

Some comments on the  
 Van der Waals equation of state

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various equations of state (Raff Table 1.2)

Table 1.2 Some commonly used equations of state

Equation of State	Functional Form	Number of Parameters
→ Ideal gas	$PV_m = RT$	0
van der Waals	$(V_m - b)(P + a/V_m^2) = RT$	2
Dieterici	$P(V_m - b)\exp[a/RTV_m] = RT$	2
Berthelot	$(V_m - b)(P + a/TV_m^2) = RT$	2
Virial	$P = RT \left[ V_m^{-1} + \sum_{n=2}^{\infty} C_n(T) V_m^{-n} \right]$	$\infty$
Beattie-Bridgman	$PV_m^2 = (1 - \gamma)RT(V_m + \beta) - \alpha,$ with $\gamma = c_0/T^3V_m$ , $\beta = b_0[1 - b/V_m]$ , and $\alpha = a_0[1 + a/V_m]$	5
Redlich-Kwong	$P = \frac{RT}{(V_m - b)} - \frac{a}{T^{1/2}V_m(V_m + b)}$	2
Reichsanstalt	$PV = RT + AP + BP^2 + CP^3 + \dots$	$\infty$

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*van der Waals equation*

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$$P_{ideal} \bar{V}_{ideal} = RT$$
$$\left( P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT$$

interpretation of parameters:

b is correction for actual volume of atoms/molecules

- volume available to molecules  $(\bar{V} - b)$  smaller than  $\bar{V}$
- b is associated with repulsive forces

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*van der Waals equation*

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$$P_{ideal} \bar{V}_{ideal} = RT$$
$$\left( P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT$$

interpretation of parameters:

a is correction for attractive forces of atoms/molecules

- a is associated with attractive forces
- $P_{bulk} \equiv P_{ideal}$  is greater than  $P \equiv P_{meas}$  measured at surface

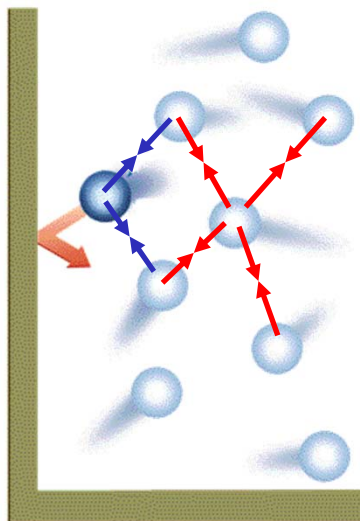
$$P_{bulk} = \left( P_{meas} + \frac{a}{\bar{V}^2} \right) \quad P_{meas} \rightarrow P_{bulk} \quad \bar{V} \rightarrow \infty$$

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*heuristic justification for attractive constant a*

- asymmetric attractive forces for molecule at surface
- molecule at surface has less momentum than molecule in bulk
- $P \equiv P_{\text{meas}} < P_{\text{bulk}}$
- $P_{\text{bulk}} = \left( P + \frac{a}{V^2} \right)$



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*van der Waals equation*

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

Table 1.1 van der Waals parameters

Gas	$b$ (L mol <sup>-1</sup> )	$a$ (L <sup>2</sup> bar mol <sup>-2</sup> )
He	0.0238	0.0346
Ne	0.01672	0.208
Ar	0.03201	1.355
Kr	0.0396	2.325
Acetylene	0.0522	4.516
N <sub>2</sub>	0.0387	1.37
H <sub>2</sub> O	0.03049	5.537
CO <sub>2</sub>	0.04286	3.658

size

polarizability

polarity

Source: Handbook of Chemistry and Physics, 78th edition, CRC Press, Boca Raton, FL, 1997-98

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*a little trash talk on VDW eqn, but instructive !!!*

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**Validity**

However, the Van der Waals model is not appropriate for rigorous quantitative calculations, remaining useful only for **teaching** and qualitative purposes.<sup>[1]</sup>

Nowadays, Eq. 2.9 belongs to **“pedagogical physics:”** it is the simplest equation that illustrates several important concepts, but its accuracy is not satisfactory.