two used here. The value of the discussion, in my mind, concerns pure pedagogy,

i.e., having concrete examples to deal with, so that when one is dealing with real data, and doing the integrations numerically, one can check the algorithm for numerical integration against these known values. And then again, perhaps there is no value at all.

VIII. REFERENCES

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