高精度状态方程

包括两相区，PVT，亥姆霍兹型

参数来源于经验，优点是极端条件也比较准确，不足是无法计算混合物 PVT

也可以用于实验数据较不广泛和较不准确的物质（参数用哪个？？？）

$$\frac{a(T,\rho)}{RT}=\frac{a^{\mathrm{id}}(T,\rho)+a^{\mathrm{R}}(T,\rho)}{RT}=\alpha^{\mathrm{id}}(\tau,\delta)+\alpha^{\mathrm{R}}(\tau,\delta) \tag{2.108}$$

$$\tau=T_c/T,\ \delta=\rho/\rho_c=\frac{m/V}{m/V_c}=V_c/V$$

$$\begin{aligned}a^{\mathrm{id}}(T,\upsilon)&=u^{\mathrm{id}}(T)-Ts^{\mathrm{id}}(T,\upsilon)\\&=\int_{T_0}^{T}c_\upsilon^{\mathrm{id}}\,\mathrm{d}T-T\int_{T_0}^{T}c_\upsilon^{\mathrm{id}}\frac{\mathrm{d}T}{T}-RT\ln\frac{\upsilon}{\upsilon_0}+a(T_0,\upsilon_0)\end{aligned} \tag{2.109}$$

or

$$a^{\mathrm{id}}(T,\rho)=\int_{T_0}^{T}c_\upsilon^{\mathrm{id}}\,\mathrm{d}T-T\int_{T_0}^{T}c_\upsilon^{\mathrm{id}}\frac{\mathrm{d}T}{T}+RT\ln\frac{\rho}{\rho_0}+a(T_0,\rho_0) \tag{2.110}$$

Table 2.3 Typical accuracy demands for technical equations of state [29].

	$\rho(P,T)$ [%]	$w^*(P,T)$ [%]	$c_p(P,T)$ [%]	$P^s(T)$ [%]	$\rho'(T)$ [%]	$\rho''(T)$ [%]
$P<30$ MPa	0.2	1–2	1–2	0.2	0.2	0.2
$P>30$ MPa	0.5	2	2	—	—	—

For nonpolar fluids [32, 33] (methane, ethane, propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane, argon, oxygen, nitrogen, ethylene, isobutane,cyclohexane, sulfur hexafluoride, carbon monoxide, carbonyl sulfide, n-decane, hydrogen sulfide, isopentane, neopentane, isohexane, krypton, n-nonane, toluene, xenon, and R116 六氟乙烷):

$$\begin{aligned}\alpha^{\mathrm{R}}(\tau,\delta)=&n_1\delta\tau^{0.25}+n_2\delta\tau^{1.125}+n_3\delta\tau^{1.5}+n_4\delta^2\tau^{1.375}+n_5\delta^3\tau^{0.25}+n_6\delta^7\tau^{0.875}\\&+n_7\delta^2\tau^{0.625}\,\mathrm{e}^{-\delta}+n_8\delta^5\tau^{1.75}\,\mathrm{e}^{-\delta}+n_9\delta\tau^{3.625}\,\mathrm{e}^{-\delta^2}+n_{10}\delta^4\tau^{3.625}\,\mathrm{e}^{-\delta^2}\\&+n_{11}\delta^3\tau^{14.5}\,\mathrm{e}^{-\delta^3}+n_{12}\delta^4\tau^{12}\,\mathrm{e}^{-\delta^3}\end{aligned} \tag{2.112}$$

For polar fluids [33, 34] (R11, R12, R22, R32, R113, R123, R125, R134a, R143a,R152a, carbon dioxide, ammonia, acetone, nitrous oxide, sulfur dioxide [35],R141b1,1-二氯-1-氟乙烷, R142b1-氯-1,1-二氟乙烷, R218 八氟丙烷, and R245fa1,1,1,3,3-五氟丙烷):

$$\begin{aligned}\alpha^{\mathrm{R}}(\tau,\delta)=&n_1\delta\tau^{0.25}+n_2\delta\tau^{1.25}+n_3\delta\tau^{1.5}+n_4\delta^3\tau^{0.25}+n_5\delta^7\tau^{0.875}+n_6\delta\tau^{2.375}\,\mathrm{e}^{-\delta}\\&+n_7\delta^2\tau^{2}\,\mathrm{e}^{-\delta}+n_8\delta^5\tau^{2.125}\,\mathrm{e}^{-\delta}+n_9\delta\tau^{3.5}\,\mathrm{e}^{-\delta^2}+n_{10}\delta\tau^{6.5}\,\mathrm{e}^{-\delta^2}\\&+n_{11}\delta^4\tau^{4.75}\,\mathrm{e}^{-\delta^2}+n_{12}\delta^2\tau^{12.5}\,\mathrm{e}^{-\delta^3}\end{aligned} \tag{2.113}$$

$$P(T,\rho)=-(\partial a/\partial\upsilon)_T=\rho RT\left[1+\delta\left(\frac{\partial\alpha^{\mathrm{R}}}{\partial\delta}\right)_\tau\right] \tag{2.114}$$

Appendix B

Coefficients for High-Precision Equations of State

Table B.1 Coefficients for nonpolar fluids (Eq. (2.113)).

	Methane	**Ethane**	**Propane**	***n*-Butane**	***n*-Pentane**
Coefficients	**1**	**2**	**3**	**4**	**5**
n_1	0.89269676	0.97628068	1.0403973	1.0626277	1.0968643
n_2	−2.5438282	−2.6905251	−2.8318404	−2.8620952	−2.9988888
n_3	0.64980978	0.73498222	0.8439381	0.88738233	0.99516887
n_4	0.020793471	−0.035366206	−0.076559592	−0.12570581	−0.16170709
n_5	0.070189104	0.084692031	0.094697373	0.10286309	0.1133446
n_6	0.00023700378	0.00024154594	0.00024796475	0.00025358041	0.00026760595
n_7	0.16653334	0.23964954	0.2774376	0.323252	0.40979882
n_8	−0.043855669	−0.042780093	−0.043846001	−0.037950761	−0.040876423
n_9	−0.1572678	−0.22308832	−0.26991065	−0.32534802	−0.38169482
n_{10}	−0.035311675	−0.051799954	−0.069313413	−0.079050969	−0.10931957
n_{11}	−0.029570024	−0.027178426	−0.029632146	−0.020636721	−0.032073223
n_{12}	0.014019842	0.011246305	0.014040127	0.0057053809	0.016877016

	***n*-Hexane**	***n*-Heptane**	***n*-Octane**	**Argon**	**Oxygen**
Coefficients	**6**	**7**	**8**	**9**	**10**
n_1	1.0553238	1.0543748	1.0722545	0.85095715	0.88878286
n_2	−2.6120616	−2.6500682	−2.4632951	−2.4003223	−2.4879433
n_3	0.76613883	0.81730048	0.65386674	0.54127841	0.59750191
n_4	−0.29770321	−0.30451391	−0.36324974	0.016919771	0.0096501817
n_5	0.11879908	0.12253869	0.1271327	0.068825965	0.071970429
n_6	0.00027922861	0.00027266473	0.00030713573	0.00021428033	0.00022337443
n_7	0.4634759	0.49865826	0.52656857	0.17429895	0.18558686
n_8	0.011433197	−0.00071432815	0.019362863	−0.033654496	−0.038129368
n_9	−0.48256969	−0.54236896	−0.58939427	−0.135268	−0.15352245
n_{10}	−0.093750559	−0.13801822	−0.14069964	−0.016387351	−0.026726815
n_{11}	−0.0067273247	−0.0061595287	−0.0078966331	−0.024987667	−0.025675299
n_{12}	−0.0051141584	0.0004860251	0.0033036598	0.0088769205	0.0095714302

(Continued)

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Table B.1 (Continued)

	Nitrogen	Ethylene	Isobutane	Cyclohexane	SF_6
Coefficients	**11**	**12**	**13**	**14**	**15**
n_1	0.92296567	0.9096223	1.0429332	1.0232354	1.2279403
n_2	−2.5575012	−2.4641015	−2.8184273	−2.9204964	−3.3035623
n_3	0.64482463	0.56175311	0.86176232	1.073663	1.2094019
n_4	0.01083102	−0.019688013	−0.10613619	−0.19573985	−0.12316
n_5	0.073924167	0.078831145	0.098615749	0.12228111	0.11044657
n_6	0.00023532962	0.00021478776	0.00023948209	0.00028943321	0.00032952153
n_7	0.18024854	0.23151337	0.30330005	0.27231767	0.27017629
n_8	−0.045660299	−0.037804454	−0.041598156	−0.04483332	−0.062910351
n_9	−0.1552106	−0.20122739	−0.29991937	−0.38253334	−0.3182889
n_{10}	−0.03811149	−0.044960157	−0.080369343	−0.089835333	−0.099557419
n_{11}	−0.031962422	−0.02834296	−0.029761373	−0.024874965	−0.036909694
n_{12}	0.015513532	0.012652824	0.01305963	0.010836132	0.019136427

	Carbon monoxide	Carbonyl sulfide	*n*-Decane	Hydrogen sulfide	Isopentane
Coefficients	**16**	**17**	**18**	**19**	**20**
n_1	0.90554	0.94374	1.0461	0.87641	1.0963
n_2	−2.4515	−2.5348	−2.4807	−2.0367	−3.0402
n_3	0.53149	0.59058	0.74372	0.21634	1.0317
n_4	0.024173	−0.021488	−0.52579	−0.050199	−0.1541
n_5	0.072156	0.082083	0.15315	0.066994	0.11535
n_6	0.00018818	0.00024689	0.00032865	0.00019076	0.00029809
n_7	0.19405	0.21226	0.84178	0.20227	0.39571
n_8	−0.043268	−0.041251	0.055424	−0.0045348	−0.045881
n_9	−0.12778	−0.22333	−0.73555	−0.2223	−0.35804
n_{10}	−0.027896	−0.050828	−0.18507	−0.034714	−0.10107
n_{11}	−0.034154	−0.028333	−0.020775	−0.014885	−0.035484
n_{12}	0.016329	0.016983	0.012335	0.0074154	0.018156

Table B.1 (Continued)

	Neopentane	**Isohexane**	**Krypton**	***n*-Nonane**	**Toluene**
Coefficients	**21**	**22**	**23**	**24**	**25**
n_1	1.1136	1.1027	0.83561	1.1151	0.96464
n_2	−3.1792	−2.9699	−2.3725	−2.702	−2.7855
n_3	1.1411	1.0295	0.54567	0.83416	0.86712
n_4	−0.10467	−0.21238	0.014361	−0.38828	−0.1886
n_5	0.11754	0.11897	0.066502	0.1376	0.11804
n_6	0.00034058	0.00027738	0.0001931	0.00028185	0.00025181
n_7	0.29553	0.40103	0.16818	0.62037	0.57196
n_8	−0.074765	−0.034238	−0.033133	0.015847	−0.029287
n_9	−0.31474	−0.43584	−0.15008	−0.61726	−0.43351
n_{10}	−0.099401	−0.11693	−0.022897	−0.15043	−0.1254
n_{11}	−0.039569	−0.019262	−0.021454	−0.012982	−0.028207
n_{12}	0.023177	0.0080783	0.0069397	0.0044325	0.014076

	Xenon	**R116**
Coefficients	**26**	**27**
n_1	0.83115	1.1632
n_2	−2.3553	−2.8123
n_3	0.53904	0.77202
n_4	0.014382	−0.14331
n_5	0.066309	0.10227
n_6	0.00019649	0.00024629
n_7	0.14996	0.30893
n_8	−0.035319	−0.028499
n_9	−0.15929	−0.30343
n_{10}	−0.027521	−0.068793
n_{11}	−0.023305	−0.027218
n_{12}	0.0086941	0.010665

Table B.2 Coefficients for polar fluids (Eq. (2.114)).

	R11	R12	R22	R32
Coefficients	**1**	**2**	**3**	**4**
n_1	1.0656383	1.0557228	0.96268924	0.92876414
n_2	−3.2495206	−3.3312001	−2.5275103	−2.4673952
n_3	0.87823894	1.0197244	0.31308745	0.40129043
n_4	0.087611569	0.084155115	0.072432837	0.055101049
n_5	0.00029950049	0.00028520742	0.00021930233	0.00011559754
n_6	0.42896949	0.39625057	0.33294864	−0.25209758
n_7	0.70828452	0.63995721	0.63201229	0.42091879
n_8	−0.017391823	−0.021423411	−0.0032787841	0.0037071833
n_9	−0.37626522	−0.36249173	−0.33680834	−0.10308607
n_{10}	0.011605284	0.001934199	−0.022749022	−0.11592089
n_{11}	−0.089550567	−0.092993833	−0.087867308	−0.044350855
n_{12}	−0.030063991	−0.024876461	−0.021108145	−0.012788805

	R113	R123	R125	R134a
Coefficients	**5**	**6**	**7**	**8**
n_1	1.0519071	1.116973	1.1290996	1.0663189
n_2	−2.8724742	−3.074593	−2.8349269	−2.449597
n_3	0.41983153	0.51063873	0.29968733	0.044645718
n_4	0.087107788	0.094478812	0.087282204	0.075656884
n_5	0.00024105194	0.00029532752	0.00026347747	0.00020652089
n_6	0.70738262	0.66974438	0.61056963	0.42006912
n_7	0.93513411	0.96438575	0.90073581	0.76739111
n_8	−0.0096713512	−0.014865424	−0.0068788457	0.0017897427
n_9	−0.52595315	−0.49221959	−0.44211186	−0.36219746
n_{10}	0.022691984	−0.022831038	−0.035041493	−0.06780937
n_{11}	−0.14556325	−0.1407486	−0.1269863	−0.10616419
n_{12}	−0.02741995	−0.025117301	−0.025185874	−0.018185791

Table B.2 (Continued)

	R143a	R152a	Carbon dioxide	Ammonia
Coefficients	**9**	**10**	**11**	**12**
n_1	1.0306886	0.95702326	0.89875108	0.7302272
n_2	−2.9497307	−2.3707196	−2.1281985	−1.1879116
n_3	0.6943523	0.18748463	−0.06819032	−0.68319136
n_4	0.071552102	0.063800843	0.076355306	0.040028683
n_5	0.00019155982	0.00016625977	0.00022053253	0.000090801215
n_6	0.079764936	0.082208165	0.41541823	−0.056216175
n_7	0.56859424	0.57243518	0.71335657	0.44935601
n_8	−0.0090946566	0.0039476701	0.00030354234	0.029897121
n_9	−0.24199452	−0.23848654	−0.36643143	−0.18181684
n_{10}	−0.070610813	−0.080711618	−0.0014407781	−0.09841666
n_{11}	−0.075041709	−0.073103558	−0.089166707	−0.055083744
n_{12}	−0.016411241	−0.015538724	−0.023699887	−0.0088983219

	Acetone	N_2O	Sulfur dioxide	R141b
Coefficients	**13**	**14**	**15**	**16**
n_1	0.90041	0.88045	0.93061	1.1469
n_2	−2.1267	−2.4235	−1.9528	−3.6799
n_3	−0.083409	0.38237	−0.17467	1.3469
n_4	0.065683	0.068917	0.061524	0.083329
n_5	0.00016527	0.00020367	0.00017711	0.00025137
n_6	−0.039663	0.13122	0.21615	0.3272
n_7	0.72085	0.46032	0.51353	0.46946
n_8	0.0092318	−0.0036985	0.010419	−0.029829
n_9	−0.17217	−0.23263	−0.25286	−0.31621
n_{10}	−0.14961	−0.00042859	−0.05472	−0.026219
n_{11}	−0.076124	−0.04281	−0.059856	−0.078043
n_{12}	−0.018166	−0.023038	−0.016523	−0.020498

(Continued)

Table B.2 (Continued)

	R142b	R218	R245fa
Coefficients	**17**	**18**	**19**
n_1	1.0038	1.327	1.2904
n_2	−2.7662	−3.8433	−3.2154
n_3	0.42921	0.922	0.50693
n_4	0.081363	0.1136	0.093148
n_5	0.00024174	0.00036195	0.00027638
n_6	0.48246	1.1001	0.71458
n_7	0.75542	1.1896	0.87252
n_8	−0.00743	−0.025147	−0.015077
n_9	−0.4146	−0.65923	−0.40645
n_{10}	−0.016558	−0.027969	−0.11701
n_{11}	−0.10644	−0.1833	−0.13062
n_{12}	−0.021704	−0.02163	−0.022952

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