

## Section A. Nomenclature Topics

### Part I. Thermodynamic Processes, Real and Ideal Gases

#### Chapter 4. Approaches for a Real Gas Dependencies Derivation

### LECTURE 5. DEPENDENCIES IN A REAL GAS

#### § 1.6. The equation of state for a real gas

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Thus, the properties of real gases in both quantitative and qualitative respects significantly differ from the properties of the ideal gasses [113, pp. 15-20]. Therefore, all results for ideal gases will be approximate and fare just at the very great rarefactions. Accordingly to that there appeared (came out, emerged) a necessity in developing the equation of state, which would precisely describe the state of a real gas. The one of such equations were obtained by the Russian scientist **N. N. Bogolubov** and American physicist **GJG. Mayer** in 1937-1946 [110, p. 163, (6-67)], [113, p. 16]

$$pv = RT \left[ 1 - \sum_{i=1}^{\infty} \frac{i}{i+1} \cdot \frac{B_i}{v^i} \right],$$

where  $B_i$  – virial coefficients, expressed through the potential energy of interaction of the given gas and its temperature.

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**Julius Robert von Mayer** (November 25, 1814 – March 20, 1878) was a German [physician](#) and [physicist](#) and one of the founders of [thermodynamics](#). He is best known for enunciating in 1841 one of the original statements of the [conservation of energy](#) or what is now known as one of the first versions of the [first law of thermodynamics](#), namely:<sup>[1][2]</sup>

**“Energy can be neither created nor destroyed”**

In 1842, Mayer described the vital [chemical process](#) now referred to as [oxidation](#) as the primary source of [energy](#) for any [living creature](#). His achievements were overlooked and priority for the discovery of the [mechanical equivalent of heat](#) was attributed to [James Joule](#) in the following year. He also proposed that plants convert light into chemical energy.

**Никола́й Никола́евич Боголю́бов** ([8 \(21\) августа 1909](#), [Нижний Новгород](#) – [13 февраля 1992](#), [Москва](#)) – выдающийся советский математик и физик-теоретик, академик [РАН \(1991\)](#), академик [АН СССР \(1953\)](#) и [АН УССР \(1948\)](#), основатель научных школ по нелинейной механике и [теоретической физике](#), с [1956 года](#) – директор лаборатории теоретической физики [Объединённого института ядерных исследований \(ОИЯИ\)](#) в [Дубне](#), с [1965](#) по [1988 год](#) – директор ОИЯИ.

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Because of the difficulties of determining the virial coefficients, usually one restricts oneself with the calculation of the first two of them. In this case the equation for the calculation has the view of [113, p. 16]

$$pv = RT \left( 1 - \frac{A}{v} - \frac{B}{v^2} \right),$$

where  $A$  and  $B$  – the first and second virial coefficients, being functions of the temperature only.

The equation by **Johannes Diderik van der Waals** is the one that the most simply and qualitatively true describes the change of state of a real gas. It is the particular (partial) case of the general equation of state by **Mayer-Bogolubov**, if one

can neglect all members containing  $\frac{1}{v}$  raised to the second power and higher in the right part. The equation by **Johannes Diderik van der Waals** was found (obtained) in 1873 and has the view of [110, P. 153, (6-36)], [113, P. 16]

$$RT = \left( p + \frac{a}{v^2} \right) (v - b), \quad (6-36)$$

where  $b$  – the smallest volume, down to which a real gas can compressed. For each of gases the value of  $b$  has a certain numerical magnitude;  $a$  – coefficient of proportionality, having a certain numerical magnitude for each separate gas independently upon the parameters of state (state variables).

**Johannes Diderik van der Waals** (November 23, 1837 – March 8, 1923) was a Dutch [theoretical physicist](#) and [thermodynamicist](#) famous for his work on an [equation of state](#) for gases and liquids.

His name is primarily associated with the [van der Waals equation of state](#) that describes the behavior of gases and their condensation to the liquid [phase](#). His name is also associated with [van der Waals forces](#) (forces between stable [molecules](#)), with [van der Waals molecules](#) (small molecular clusters bound by van der Waals forces), and with [van der Waals radii](#) (sizes of molecules).

He became the first [physics](#) professor of the [University of Amsterdam](#) when it opened in 1877 and won the 1910 Nobel Prize in physics.

Most textbooks give two different [derivations](#) [[http://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation](http://en.wikipedia.org/wiki/Van_der_Waals_equation)]. One is the conventional derivation that goes back to van der Waals and the other is a statistical mechanics derivation. The latter has the major advantage that it makes explicit the intermolecular potential, which is neglected in the first derivation. The conventional van der Waals equation is a mechanical equation of state, which cannot be used to specify all thermodynamic functions, while the statistical mechanical derivation yields the partition function for the system, which does allow all thermodynamic functions to be specified, including the mechanical equation of state [[http://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation](http://en.wikipedia.org/wiki/Van_der_Waals_equation)].

The **excluded volume per particle** (of average diameter  $d$  or radius  $r$ ) is [121, pp. 152-156] equal to the volume of the sphere of the radius  $d$

$$V_{sf} = \int_{-d}^d S dx,$$

where  $S$  – the area of the circle in the intersection of the sphere with the plane perpendicular to the axis of  $Ox$  at the distance of  $x$  from its center of  $O$  (fig. ).

$$S = \pi r_c^2,$$

where  $r_c$  – the radius of the circle.

$$r_c^2 = d^2 - x^2, \quad r_c = \sqrt{d^2 - x^2} = r_c(x).$$

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(fig. )

Then,

$$S = \pi(d^2 - x^2) = S(x), \quad V_{sf} = \int_{-d}^d \pi(d^2 - x^2) dx.$$

$$\begin{aligned} V_{sf} &= \pi \int_{-d}^d (d^2 - x^2) dx = \pi \left[ d^2 x - \frac{x^3}{3} \right]_{-d}^d = \pi \left[ d^3 + d^3 - \left( \frac{d^3}{3} + \frac{d^3}{3} \right) \right] = \\ &= \pi \left[ 2d^3 - 2 \frac{d^3}{3} \right] = 2\pi d^3 \left[ 1 - \frac{1}{3} \right] = 2\pi d^3 \frac{2}{3} = \frac{4}{3} \pi d^3. \end{aligned}$$

The volume of the particle

$$V_p = \frac{4}{3} \pi \left( \frac{d}{2} \right)^3 = \frac{1}{6} \pi d^3.$$

$$\frac{V_{sf}}{V_p} = \frac{\frac{4}{3} \pi d^3}{\frac{1}{6} \pi d^3} = \frac{4}{3} \cdot \frac{6}{1} = 8.$$

Since, that just two of particles collide (have a collision); because accordingly to the special calculations of the theory of probabilities the collisions of three, four and more molecules may happen (occur, take place, arise) fairly seldom (rather

(quite, relatively, somewhat, to a certain extent) rare); for all molecules, consisting the compound (composition, complex) of the considered volume, the **excluded volume**

$$b = 4V_s,$$

where  $V_s$  – the volume of all  $N$  molecules of themselves; which was divided by 2 to prevent overcounting [[http://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation](http://en.wikipedia.org/wiki/Van_der_Waals_equation)]. So  $b$  is four times the proper volume of all the particles. It was a point of concern to van der Waals that the factor four yields actually an upper bound, empirical values for  $b$  are usually lower. Of course, molecules are not infinitely hard, as van der Waals thought, but are often fairly soft [[http://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation](http://en.wikipedia.org/wiki/Van_der_Waals_equation)].

Thus, taking dimensions of molecules into a consideration in the equation of state for a real gas means making allowance for the forces of pushing. Therefore, the real volume for possible motion shrinks

$$RT = p(v - b).$$

Next, we introduce a pairwise attractive force between the particles [[http://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation](http://en.wikipedia.org/wiki/Van_der_Waals_equation)]. Van der Waals assumed that, notwithstanding the existence of this force, the density of the fluid is homogeneous. Further he assumed that the range of the attractive force is so small that the great majority of the particles do not feel that the container is of finite size. That is, the bulk of them have more attracting particles to their right than to their left when they are relatively close to the left-hand wall of the container. The same statement holds with left and right interchanged. Given the homogeneity of the fluid, the bulk of the particles do not experience a net force pulling them to the right or to the left. This is different for the particles in **surface layers directly adjacent to the walls**. They feel a net force from the bulk particles pulling them into the container, because this force is not compensated by particles on the side where the wall is (another assumption here is that there is no interaction between walls and particles, which is not true as can be seen from the phenomenon of droplet formation; most types of liquid show adhesion). This net force decreases the force exerted onto the wall by the particles in the surface layer. The net force on a surface particle, pulling it

into the container, is proportional to the number density  
[\[http://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation\]](http://en.wikipedia.org/wiki/Van_der_Waals_equation)

$$n = \frac{N}{v}.$$

Thus, inside the volume occupied by the particles of a real gas, in addition to regular pressure there is also a pressure, stipulated (conditioned, predetermined, set) by the forces of intermolecular interaction. This pressure is called the **inside (inner) pressure**. The **total pressure inside gas** is the sum of the **walls pressure** and inside pressure  $p'$  [121, p. 154].

Having considered the **sphere of molecular action**, picking up (choosing) two layers 1 and 2 adjacent directly to the wall, the thickness of each is equal to the radius of the sphere of molecular action, we get the expression of the inside pressure proportional to the concentrations  $n_1$  and  $n_2$  in the layers 1 and 2 correspondingly

$$p' \sim n_1 n_2.$$

The layers 1 and 2 are rather thin – the magnitude of their value is of the  $10^{-7}$  cm order. Therefore with the great degree of accuracy

$$n_1 = n_2 = n.$$

$$p' \sim n^2.$$

Hence,

$$p' \sim \frac{N}{v^2} \text{ or } p' = \frac{a}{v^2},$$

where  $a$  – coefficient, includes all constants and the constant of proportionality amongst them [121, p. 155].

Therefore [113, p. 16], [110, p. 153, (6-36)]

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT. \quad (6-36)$$

It is of some historical interest to point out that van der Waals in his Nobel Prize lecture gave credit to **Pierre-Simon Laplace** [\[Laplace\]](http://en.wikipedia.org/wiki/Pierre-Simon_Laplace) for the argument that pressure is reduced proportional to the square of the density [\[http://en.wikipedia.org/wiki/Van\\_der\\_Waals\\_equation\]](http://en.wikipedia.org/wiki/Van_der_Waals_equation). Considering after the

dependence of the proportionality of the net force upon the number density, one might find that the number of particles in the surface layers is, again by assuming homogeneity, also proportional to the density. In total, the force on the walls is decreased by a factor proportional to the square of the density, and the pressure (force per unit surface) is decreased by the corresponding member.

**Pierre-Simon, marquis de Laplace** [<http://en.wikipedia.org/wiki/Laplace>] (pronounced: [\[lə'plɑ:s\]](#); 23 March 1749 – 5 March 1827) was a French [mathematician](#) and [astronomer](#) whose work was pivotal to the development of mathematical [astronomy](#) and [statistics](#). He summarized and extended the work of his predecessors in his five volume *Mécanique Céleste* ([Celestial Mechanics](#)) (1799–1825). This work translated the geometric study of [classical mechanics](#) to one based on [calculus](#), opening up a broader range of problems. In statistics, the so-called [Bayesian interpretation](#) of probability was mainly developed by Laplace.<sup>[1]</sup>

He formulated [Laplace's equation](#), and pioneered the [Laplace transform](#) which appears in many branches of [mathematical physics](#), a field that he took a leading role in forming. The [Laplacian differential operator](#), widely used in mathematics, is also named after him.

He restated and developed the [nebular hypothesis](#) of the [origin of the solar system](#) and was one of the first scientists to postulate the existence of [black holes](#) and the notion of [gravitational collapse](#).

He is remembered as one of the greatest scientists of all time, sometimes referred to as a *French [Newton](#)* or *Newton of France*, with a phenomenal natural mathematical faculty superior to any of his contemporaries.<sup>[2]</sup>

He became a count of the [First French Empire](#) in 1806 and was named a [marquis](#) in 1817, after the [Bourbon Restoration](#).

The equation by van der Waals qualitatively true reflects the states of real substances in the liquid and gaseous form (aggregate state). For two-phase states it is inapplicable (unsuitable, unusable, useless, inappropriate). For one mole of a gas the equation by van der Waals is written in the view of [113, p. 17]

$$8.314T = \left( p + \frac{a_{\mu}}{v_{\mu}^2} \right) (v_{\mu} - b_{\mu}).$$

If in the equation by van der Waals it is to open parentheses (brackets) and arrange the obtained members in the order of decreasing the power of  $v$

$$v^2 RT = (pv^2 + a)(v - b) = pv^3 + av - pbv^2 - ab = pv^3 - pbv^2 + av - ab,$$

then we get the equation of the third power with respect to the specific volume of gas

$$pv^3 - pbv^2 + av - ab - v^2 RT = pv^3 - (pb + RT)v^2 + av - ab = 0.$$

It is known from mathematics that such an equation at some given values of  $p$  and  $T$  should have three roots. At this there can be the next three cases:

1. All of the three roots are different and real;
2. All of the three roots are real and equal to each other;
3. One of the roots is real and the two are imaginary (complex).

In the last case it is only the one real root has the real meaning because imaginary roots do not have any physical sense [113, P. 17].

The isotherms that correspond to the equation by van der Waals are shown on the  $pv$ -diagram (fig. 2.3). The curves on fig. 2.3 are plotted for nitrogen gas with the parameters of [110, p. 152, T. 6-8]

$$RN2 = 296.727$$

$$TkN2 := -147 + 273.15$$

$$TkN2 = 126.15$$

$$pkN2 := 3.39 \cdot 10^6$$

[110, p. 155, (6-43), (6-47)]

$$aN2 := \frac{27}{64} \cdot \frac{RN2^2 \cdot TkN2^2}{pkN2}$$

$$aN2 = 174.371$$

[110, p. 155, (6-43)]

$$bN2 := \frac{vkN2}{3}$$

[110, p. 155, (6-44)]

$$\left( pkN2 + \frac{a}{vk^2} \right) \left( vk - \frac{vk}{3} \right) = RN2 \cdot TkN2 \text{ solve, vk} \rightarrow \left[ \begin{array}{l} \frac{1}{4 \cdot pkN2} \cdot \left[ 3 \cdot RN2 \cdot TkN2 + \left( 9 \cdot RN2^2 \cdot TkN2^2 - 16 \cdot pkN2 \cdot a \right)^{\frac{1}{2}} \right] \\ \frac{1}{4 \cdot pkN2} \cdot \left[ 3 \cdot RN2 \cdot TkN2 - \left( 9 \cdot RN2^2 \cdot TkN2^2 - 16 \cdot pkN2 \cdot a \right)^{\frac{1}{2}} \right] \end{array} \right]$$



$$\left( \text{pkN2} + \frac{\text{aN2}}{\text{vk}^2} \right) \left( \text{vk} - \frac{\text{vk}}{3} \right) = \text{RN2} \cdot \text{TkN2} \text{ solve, vk} \rightarrow \left( \begin{array}{l} 4.140724960205415853510^{-3} \\ 1.242217488061624756010^{-2} \end{array} \right)$$

$$\text{vkN2} := \frac{1}{4 \cdot \text{pkN2}} \cdot \left[ 3 \cdot \text{RN2} \cdot \text{TkN2} - \left( 9 \cdot \text{RN2}^2 \cdot \text{TkN2}^2 - 16 \cdot \text{pkN2} \cdot \text{aN2} \right)^{\frac{1}{2}} \right]$$

$$\text{vkN2} = 4.14072496 \times 10^{-3}$$

$$\text{pkN2} := \frac{1}{27} \cdot \frac{\text{aN2}}{\left( \frac{\text{vkN2}}{3} \right)^2}$$

$$\text{pkN2} = 3.39 \times 10^6$$

$$\text{bN2} := \frac{\text{vkN2}}{3}$$

$$\text{bN2} = 1.38 \times 10^{-3}$$

[110, p. 155, (6-44)]

$$\text{pkN2} := \frac{1}{27} \cdot \frac{\text{aN2}}{(\text{bN2})^2}$$

$$\text{pkN2} = 3.39 \times 10^6$$

[110, p. 155, (6-45)]

$$\text{TkN2} := \frac{8 \cdot \text{aN2}}{27 \cdot \text{bN2} \cdot \text{RN2}}$$

$$\text{TkN2} = 126.15$$

[110, p. 156, (6-46)]

$$\text{vkN2} := 3 \cdot \text{bN2}$$

$$\text{vkN2} = 4.141 \times 10^{-3}$$

[110, p. 156, (6-46)]

$$\text{TN2} := \left( \begin{array}{l} 100 \\ 105 \\ 110 \\ 115 \\ 120 \\ \text{TkN2} \\ 130 \\ 135 \\ 140 \end{array} \right)$$

$$p_{N2T120}(v) := \frac{RN2 \cdot TN2_4 \cdot v^2 + a_{N2} \cdot b_{N2} - a_{N2} \cdot v}{v^3 - b_{N2} \cdot v^2}$$

$$p_{N2Tk}(v) := \frac{RN2 \cdot TN2_5 \cdot v^2 + a_{N2} \cdot b_{N2} - a_{N2} \cdot v}{v^3 - b_{N2} \cdot v^2}$$

[Chapter\_2.mcd]

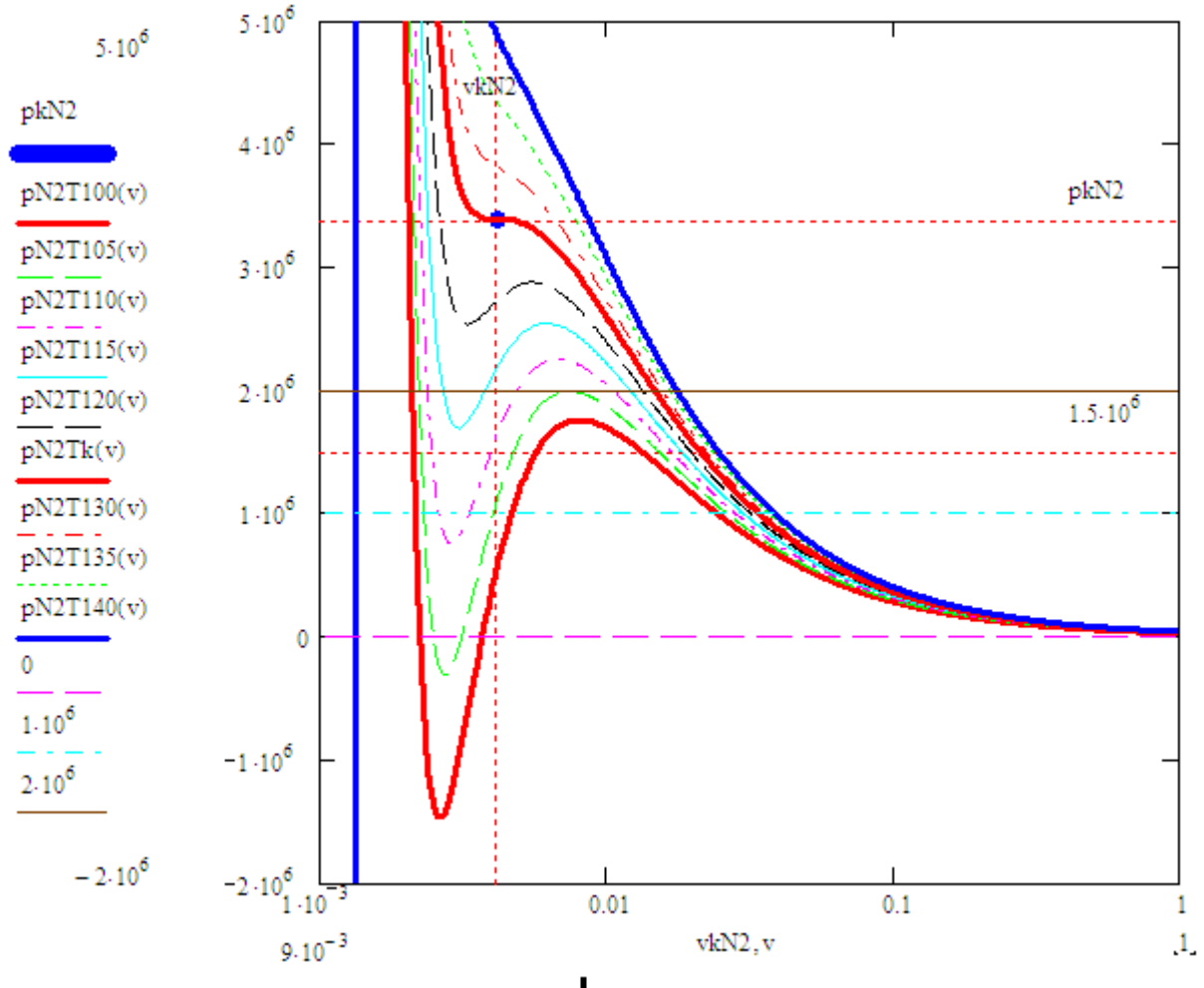


Fig. 2.3

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The constants of  $a$  and  $b$  for the equation by **Johannes Diderik van der Waals** are calculated with the help of the equations of [110, p. 152, (6-34), (6-35)]

$$\left(\frac{\partial p}{\partial v}\right)_T^{cr} = 0; \tag{6-34}$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T^{cr} = 0; \quad (6-35)$$

since in **the critical state**  $K$  (see fig. 2.3), as experiments show that (as that known from (shown by) experiments), the critical isotherm of

$$T_{cr} = \text{const}$$

has the horizontal tangent line and the over-bending (bend, bend-over) point.

The famous English physicist **T. Andrews** in his experiments with the carbon-dioxide gas concerned about the relations between  $p$ ,  $v$ , and  $T$ , in 1857-1869, established (discovered, revealed) that the higher the temperature, at which the dependence of  $v$  upon  $p$  is measured, the less difference is between the specific volumes of the gaseous and liquid phases [110, pp. 150-151, fig. 6-10, 6-11, (6-32), (6-33)].

Further, it was discovered **the critical state**  $K$ , where gases undergo unstable conditions state; as for the mutually reversible “liquid-gas” and “gas-liquid” transitions (transformations, conversions, transfers) requiring both isothermal and isobaric circumstances (situations); with the horizontal isobaric-isothermal partition degrading into the point.

Let us find the constants of  $a$ ,  $b$  and with the help of them **the critical parameters of state**. Expressing the pressure of  $p$  in the view of the real function of  $v$  from the equation by **Johannes Diderik van der Waals** we have

$$(pv^2 + a)(v - b) = RTv^2 = pv^3 - pbv^2 + av - ab = p(v^3 - bv^2) + av - ab,$$

$$p(v) = \frac{RTv^2 - av + ab}{v^3 - bv^2}.$$

The first derivative of  $p(v)$  with respect to  $v$  at  $T = \text{const}$  will be equal to zero at the point of  $K$  (see fig. 2.3) upon the critical isotherm. Thus,

$$\left(\frac{\partial p}{\partial v}\right)_T^{cr} = \left\{ \frac{\partial}{\partial v} [p(v)] \right\}_T^{cr} = 0,$$

$$\left(\frac{\partial p}{\partial v}\right)_T^{cr} = \left[ \frac{\partial}{\partial v} \left( \frac{RTv^2 - av + ab}{v^3 - bv^2} \right) \right]_T^{cr} = 0,$$

$$\left(\frac{\partial p}{\partial v}\right)_T^{cr} = \frac{(2RTv - a)(v^3 - bv^2) - (RTv^2 - av + ab)(3v^2 - 2bv)}{(v^3 - bv^2)^2} = 0,$$

$$\left(\frac{\partial p}{\partial v}\right)_T^{cr} = \frac{2RTv^4 - av^3 - 2bRTv^3 + abv^2}{(v^3 - bv^2)^2} + \frac{-3RTv^4 + 2bRTv^3 + 3av^3 - 2abv^2 - 3abv^2 + 2ab^2v}{(v^3 - bv^2)^2} = 0,$$

$$\left(\frac{\partial p}{\partial v}\right)_T^{cr} = \frac{-RTv^4 + 2av^3 - 4abv^2 + 2ab^2v}{(v^3 - bv^2)^2} = 0. \quad (6-34a)$$

Therefore

$$-RTv^4 + 2av^3 - 4abv^2 + 2ab^2v = 0.$$

Canceling for  $v \neq 0$ , we will get

$$-RTv^3 + 2av^2 - 4abv + 2ab^2 = 0. \quad (6-34b)$$

The second derivative of  $p(v)$  with respect to  $v$  at  $T = \text{const}$  will also be equal to zero at the point of  $K$  (see fig. 2.3) upon the critical isotherm. Thus, applying the (6-34a)

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T^{cr} = \left[\frac{\partial}{\partial v}\left(\frac{\partial p}{\partial v}\right)\right]_T^{cr} = \left[\frac{\partial}{\partial v}\left(\frac{-RTv^4 + 2av^3 - 4abv^2 + 2ab^2v}{(v^3 - bv^2)^2}\right)\right]_T^{cr} = 0,$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T^{cr} = \frac{(-4RTv^3 + 6av^2 - 8abv + 2ab^2)(v^3 - bv^2)^2}{[(v^3 - bv^2)^2]^2} - \frac{2(-RTv^4 + 2av^3 - 4abv^2 + 2ab^2v)(v^3 - bv^2)(3v^2 - 2bv)}{[(v^3 - bv^2)^2]^2} = 0,$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T^{cr} = \frac{(-4RTv^3 + 6av^2 - 8abv + 2ab^2)(v^3 - bv^2)}{(v^3 - bv^2)^3} - \frac{2(-RTv^4 + 2av^3 - 4abv^2 + 2ab^2v)(3v^2 - 2bv)}{(v^3 - bv^2)^3} = 0,$$

$$\begin{aligned}
\left(\frac{\partial^2 p}{\partial v^2}\right)_T^{cr} &= \frac{-4RTv^6 + 4bRTv^5 + 6av^5 - 6abv^4}{(v^3 - bv^2)^3} + \\
&+ \frac{-8abv^4 + 8ab^2v^3 + 2ab^2v^3 - 2ab^3v^2}{(v^3 - bv^2)^3} - \\
&- \frac{-6RTv^6 + 4bRTv^5 + 12av^5 - 8abv^4}{(v^3 - bv^2)^3} - \\
&- \frac{-24abv^4 + 16ab^2v^3 + 12ab^2v^3 - 8ab^3v^2}{(v^3 - bv^2)^3} = 0, \\
\left(\frac{\partial^2 p}{\partial v^2}\right)_T^{cr} &= \frac{2RTv^6 - 6av^5 + 18abv^4 - 18ab^2v^3 + 6ab^3v^2}{(v^3 - bv^2)^3} = 0. \tag{6-35a}
\end{aligned}$$

Therefore

$$2RTv^6 - 6av^5 + 18abv^4 - 18ab^2v^3 + 6ab^3v^2 = 0.$$

Or, canceling for  $2v^2 \neq 0$ , we will get

$$RTv^4 - 3av^3 + 9abv^2 - 9ab^2v + 3ab^3 = 0. \tag{6-35b}$$

Now, in order to get the desired constants of  $a$  and  $b$ , we have the system of two equations obtained, that is of the (6-34b) and (6-35b), with the two unknown values

$$\left. \begin{aligned}
-RTv^3 + 2av^2 - 4abv + 2ab^2 &= 0, \\
RTv^4 - 3av^3 + 9abv^2 - 9ab^2v + 3ab^3 &= 0.
\end{aligned} \right\} \tag{a}$$

Then, from the first equation of the system (a), i.e., from the (6-34b), for  $a$ , we get the expression of

$$a = \frac{RTv^3}{2(v^2 - 2bv + b^2)}. \tag{b}$$

Substituting this relation of (b) for the  $a$  into the second equation of the system of (a), i.e., into the formula of (6-35b), we will find

$$RTv^4 - 3\left(\frac{RTv^3}{2(v^2 - 2bv + b^2)}\right)v^3 + 9\left(\frac{RTv^3}{2(v^2 - 2bv + b^2)}\right)bv^2 -$$

$$-9\left(\frac{RTv^3}{2(v^2 - 2bv + b^2)}\right)b^2v + 3\left(\frac{RTv^3}{2(v^2 - 2bv + b^2)}\right)b^3 = 0. \quad (c)$$

Transforming the expression of (c), in the way of cancelling it for  $RTv^3 \neq 0$ , we will obtain

$$v - \frac{3v^3}{2(v^2 - 2bv + b^2)} + \frac{9bv^2}{2(v^2 - 2bv + b^2)} - \frac{9b^2v}{2(v^2 - 2bv + b^2)} + \frac{3b^3}{2(v^2 - 2bv + b^2)} = 0.$$

Then, rearranging this formula, by reducing all its fractions to the common denominator of

$$2(v^2 - 2bv + b^2),$$

we have the relation of

$$\frac{2v(v^2 - 2bv + b^2) - 3v^3 + 9bv^2 - 9b^2v + 3b^3}{2(v^2 - 2bv + b^2)} = 0.$$

Therefore

$$\begin{aligned} 2v(v^2 - 2bv + b^2) - 3v^3 + 9bv^2 - 9b^2v + 3b^3 &= 0, \\ 2v^3 - 4bv^2 + 2b^2v - 3v^3 + 9bv^2 - 9b^2v + 3b^3 &= 0, \\ -v^3 + 5bv^2 - 7b^2v + 3b^3 &= 0. \end{aligned} \quad (d)$$

From here, foreseeing (envisaging, predicting) the existence of the linear multiplier [Бронштейн И. Н., Семендяев К. А. Справочник по математике для инженеров и учащихся втузов. М.: «Наука». Главная редакция физико-математической литературы, 1981. – 720 с., p. 169] in the view of

$$v - 3b,$$

in fact, relishing the prospect of having a binomial multiplier at the rest of the division, we can have

$$\begin{aligned} \frac{v^3 - 5bv^2 + 7b^2v - 3b^3}{v - 3b} &= v^2 + \frac{-2bv^2 + 7b^2v - 3b^3}{v - 3b} = \\ &= v^2 - 2bv + \frac{b^2v - 3b^3}{v - 3b} = v^2 - 2bv + b^2. \end{aligned}$$

Thus, we have succeeded (that happened as expected) to split the equation of (d) into the multipliers of

$$v - 3b \quad \text{and} \quad v^2 - 2bv + b^2 = (v - b)^2.$$

Which means

$$v^3 - 5bv^2 + 7b^2v - 3b^3 = (v - 3b)(v^2 - 2bv + b^2) = (v - 3b)(v - b)^2 = 0.$$

Then, the roots of the equation of (d) are

$$v_1 = 3b, \quad v_{2,3} = b.$$

Thus, [110, p. 156, (6-47)]

$$v_{cr} = 3b, \tag{6-47}$$

since  $v$  cannot equal  $b$ , or, which is the same

$$v - b \neq 0.$$

From where [110, p. 155, (6-44)]

$$b = \frac{v_{cr}}{3}. \tag{6-44}$$

Then, from the relation of (b) we might find the constant of  $a$  as the function of the critical volume  $v_{cr}$  and the temperature  $T_{cr}$  substituting for  $b$  its expression of (6-44) into the equation of (b)

$$a = \frac{RT_{cr}v_{cr}^3}{2\left[v_{cr}^2 - 2\left(\frac{v_{cr}}{3}\right)v_{cr} + \left(\frac{v_{cr}}{3}\right)^2\right]} = \frac{RT_{cr}v_{cr}^3}{2\left(v_{cr}^2 - \frac{2v_{cr}^2}{3} + \frac{v_{cr}^2}{9}\right)}. \tag{b1}$$

Having cancelled the  $v_{cr}^2 \neq 0$ , we are getting

$$a = \frac{RT_{cr}v_{cr}}{2 - \frac{4}{3} + \frac{2}{9}} = \frac{RT_{cr}v_{cr}}{\frac{18 - 12 + 2}{9}} = \frac{9}{8}RT_{cr}v_{cr}. \tag{b2}$$

On the other hand substituting (6-47) for  $v_{cr}$  into (b) gives

$$a = \frac{RT_{cr}(3b)^3}{2\left[(3b)^2 - 2b(3b) + b^2\right]} = \frac{RT_{cr}27b^3}{18b^2 - 12b^2 + 2b^2}. \tag{b3}$$

Having cancelled the  $b^2 \neq 0$ , we are getting

$$a = \frac{RT_{cr}27b}{18 - 12 + 2} = \frac{27}{8}RT_{cr}b. \tag{b4}$$

Both equations (b2) and (b4) yield the same result since of (6-44)

$$a = \frac{27}{8} RT_{cr} \frac{v_{cr}}{3} = \frac{9}{8} RT_{cr} v_{cr}. \quad (b5)$$

The other interest is to obtain the constant of  $a$  as the function of  $T_{cr}$  and  $p_{cr}$ . For that reason we use the equation by van der Waals to tie (attach, connect) the constant of  $a$  and the critical pressure of  $p_{cr}$ . Namely, let us substitute (6-44) for the constant of  $b$  into (6-36)

$$\left( p_{cr} + \frac{a}{v_{cr}^2} \right) \left( v_{cr} - \frac{v_{cr}}{3} \right) = RT_{cr}.$$

From where we will find

$$\left( \frac{p_{cr} v_{cr}^2 + a}{v_{cr}^2} \right) \left( \frac{3v_{cr} - v_{cr}}{3} \right) = RT_{cr},$$

$$2v_{cr} (p_{cr} v_{cr}^2 + a) = 3RT_{cr} v_{cr}^2,$$

$$2p_{cr} v_{cr}^3 + 2a v_{cr} = 3RT_{cr} v_{cr}^2.$$

Let us cancel the  $v_{cr} \neq 0$

$$2p_{cr} v_{cr}^2 + 2a = 3RT_{cr} v_{cr}.$$

Thus, we have got

$$a = \frac{3}{2} RT_{cr} v_{cr} - p_{cr} v_{cr}^2. \quad (b6)$$

From the equation of (b2) or (b5)

$$v_{cr} = \frac{8}{9} \frac{a}{RT_{cr}}. \quad (b7)$$

Let us substitute it for  $v_{cr}$  into the expression of (b6)

$$a = \frac{3}{2} RT_{cr} \left( \frac{8}{9} \frac{a}{RT_{cr}} \right) - p_{cr} \left( \frac{8}{9} \frac{a}{RT_{cr}} \right)^2. \quad (b8)$$

Having simplified the relation of (b8) by having cancelled the  $RT_{cr}$  and  $a \neq 0$

$$1 = \frac{3}{2} \left( \frac{8}{9} \right) - p_{cr} \left( \frac{8}{9} \right)^2 \frac{a}{(RT_{cr})^2},$$



$$p_{cr} \left( \frac{8}{9} \right)^2 \frac{a}{(RT_{cr})^2} = \frac{24-18}{18} = \frac{1}{3}, \quad (b9)$$

we gain (obtain, get) [110, p. 155, (6-43)]

$$a = \frac{27 R^2 T_{cr}^2}{64 p_{cr}}. \quad (6-43)$$

Critical pressure and temperature through the constants of  $a$  and  $b$  then can be expressed in the following (next) way. From (b9) or (6-43)

$$p_{cr} = \frac{27 R^2 T_{cr}^2}{64 a}.$$

From the equation of (b4) it is easily to have [110, p. 156, (6-46)]

$$T_{cr} = \frac{8}{27} \frac{a}{Rb}. \quad (6-46)$$

Substituting it for  $T_{cr}$  into the previous (preceding) formula we find

$$p_{cr} = \frac{27 R^2}{64 a} \left( \frac{8}{27} \frac{a}{Rb} \right)^2,$$

then transforming (rearranging) it, we finally get [110, p. 155, (6-45)]

$$p_{cr} = \frac{1}{27} \frac{a}{b^2}. \quad (6-45)$$

The position of a specific (concrete, real, existing, actual, material, physical) partition (part) isothermal-isobaric line in between the monotonous branches of the wavy curves is found on the condition of the so called **Maxwell's rule** [110, pp. 154-155, fig. 6-15, (6-40)-(6-42)], the sense of which is next. If one can consider that a particular isotherm yields the same integral as the corresponding isobar does for the same part of the wavy curve (curly line), then it is acceptable to believe them (isotherm and isobar) forming a reversible cycle with the two isotherms; one of them is wavy and the other is isobaric, and both of them yield the same square (area) under their lines.

The isobar  $AB$ , intersecting the isotherm, gives the three real values of volume in the point of  $A$ ,  $R$ , and  $B$  (at the three different real roots) [113, p. 17].

The biggest root, which is equaled to the specific volume at the point of  $B$ , relate (pertain) to the vapor (gaseous) state of the substance, and the least one (at the point of  $A$ ) – to the liquid state.

\* \* \* \* \*

At some certain temperature, which is called the **critical temperature**, the isotherm does not have the wavy part [113, p. 18]. There is only the point of bend (twist), the touching line to which should be horizontal. This corresponds the second case of the equation by van der Waals solution mentioned above when all of the three roots are real and equal to each other (the point of  $K$  on the fig. 2.3, 2.3. a)).

At temperatures higher than critical, isotherms will have a monotonous character. Here, there will be just one real root. If we connect the points of  $A$ ,  $A_1$ ,  $A_2$  and so on, then we will get the curve where the liquid is at the state of boiling (the **boundary curve of liquid** – the curve of  $AK$ ). The curve of  $BK$  is called the **boundary curve of vapor**. Thus, for a real substance the  $p\nu$ -diagram can be divided into three specific zones [113, p. 18]:

1. The area of the liquid state, lying to the left from the curve of  $AK$  ;
2. The area of the two-phase state (wet vapor), situated between the curves of  $AK$  and  $BK$  ;
3. The area of the superheated vapor, placed to right from the curve of  $BK$  and above (higher than) the point of  $K$  .

\* \* \* \* \*

Fig. 2.3a

Conventionally the area of liquid is bounded from the above with the line of  $CK$ , representing the critical isobar [113, p. 19].

The **critical state of substance** was discovered for the first time by **D. I. Mendeleev** in 1861. *He called the critical temperature the absolute temperature of boiling.*

**Дми́трий Ива́нович Менделеев** [<http://ru.wiki>] (27 января [[8 февраля](#)] 1834, [Тобольск](#) — 20 января [[2 февраля](#)] 1907, [Санкт-Петербург](#)) — [русский учёный-энциклопедист](#), общественный деятель. [Химик](#), [физикохимик](#), [физик](#), [метролог](#), [экономист](#), [технолог](#), [геолог](#), [метеоролог](#), [педагог](#), [воздухоплаватель](#), [приборостроитель](#). [Профессор Санкт-Петербургского университета](#); [член-корреспондент](#) по разряду «физический» [Императорской Санкт-Петербургской Академии наук](#). Среди наиболее известных открытий — [периодический закон химических элементов](#), один из [фундаментальных законов мироздания](#), неотъемлемый для всего [естествознания](#).

At big densities the equation by van der Waals gives considerable mistakes, related to the fact that at its derivation there had not been taken into the consideration the phenomena of the force association and dissociation on molecules under the influence of the intermolecular forces of interaction [113, p. 19]. Besides (moreover), it was proven with experiments that the coefficients of  $a$  and  $b$ , introduced into the equation by van der Waals, are described with rather complicated dependences upon the temperature and pressure.

Russian scientists **M. P. Vukalovich** and **I. I. Novikov** in 1939 proposed (suggested) a new universal equation of state for a real gas, which makes allowance for the phenomenon of the forced association of molecules, and the equation has the view of [113, p. 19]

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \left[1 - \frac{C}{vT^{\frac{3+2m}{2}}}\right],$$

where  $a$  and  $b$  – the constants of the equation by van der Waals;  $C$ ,  $m$  – constants, determined on the basis of experiments [113, p. 20].