Расчет конфигурационного интеграла для реальных газов

$$Z_V = \int\limits_q \iiint\limits_{......} e^{-\frac{\sum\limits_{ij} U_{ij}}{kT}} dq... = \int\limits_q \iiint\limits_{.......} \left(\prod_{ij} e^{-\frac{U_{ij}}{kT}} \right) dq... \qquad (1)$$

$$e^{-\frac{U_{ij}}{kT}} = 1 + f_{ij}$$

$$Z_V = \int\limits_q \iiint\limits_{.....} \left(\prod_{ij} e^{-\frac{U_{ij}}{kT}} \right) dq... = \int\limits_q \iiint\limits_{....} \left(\prod_{ij} (1 + f_{ij}) \right) dq... =$$

$$= \int\limits_q \iiint\limits_{....} \left(1 + \sum_{i,j} f_{ij} + \sum_{ij,kl} f_{ij} f_{kl} .... \right) dq... \qquad (2)$$

$$Z_V \approx \int\limits_q \iiint\limits_{....} \left(1 + \sum_{ij} f_{ij} \right) dq....$$

$$Z_V = \int\limits_q \iiint\limits_{...} \left(1 + \sum_{ij} f_{ij} \right) dq... = V^N + V^{N-2} \iint\limits_q \sum_{ij} f_{ij} dq_i dq_j =$$

$$V^N + V^{N-2} \frac{N^2}{2} \iint\limits_q f_{ij} dq_i dq_j \qquad (3)$$

$$r_{ij} = q_j - q_i; \quad dr_{ij} = dq_j$$

$$\int_q \iint_{....} f_{ij} dq_{i,x} dq_{i,y} dq_{i,z} dq_{j,x} dq_{j,y} dq_{j,z} = V \iiint_r f_{ij} dr_{ij,x} dr_{ij,y} dr_{ij,z} \tag{4}$$

$$dr_{ij,x} dr_{ij,y} dr_{ij,z} = r^2 dr \sin\theta d\theta d\varphi$$

$$\iiint_r f_{ij} dr_{ij,x} dr_{ij,y} dr_{ij,z} = \iiint_{r,\theta,\varphi} f_{ij} r^2 dr \sin\theta d\theta d\varphi$$

$$r^2 dr \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi = 2 \times 2\pi r^2 dr = 4\pi r^2 dr$$

$$Z_V = V^N + V^{N-1} \frac{N^2}{2} \int_0^{\infty} f_{ij} 4\pi r^2 dr \tag{5}$$

$$Z_V = V^N + V^N \frac{N^2}{2V} \beta = V^N \left(1 + \frac{N^2}{2V} \beta \right) \tag{6}$$

$$\ln Z_V = N \ln V + \ln\left(1 + \frac{N^2}{2V} \beta \right) = N \ln V + \frac{N^2}{2V} \beta \tag{7}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{NkT}{V} - \frac{kTN^2\beta}{2V^2};$$
$$\frac{pV}{RT} = 1 - \frac{N\beta}{2V} \qquad (8)$$

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} \ldots.$$

$$B(T) = -\frac{N\beta}{2} = -\frac{N}{2}\int_0^\infty f_{ij} 4\pi r^2 dr = 2\pi N \int_0^\infty \left(1 - e^{-\frac{U_{ij}}{kT}}\right) r^2 dr \qquad (9)$$

$U_{ij} = \infty$ при $0 \le r < r_0$ и $U_{ij} = -c/r^6$ при $r_0 \le r < \infty$ (10)

$f_{ij} = \exp(-U_{ij}/kT) - 1 = \exp(\frac{c}{kT*r^6}) - 1$ при $r_0 \le r < \infty$ (11)

$$f_{ij} = \frac{c}{kT*r^6}$$

$$0 \le r < r_0; \int_0^{r_0} f_{ij} 4\pi r^2 dr = -\frac{4}{3}\pi r_0^3 \qquad (12)$$

$$r_0 \le r < \infty; \int_{r_0}^{\infty} \mathrm{f_{ij}}\, 4\pi \mathrm{r}^2 \mathrm{dr} = \int_{r_0}^{\infty} \frac{\mathrm{c}*4\pi \mathrm{r}^2}{\mathrm{r}^6 * \mathrm{kT}} \mathrm{dr} = \frac{4\pi \mathrm{c}}{\mathrm{kT}} \int_{r_0}^{\infty} \frac{1}{\mathrm{r}^4} \mathrm{dr} =$$

$$= -\frac{4\pi c}{kT}\frac{1}{3} \times \frac{1}{r^3} \Big|_{r_0}^{\infty} = \frac{4\pi c}{3kT} \times \frac{1}{r_0^3} \tag{13}$$

$$\beta = \int_0^{\infty} \mathrm{f_{ij}} * 4\pi \mathrm{r}^2 \mathrm{dr} = -\frac{4}{3}\pi \mathrm{r}_0^3 + \frac{4\pi \mathrm{c}}{3\mathrm{kTr}_0^3} \tag{14}$$

$$\ln Z_V = N \ln V + \frac{N^2 * \left(-\frac{4}{3}\pi \mathrm{r}_0^3 + \frac{4\pi \mathrm{c}}{3\mathrm{kTr}_0^3} \right)}{2V} \tag{15}$$

$$\mathrm{p} = \mathrm{kT}\left(\frac{\partial \ln Z_v}{\partial V}\right)_{\mathrm{T}} = \frac{\mathrm{NkT}}{\mathrm{V}} - \frac{\mathrm{kTN}^2 * \left(-\frac{4}{3}\pi \mathrm{r}_0^3 + \frac{4\pi \mathrm{c}}{3\mathrm{kTr}_0^3} \right)}{2\mathrm{V}^2} \tag{16}$$

$$\frac{\mathrm{pV}}{\mathrm{RT}} = 1 - \frac{\mathrm{N} * \left(-\frac{4}{3}\pi \mathrm{r}_0^3 + \frac{4\pi \mathrm{c}}{3\mathrm{kTr}_0^3} \right)}{2\mathrm{V}} \tag{17}$$

$$\mathrm{B}(\mathrm{T}) = 2\pi \mathrm{N} * \left(\frac{\mathrm{r}_0^3}{3} - \frac{\mathrm{c}}{3\mathrm{kTr}_0^3} \right) = b_W - \frac{a_W}{RT} \tag{18}$$

$$b_W = \frac{2\pi N r_0^3}{3};\ a_W = \frac{2\pi N^2 c}{3 r_0^3} \tag{19}$$

$$(p + \frac{2\pi c N}{3 r_0^3 V^2}) * (V - \frac{2\pi N^2 r_0^3}{3}) = RT \tag{20}$$