

COMPUTER PROGRAM FOR DETERMINATION OF THERMODYNAMIC PROPERTIES OF FLUIDS

GY. VARSÁNYI

Department of Physical Chemistry
Technical University, H-1521 Budapest

Received March 1, 1989

Abstract

The charts for reduced compressibility coefficients published in [1] have been completed by a table referring to a fluid of critical compressibility coefficient 0.302. The new table has been constructed using the data of helium. The isotherms have been divided into pressure intervals within which they have been described by maximum fourth order functions. The compressibility coefficients along the isobars have been then interpolated by quadratic functions of temperature. An additional requirement for the interpolation formulae was to yield a smooth inversion curve. The formulae can be used also for the calculation of fugacity coefficients and molar enthalpies. Two computer programs have been elaborated for these calculations.

Introduction

Although computerizable equations of state have been published for many fluids such equations are not available for the majority of substances. In these cases the rule of corresponding states is a useful tool which allows one to calculate the pressure, the volume and the temperature of fluids. This method applies charts or diagrams containing common compressibility coefficients for different substances as a function of the reduced pressure p_r , the reduced temperature T_r and the critical compressibility coefficient Z_c . Obviously, this approximative method has an inherent inaccuracy, and in order not to increase it one has to perform the threefold interpolation (by p_r , T_r and Z_c) precisely. The compressibility coefficient charts published in a former paper [1] have been computed using thermodynamic data of NH_3 , C_2H_4 and air. In the present work new interpolation formulae have been developed and employed completing at the same time the above charts by new data.

The reduced compressibility chart of helium

In constructing the chart the data of International Thermodynamic Tables of the Fluid State, Vol. 4 [2] were used. The chart containing the reduced compressibility coefficients of helium extends to much wider pressure and temperature range than the charts relating to ammonia (Table 1), ethylene

Table 1
 Chart of generalized reduced compressibility function
 $Z_c = 0.302$ (Helium)

P_r T_r	0.01	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.15
0.5	0.003	0.029	0.058	0.087	0.115	0.143	0.171	0.200	0.228	0.256	0.283	0.297	0.311	0.324
0.6	0.989	0.887	0.049	0.074	0.099	0.123	0.146	0.171	0.194	0.218	0.241	0.253	0.264	0.276
0.7	0.992	0.922	0.828	0.067	0.089	0.110	0.131	0.152	0.173	0.194	0.214	0.225	0.235	0.245
0.8	0.995	0.944	0.881	0.806	0.730	0.103	0.123	0.142	0.161	0.179	0.198	0.207	0.216	0.225
0.9	0.996	0.957	0.912	0.862	0.804	0.739	0.669	0.142	0.161	0.178	0.195	0.203	0.210	0.218
0.92	0.996	0.960	0.916	0.869	0.816	0.757	0.691	0.620	0.164	0.181	0.197	0.204	0.211	0.218
0.94	0.996	0.962	0.921	0.876	0.828	0.773	0.711	0.644	0.167	0.185	0.199	0.206	0.213	0.220
0.96	0.996	0.963	0.925	0.883	0.838	0.787	0.730	0.667	0.604	0.190	0.202	0.209	0.216	0.222
0.98	0.997	0.965	0.928	0.889	0.847	0.800	0.746	0.692	0.636	0.555	0.225	0.220	0.220	0.225
1.00	0.997	0.967	0.932	0.895	0.856	0.812	0.762	0.712	0.660	0.584	0.302	0.259	0.225	0.229
1.01	0.997	0.968	0.934	0.898	0.859	0.817	0.770	0.721	0.670	0.597	0.478	0.408	0.329	0.304
1.02	0.997	0.968	0.935	0.900	0.863	0.822	0.777	0.730	0.680	0.610	0.503	0.437	0.361	0.328
1.03	0.997	0.969	0.937	0.903	0.866	0.827	0.784	0.738	0.691	0.623	0.526	0.466	0.397	0.357
1.04	0.997	0.970	0.938	0.905	0.870	0.832	0.791	0.746	0.701	0.636	0.549	0.494	0.436	0.393
1.05	0.997	0.970	0.940	0.907	0.873	0.837	0.797	0.754	0.709	0.649	0.571	0.521	0.471	0.424
1.06	0.997	0.971	0.941	0.909	0.876	0.841	0.803	0.761	0.717	0.661	0.592	0.546	0.498	0.451
1.07	0.997	0.972	0.942	0.912	0.879	0.845	0.809	0.768	0.725	0.672	0.612	0.569	0.523	0.475
1.08	0.997	0.972	0.944	0.914	0.882	0.849	0.814	0.775	0.733	0.683	0.628	0.588	0.545	0.499
1.09	0.997	0.973	0.945	0.916	0.885	0.853	0.819	0.781	0.740	0.693	0.642	0.606	0.566	0.523
1.10	0.997	0.974	0.946	0.918	0.888	0.857	0.824	0.787	0.748	0.703	0.655	0.623	0.587	0.548
1.12	0.998	0.975	0.948	0.921	0.893	0.863	0.832	0.798	0.762	0.723	0.678	0.654	0.627	0.596
1.14	0.998	0.976	0.951	0.925	0.898	0.869	0.840	0.808	0.775	0.739	0.699	0.678	0.655	0.630
1.16	0.998	0.977	0.953	0.928	0.902	0.875	0.848	0.818	0.787	0.754	0.719	0.700	0.680	0.659
1.18	0.998	0.978	0.955	0.931	0.906	0.881	0.855	0.827	0.798	0.767	0.735	0.718	0.701	0.682
1.20	0.998	0.979	0.956	0.934	0.910	0.886	0.861	0.835	0.808	0.779	0.749	0.734	0.718	0.701
1.3	0.998	0.982	0.964	0.946	0.927	0.908	0.888	0.868	0.847	0.826	0.803	0.792	0.780	0.769
1.4	0.999	0.985	0.970	0.955	0.940	0.924	0.908	0.892	0.876	0.859	0.841	0.833	0.824	0.815
1.5	0.999	0.988	0.975	0.962	0.950	0.937	0.924	0.911	0.897	0.883	0.870	0.863	0.856	0.849
1.6	0.999	0.990	0.979	0.968	0.958	0.947	0.936	0.925	0.914	0.903	0.891	0.886	0.880	0.874
1.7	0.999	0.991	0.982	0.973	0.964	0.955	0.946	0.936	0.927	0.918	0.908	0.904	0.899	0.894
1.8	0.999	0.992	0.985	0.977	0.969	0.961	0.954	0.946	0.938	0.930	0.922	0.918	0.914	0.910
1.9	0.999	0.993	0.987	0.980	0.973	0.967	0.960	0.953	0.947	0.940	0.933	0.930	0.927	0.923

$\frac{P_r}{T_r}$	1.2	1.25	1.3	1.35	1.4	1.45	1.5	1.6	1.7	1.8	1.9	2.0	2.2	2.4
0.5	0.338	0.351	0.365	0.378	0.392	0.405	0.419	0.446	0.472	0.499	0.525	0.551	0.604	0.656
0.6	0.287	0.299	0.310	0.322	0.333	0.344	0.356	0.378	0.401	0.423	0.445	0.467	0.511	0.555
0.7	0.255	0.265	0.275	0.285	0.295	0.305	0.315	0.334	0.354	0.373	0.393	0.412	0.450	0.488
0.8	0.234	0.243	0.252	0.261	0.270	0.279	0.288	0.305	0.323	0.340	0.358	0.375	0.409	0.442
0.9	0.225	0.233	0.241	0.249	0.257	0.265	0.274	0.290	0.305	0.321	0.337	0.352	0.383	0.413
0.92	0.225	0.232	0.240	0.247	0.255	0.264	0.272	0.288	0.303	0.319	0.334	0.349	0.379	0.409
0.94	0.227	0.234	0.240	0.248	0.256	0.264	0.272	0.287	0.302	0.317	0.332	0.347	0.377	0.405
0.96	0.229	0.237	0.244	0.251	0.259	0.266	0.273	0.288	0.302	0.317	0.331	0.346	0.374	0.402
0.98	0.232	0.241	0.249	0.256	0.262	0.269	0.276	0.290	0.303	0.317	0.331	0.345	0.372	0.400
1.00	0.236	0.246	0.254	0.260	0.267	0.275	0.280	0.292	0.304	0.316	0.330	0.344	0.371	0.398
1.01	0.285	0.271	0.262	0.263	0.269	0.275	0.282	0.294	0.305	0.316	0.330	0.344	0.371	0.397
1.02	0.302	0.282	0.268	0.267	0.272	0.277	0.285	0.296	0.306	0.317	0.331	0.344	0.371	0.397
1.03	0.323	0.296	0.276	0.272	0.275	0.280	0.288	0.298	0.308	0.318	0.332	0.345	0.371	0.396
1.04	0.351	0.315	0.288	0.278	0.278	0.283	0.291	0.300	0.310	0.320	0.333	0.346	0.371	0.396
1.05	0.379	0.337	0.302	0.284	0.281	0.286	0.295	0.303	0.313	0.323	0.335	0.347	0.372	0.396
1.06	0.404	0.361	0.320	0.297	0.291	0.295	0.301	0.308	0.317	0.327	0.338	0.349	0.373	0.397
1.07	0.429	0.384	0.341	0.318	0.309	0.310	0.313	0.317	0.323	0.331	0.341	0.351	0.374	0.397
1.08	0.454	0.410	0.367	0.343	0.332	0.330	0.328	0.329	0.331	0.336	0.344	0.353	0.375	0.398
1.09	0.479	0.437	0.396	0.371	0.358	0.350	0.344	0.341	0.339	0.341	0.347	0.356	0.376	0.398
1.10	0.504	0.466	0.428	0.402	0.385	0.376	0.369	0.355	0.348	0.346	0.351	0.358	0.378	0.399
1.12	0.560	0.523	0.491	0.466	0.445	0.427	0.412	0.386	0.369	0.360	0.361	0.365	0.382	0.401
1.14	0.603	0.574	0.546	0.523	0.498	0.475	0.453	0.418	0.391	0.377	0.374	0.376	0.388	0.406
1.16	0.638	0.615	0.592	0.568	0.541	0.515	0.490	0.450	0.418	0.399	0.392	0.390	0.398	0.412
1.18	0.664	0.644	0.623	0.601	0.576	0.549	0.524	0.483	0.450	0.428	0.416	0.411	0.411	0.420
1.20	0.684	0.666	0.647	0.627	0.604	0.580	0.558	0.519	0.486	0.461	0.445	0.435	0.426	0.430
1.3	0.757	0.744	0.732	0.720	0.707	0.694	0.681	0.655	0.629	0.603	0.578	0.559	0.527	0.508
1.4	0.806	0.797	0.788	0.778	0.769	0.760	0.750	0.731	0.712	0.694	0.676	0.658	0.627	0.602
1.5	0.842	0.834	0.827	0.820	0.813	0.805	0.798	0.784	0.769	0.755	0.741	0.726	0.700	0.677
1.6	0.868	0.863	0.857	0.851	0.845	0.839	0.834	0.822	0.810	0.799	0.787	0.776	0.755	0.735
1.7	0.889	0.885	0.880	0.875	0.870	0.866	0.861	0.851	0.842	0.832	0.823	0.814	0.796	0.779
1.8	0.906	0.902	0.898	0.894	0.890	0.886	0.882	0.874	0.866	0.859	0.851	0.843	0.828	0.814
1.9	0.920	0.916	0.913	0.910	0.906	0.903	0.900	0.893	0.886	0.880	0.873	0.867	0.854	0.842

Table 1. (Contd)

Chart of generalized reduced compressibility function
 $Z_c = 0.302$ (Helium)

P_r T_r	2.6	2.8	3.0	3.5	4.0	4.5	5	6	7	8	9	10	15	20
0.5	0.707	0.758	0.809	0.935	1.059	1.181	1.302	1.539	1.771	1.999	2.223	2.443	3.497	4.487
0.6	0.598	0.641	0.684	0.789	0.892	0.995	1.095	1.293	1.487	1.677	1.863	2.047	2.927	3.757
0.7	0.525	0.563	0.599	0.691	0.780	0.868	0.955	1.126	1.293	1.456	1.617	1.775	2.534	3.247
0.8	0.476	0.509	0.541	0.622	0.701	0.779	0.855	1.006	1.153	1.296	1.437	1.576	2.242	2.870
0.9	0.443	0.472	0.502	0.574	0.645	0.715	0.783	0.918	1.049	1.177	1.303	1.427	2.021	2.582
0.92	0.438	0.467	0.496	0.567	0.636	0.704	0.772	0.903	1.032	1.157	1.281	1.402	1.983	2.532
0.94	0.434	0.463	0.491	0.560	0.628	0.695	0.761	0.889	1.015	1.138	1.259	1.378	1.947	2.485
0.96	0.430	0.458	0.486	0.554	0.620	0.686	0.750	0.876	1.000	1.120	1.239	1.355	1.913	2.439
0.98	0.427	0.454	0.481	0.548	0.613	0.677	0.740	0.864	0.985	1.103	1.219	1.333	1.879	2.396
1.00	0.425	0.451	0.478	0.543	0.606	0.669	0.731	0.852	0.971	1.087	1.201	1.313	1.848	2.354
1.01	0.424	0.450	0.476	0.540	0.603	0.665	0.727	0.847	0.964	1.079	1.192	1.302	1.833	2.334
1.02	0.423	0.449	0.474	0.538	0.600	0.662	0.723	0.841	0.958	1.071	1.183	1.292	1.818	2.314
1.03	0.422	0.448	0.473	0.536	0.598	0.658	0.718	0.836	0.951	1.064	1.174	1.283	1.803	2.295
1.04	0.422	0.447	0.472	0.534	0.595	0.655	0.714	0.831	0.945	1.056	1.166	1.274	1.789	2.276
1.05	0.421	0.446	0.471	0.532	0.592	0.652	0.711	0.826	0.939	1.049	1.158	1.264	1.775	2.258
1.06	0.421	0.445	0.470	0.530	0.590	0.649	0.707	0.821	0.933	1.042	1.150	1.255	1.761	2.239
1.07	0.421	0.445	0.469	0.528	0.587	0.646	0.703	0.816	0.927	1.035	1.142	1.246	1.748	2.221
1.08	0.421	0.444	0.468	0.527	0.585	0.643	0.700	0.812	0.921	1.029	1.134	1.238	1.734	2.204
1.09	0.421	0.444	0.467	0.525	0.583	0.640	0.696	0.807	0.916	1.022	1.127	1.229	1.722	2.187
1.10	0.421	0.444	0.467	0.524	0.581	0.637	0.693	0.803	0.911	1.016	1.119	1.221	1.709	2.170
1.12	0.422	0.444	0.466	0.522	0.577	0.632	0.687	0.795	0.900	1.004	1.105	1.205	1.684	2.137
1.14	0.425	0.445	0.466	0.520	0.574	0.628	0.681	0.787	0.890	0.992	1.092	1.190	1.661	2.106
1.16	0.429	0.448	0.467	0.519	0.571	0.624	0.676	0.779	0.881	0.981	1.079	1.175	1.638	2.075
1.18	0.434	0.451	0.469	0.518	0.569	0.620	0.671	0.773	0.872	0.970	1.067	1.161	1.616	2.046
1.20	0.440	0.455	0.472	0.518	0.567	0.617	0.667	0.766	0.864	0.960	1.055	1.148	1.595	2.018
1.3	0.499	0.498	0.503	0.531	0.568	0.610	0.653	0.741	0.829	0.917	1.004	1.089	1.501	1.891
1.4	0.583	0.570	0.563	0.565	0.585	0.616	0.650	0.727	0.805	0.885	0.964	1.043	1.423	1.785
1.5	0.659	0.643	0.631	0.616	0.619	0.636	0.660	0.723	0.790	0.862	0.934	1.006	1.358	1.695
1.6	0.717	0.702	0.690	0.672	0.664	0.663	0.682	0.729	0.784	0.847	0.912	0.977	1.303	1.617
1.7	0.764	0.750	0.738	0.718	0.709	0.706	0.712	0.743	0.785	0.840	0.897	0.956	1.257	1.551
1.8	0.801	0.789	0.778	0.758	0.747	0.743	0.746	0.764	0.794	0.839	0.889	0.942	1.219	1.494
1.9	0.831	0.820	0.810	0.791	0.780	0.775	0.775	0.786	0.809	0.846	0.887	0.935	1.187	1.445

$\frac{P_r}{T_r}$	25	30	35	40	45	50	60	70	80	90	100	150	200	250	300
0.6	4.551	5.313													
0.7	3.931	4.588	5.227	5.842											
0.8	3.471	4.050	4.610	5.154											
0.9	3.118	3.635	4.136	4.622	5.097	5.561	6.462								
0.92	3.057	3.563	4.054	4.530	4.995	5.450	6.332								
0.94	2.999	3.496	3.975	4.442	4.897	5.343	6.207								
0.96	2.943	3.429	3.899	4.357	4.803	5.240	6.087								
0.98	2.889	3.365	3.827	4.275	4.714	5.141	5.971								
1.00	2.838	3.305	3.757	4.197	4.626	5.046	5.861								
1.01	2.814	3.276	3.724	4.159	4.584	5.001	5.807								
1.02	2.789	3.247	3.691	4.122	4.543	4.956	5.755								
1.03	2.766	3.219	3.659	4.086	4.503	4.911	5.703								
1.04	2.742	3.192	3.627	4.050	4.464	4.868	5.653								
1.05	2.719	3.164	3.596	4.015	4.425	4.825	5.603								
1.06	2.697	3.138	3.565	3.981	4.386	4.782	5.553	6.296	7.017						
1.07	2.675	3.111	3.535	3.947	4.348	4.741	5.503	6.241	6.956						
1.08	2.653	3.086	3.505	3.913	4.312	4.701	5.456	6.188	6.896						
1.09	2.632	3.061	3.476	3.881	4.276	4.661	5.410	6.135	6.838						
1.10	2.611	3.036	3.448	3.849	4.240	4.623	5.364	6.083	6.780						
1.12	2.571	2.988	3.393	3.787	4.171	4.547	5.276	5.983	6.667						
1.14	2.532	2.942	3.340	3.727	4.105	4.474	5.191	5.886	6.558						
1.16	2.494	2.897	3.289	3.669	4.041	4.404	5.108	5.791	6.451	7.093	7.722				
1.18	2.458	2.854	3.239	3.613	3.979	4.336	5.029	5.700	6.349	6.981	7.598				
1.20	2.423	2.813	3.191	3.559	3.919	4.270	4.952	5.612	6.251	6.873	7.481				
1.3	2.265	2.626	2.975	3.316	3.648	3.972	4.602	5.213	5.804	6.380	6.942				
1.4	2.132	2.467	2.791	3.107	3.416	3.718	4.303	4.871	5.420	5.956	6.478				
1.5	2.018	2.330	2.633	2.928	3.216	3.498	4.045	4.575	5.088	5.589	6.077				
1.6	1.920	2.212	2.496	2.773	3.043	3.307	3.820	4.317	4.798	5.267	5.725	7.887			
1.7	1.835	2.110	2.376	2.636	2.890	3.139	3.622	4.090	4.543	4.985	5.416	7.451			
1.8	1.761	2.019	2.271	2.516	2.756	2.991	3.447	3.889	4.317	4.734	5.142	7.061	8.844		
1.9	1.696	1.940	2.178	2.410	2.637	2.859	3.291	3.710	4.115	4.510	4.897	6.718	8.405		

Table I. (Contd.)

$Z_c = 0.302$ (Helium)

Table 1 (Contd.) $Z_c = 0.302$ (Helium)

P_r T_r	2.6	2.8	3.0	3.5	4.0	4.5	5.0	6	7	8	9	10	15	20
2.0	0.855	0.846	0.837	0.820	0.808	0.802	0.801	0.808	0.826	0.855	0.890	0.930	1.162	1.402
2.5	0.928	0.923	0.919	0.909	0.901	0.896	0.893	0.893	0.900	0.914	0.932	0.952	1.094	1.264
3.0	0.964	0.962	0.960	0.955	0.951	0.948	0.946	0.945	0.948	0.956	0.966	0.979	1.075	1.198
4	0.996	0.996	0.996	0.995	0.995	0.996	0.997	0.999	1.002	1.008	1.014	1.022	1.077	1.150
5	1.007	1.008	1.008	1.010	1.012	1.014	1.015	1.020	1.024	1.030	1.036	1.042	1.083	1.136
6	1.012	1.012	1.013	1.016	1.018	1.020	1.023	1.028	1.033	1.039	1.045	1.051	1.086	1.128
8	1.014	1.015	1.016	1.018	1.021	1.024	1.026	1.032	1.037	1.043	1.048	1.054	1.084	1.116
10	1.013	1.014	1.015	1.018	1.020	1.023	1.025	1.030	1.035	1.040	1.046	1.051	1.077	1.104
15	1.010	1.011	1.012	1.014	1.016	1.018	1.020	1.024	1.028	1.032	1.036	1.040	1.060	1.080
20	1.008	1.009	1.010	1.011	1.013	1.014	1.016	1.019	1.022	1.025	1.028	1.032	1.047	1.063
25	1.007	1.007	1.008	1.009	1.010	1.012	1.013	1.016	1.018	1.021	1.023	1.026	1.039	1.051
30	1.006	1.006	1.006	1.008	1.009	1.010	1.011	1.013	1.015	1.017	1.019	1.022	1.032	1.043
35	1.005	1.005	1.006	1.006	1.007	1.008	1.009	1.011	1.013	1.015	1.017	1.018	1.028	1.037
40	1.004	1.005	1.005	1.006	1.007	1.007	1.008	1.010	1.011	1.013	1.015	1.016	1.024	1.032
45	1.004	1.004	1.004	1.005	1.006	1.006	1.007	1.009	1.010	1.011	1.013	1.014	1.021	1.028
50	1.003	1.004	1.004	1.004	1.005	1.006	1.007	1.008	1.009	1.010	1.012	1.013	1.019	1.025
60	1.003	1.003	1.003	1.004	1.004	1.005	1.005	1.006	1.007	1.008	1.009	1.010	1.016	1.021
70	1.002	1.002	1.003	1.003	1.003	1.004	1.004	1.005	1.006	1.007	1.008	1.009	1.013	1.017
80	1.002	1.002	1.002	1.003	1.003	1.003	1.004	1.005	1.005	1.006	1.007	1.008	1.011	1.015
90	1.002	1.002	1.002	1.003	1.003	1.003	1.003	1.004	1.005	1.005	1.006	1.007	1.010	1.013
100	1.001	1.002	1.002	1.002	1.002	1.003	1.003	1.004	1.004	1.005	1.005	1.006	1.009	1.011
120	1.001	1.001	1.001	1.002	1.002	1.002	1.002	1.003	1.003	1.004	1.004	1.005	1.007	1.009
140	1.001	1.001	1.001	1.001	1.002	1.002	1.002	1.002	1.003	1.003	1.003	1.004	1.006	1.008
160	1.001	1.001	1.001	1.001	1.001	1.001	1.002	1.002	1.002	1.003	1.003	1.003	1.005	1.006
180	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.002	1.002	1.002	1.003	1.003	1.004	1.006
200	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.002	1.002	1.002	1.003	1.004	1.005
220	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.002	1.002	1.002	1.002	1.003	1.004
240	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.002	1.002	1.003	1.004
260	1.000	1.000	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.002	1.002	1.003

$\frac{P_r}{T_r}$	25	30	35	40	45	50	60	70	80	90	100	150	200	250	300
2.0	1.639	1.870	2.096	2.316	2.531	2.742	3.152	3.550	3.935	4.311	4.677	6.408	8.011		
2.5	1.441	1.619	1.795	1.968	2.138	2.306	2.632	2.950	3.258	3.559	3.853	5.241	6.528	7.741	8.898
3.0	1.332	1.471	1.611	1.751	1.889	2.026	2.295	2.558	2.814	3.065	3.310	4.470	5.548	6.565	7.538
4	1.235	1.325	1.419	1.515	1.612	1.709	1.902	2.094	2.282	2.468	2.650	3.520	4.334	5.104	5.840
5	1.196	1.261	1.329	1.400	1.472	1.544	1.691	1.838	1.984	2.129	2.273	2.964	3.616	4.236	4.829
6	1.175	1.226	1.280	1.335	1.391	1.448	1.565	1.682	1.800	1.917	2.034	2.603	3.145	3.663	4.160
8	1.150	1.186	1.224	1.263	1.302	1.342	1.424	1.507	1.591	1.674	1.758	2.171	2.571	2.958	3.331
10	1.132	1.161	1.191	1.221	1.252	1.283	1.347	1.411	1.476	1.541	1.605	1.927	2.241	2.546	2.844
15	1.100	1.120	1.140	1.161	1.181	1.202	1.244	1.286	1.328	1.370	1.412	1.619	1.822	2.020	2.213
20	1.078	1.094	1.110	1.125	1.141	1.157	1.188	1.219	1.251	1.282	1.314	1.468	1.619	1.765	1.907
25	1.064	1.077	1.089	1.102	1.115	1.127	1.152	1.178	1.203	1.228	1.253	1.376	1.496	1.612	1.725
30	1.054	1.064	1.075	1.085	1.096	1.106	1.127	1.148	1.169	1.190	1.211	1.313	1.413	1.510	1.604
35	1.046	1.055	1.064	1.073	1.082	1.091	1.109	1.127	1.145	1.162	1.180	1.267	1.352	1.435	1.515
40	1.040	1.048	1.056	1.064	1.072	1.079	1.095	1.110	1.126	1.141	1.157	1.232	1.306	1.378	1.448
45	1.035	1.042	1.049	1.056	1.063	1.070	1.084	1.097	1.111	1.125	1.138	1.205	1.270	1.333	1.395
50	1.032	1.038	1.044	1.050	1.056	1.063	1.075	1.087	1.099	1.111	1.123	1.183	1.241	1.297	1.353
60	1.026	1.031	1.036	1.041	1.046	1.051	1.061	1.071	1.081	1.091	1.101	1.149	1.197	1.243	1.288
70	1.022	1.026	1.030	1.035	1.039	1.043	1.051	1.060	1.068	1.076	1.085	1.125	1.165	1.204	1.242
80	1.019	1.022	1.026	1.030	1.033	1.037	1.044	1.051	1.059	1.066	1.073	1.107	1.142	1.175	1.207
90	1.016	1.020	1.023	1.026	1.029	1.032	1.039	1.045	1.051	1.057	1.063				
100	1.014	1.017	1.019	1.023	1.026	1.028	1.034	1.040	1.045	1.051	1.056				
120	1.012	1.014	1.016	1.018	1.021	1.023	1.027	1.032	1.036	1.041	1.045				
140	1.010	1.011	1.013	1.015	1.017	1.019	1.023	1.026	1.030	1.034	1.037				
160	1.008	1.010	1.011	1.013	1.014	1.016	1.019	1.022	1.025	1.028	1.031				
180	1.007	1.008	1.010	1.011	1.012	1.014	1.016	1.019	1.022	1.024	1.027				
200	1.006	1.007	1.008	1.010	1.011	1.012	1.014	1.017	1.019	1.021	1.024				
220	1.005	1.006	1.007	1.009	1.010	1.011	1.013	1.015	1.017	1.019	1.021				
240	1.005	1.006	1.007	1.008	1.008	1.009	1.011	1.013	1.015	1.017	1.018				
260	1.004	1.005	1.006	1.007	1.008	1.008	1.010	1.012	1.013	1.015	1.017				

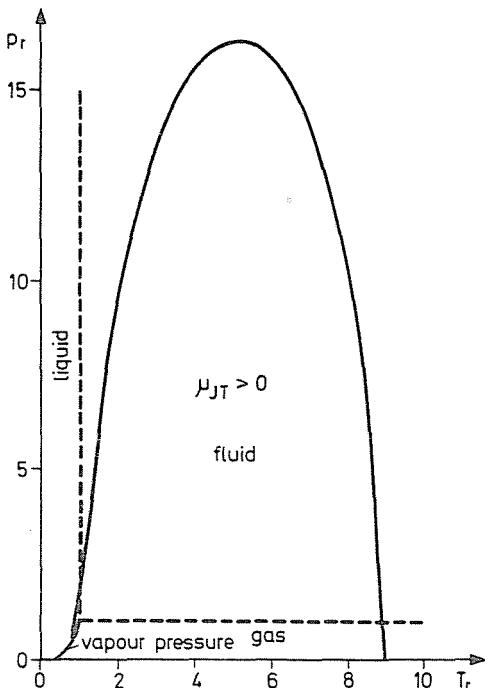


Fig. 1

and air. Because of the extremely low critical pressure and temperature of helium its reduced coefficients can be on the other hand very high. The complete inversion curve of helium could also be drawn.

Interpolation formulae to calculate compressibility coefficients

The isotherms have been produced as a power series of p_r . Maximum fourth order polynomials have been employed. As, however, a complete isotherm cannot be described accurately by a fourth order polynomial the isotherms have been divided into pressure intervals. Taken into consideration the isotherm patterns the following p_r values were taken for constant limits of the intervals: 0.5, 1, 1.25, 1.5, 2, 3, 6, 15 and 50. For each interval the following power series have been defined by least square fitting

$$Z_o = A_o + B_o p_r + C_o p_r^2 + D_o p_r^3 + E_o p_r^4 \quad (1)$$

Between the isotherms one has then to interpolate for the required temperature. For this interpolation quadratic functions have been applied. In the chosen pressure and temperature interval the following interpolation

formula has been used

$$q = p + rT_r + sT_r^2 \quad (2)$$

From the difference of power series belonging to the first and the last isotherm of the temperature interval a new power series ΔZ holding to the whole temperature interval has been obtained

$$\Delta Z = A_d + B_d p_r + C_d p_r^2 + D_d p_r^3 + E_d p_r^4 \quad (3)$$

where $A_d = A_f - A_o$, $B_d = B_f - B_o$, etc. (A_f , B_f , etc. are coefficients of the power series relating to the end of the temperature interval.) From these, for any pressure and temperature

$$Z = Z_o + q\Delta Z \quad (4)$$

In a pressure interval, however, q also varies with the pressure so that p , r and s have to be produced in the function of pressure. These power series of fourth power at maximum are

$$p = A_p + B_p p_r + C_p p_r^2 + D_p p_r^3 + E_p p_r^4 \quad (5)$$

$$r = A_r + B_r p_r + C_r p_r^2 + D_r p_r^3 + E_r p_r^4 \quad (6)$$

$$s = A_s + B_s p_r + C_s p_r^2 + D_s p_r^3 + E_s p_r^4 \quad (7)$$

By chance p and r depend on s so that only s had to be produced by the least square method.

Let us define a relative temperature: $\vartheta = T_r - T_{ro}$. According to Eq. (4) at the beginning of the interval q equals to 0 while at the end it is equal to 1. Introducing this relative temperature

$$q = \rho\vartheta + \sigma\vartheta^2 \quad (8)$$

Substituting ϑ into Eq. (8)

$$\begin{aligned} q &= \rho T_r - \rho T_{ro} + \sigma T_r^2 - 2\sigma T_r T_{ro} + \sigma T_{ro}^2 = T_{ro}(\sigma T_{ro} - \rho) + \\ &\quad + (\rho - 2\sigma T_{ro})T_r + \sigma T_r^2 \end{aligned} \quad (9)$$

Comparing to Eq. (2)

$$p = T_{ro}(\sigma T_{ro} - \rho) \quad (10)$$

$$r = \rho - 2\sigma T_{ro} \quad (11)$$

$$s = \sigma \quad (12)$$

Writing Eq. (8) for the whole interval

$$q = \rho(T_{rf} - T_{ro}) + s(T_{rf} - T_{ro})^2 = 1 \quad (13)$$

Hence

$$\rho = \frac{1}{\Delta T_r} - s \Delta T_r \quad (14)$$

where ΔT_r is the whole temperature interval. Substituting Eq. (14) into Eq. (10) and (11)

$$p = T_{ro} \left(s T_{rf} - \frac{1}{\Delta T_r} \right) \quad (15)$$

$$r = \frac{1}{\Delta T_r} - s(T_{ro} + T_{rf}) \quad (16)$$

The coefficients of power series (5) and (6), respectively, are equal to

$$A_p = T_{ro} \left(A_s T_{rf} - \frac{1}{\Delta T_r} \right); \quad B_p = T_{ro} T_{rf} B_s; \quad C_p = T_{ro} T_{rf} C_s; \quad \text{etc.} \quad (17)$$

$$A_r = \frac{1}{\Delta T_r} - A_s(T_{ro} + T_{rf}); \quad B_r = -B_s(T_{ro} + T_{rf}); \quad \text{etc.} \quad (18)$$

The inversion temperature

The Joule–Thomson coefficient is defined as

$$\mu_{JT} = \frac{RT_r T}{C_{mp}} \left(\frac{\partial Z}{\partial T_r} \right)_{p_r}. \quad (19)$$

Differentiating Eq. (4) and substituting it into Eq. (19)

$$\mu_{JT} = \frac{RT_r T}{C_{mp}} \frac{dq}{dT_r} \Delta Z. \quad (20)$$

At the inversion temperature the Joule–Thomson coefficient is 0 what is fulfilled when $dq/dT_r = 0$. After differentiating the condition of limiting value, according to Eq. (2)

$$T_{ri} = - \frac{r}{2s} \quad (21)$$

Substituting Eq. (16) into Eq. (21)

$$T_{ri} = \frac{(T_{rf}^2 - T_{ro}^2)s - 1}{2s\Delta T_r} \quad (22)$$

that is

$$T_{ri} - T_{ro} = \frac{(\Delta T_r)^2 s - 1}{2s\Delta T_r} \equiv \vartheta_i \quad (23)$$

It means that if there are inversion temperatures in a given pressure and temperature interval s cannot be chosen arbitrarily but according to Eq. (23)

$$s = \frac{1}{(\Delta T_r)^2 - 2\vartheta_i \Delta T_r} \quad (24)$$

The choice of temperature intervals and the diminishing of the pressure intervals

The temperature intervals have been chosen to obtain the compressibility coefficients, applying Eq. (2), whith a maximum error of 2%. In the sense of the same requirement the pressure intervals had also to be diminished even inside the pressure limits given earlier, particularly near to the critical pressure ($p_r=1$) or in the region of the isotherm minima. The reproduction of the inversion temperatures, however, laid also further requirements. As p and r depend on s the temperature change of the compressibility coefficients along an isobar had to be characterized only by s . Applying the least square method to Eq. (8)

$$\frac{d}{dp} \sum (q - \rho\vartheta - s\vartheta^2)^2 = 0 \quad (25)$$

$$\sum q\vartheta = \rho \sum \vartheta^2 + s \sum \vartheta^3 = \frac{\sum \vartheta^2}{\Delta T_r} - s \Delta T_r \sum \vartheta^2 + s \sum \vartheta^3 \quad (26)$$

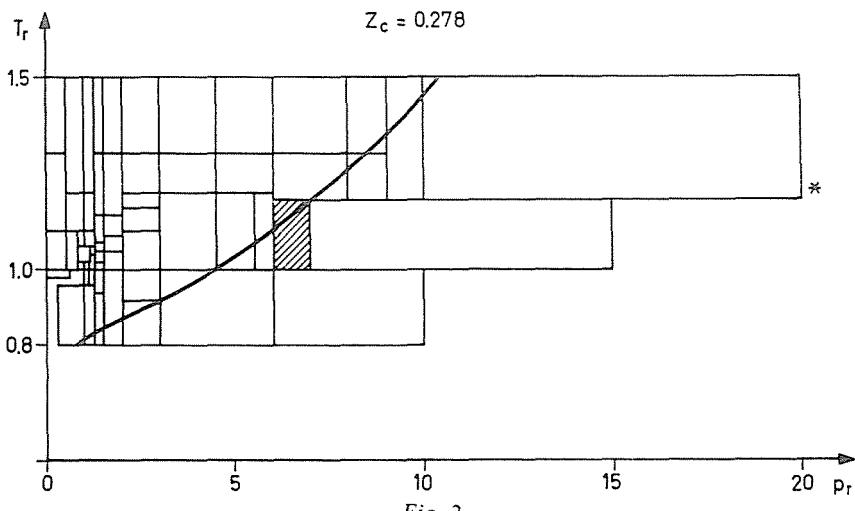


Table 2

	A	B	C	D	E
Z_0	0.029	0.146672	$-4.0364 \cdot 10^{-3}$	$1.79 \cdot 10^{-4}$	$-3.418 \cdot 10^{-6}$
Z	0.1721	-0.044301	$3.5077 \cdot 10^{-3}$	$-1.8094 \cdot 10^{-4}$	$3.534 \cdot 10^{-6}$
p	-1206623.889	689441.2444	-147735.1882	14070.01792	-502.50064
r	2229181.799	-1273713.485	272934.5002	-25993.76192	928.34864
s	-1022557.91	584272.241	-125199.312	11923.744	-425.848

For $p_r=6$ s equals to -470 and $\vartheta_i=0.0959$. As $T_r=1$ in this interval, T_r^i will be 1.00959.

Hence

$$s = \frac{\Sigma \vartheta - \frac{\Sigma \vartheta^2}{\Delta T_r}}{\Sigma \vartheta^3 - \Delta T_r \Sigma \vartheta^2} \quad (27)$$

The s parameters determined for different isobars could be constructed as a power series of p_r (see Eq. (7)).

The intervals had to be diminished not only because of the not satisfying accuracy of power series (1), (2) and (7) but also in order to describe precisely the inversion curve. Eq. (2) is a quadratic function which equals to 0 at the beginning and to 1 at the end of the interval so that a minimum can occur only in the first half and a maximum only in the second half of the interval. In addition, in the given pressure interval the inversion temperature cannot pass through the middle of the temperature interval changing the pressure because at this point $\vartheta_i = \Delta T_r/2$ and according to Eq. (24) $s = \infty$ jumping from $+\infty$ into $-\infty$ or reversely by changing pressure. Obviously this cannot be described by a quartic function. Fig. 2 shows the intervals chosen according to such principles for fluids characterized by $Z_c=0.278$. The inversion curve is also drawn in the figure. Table 2 gives the coefficients of power series (1), (3), (5), (6) and (7) for the striped field in the figure as an example.

Calculation of fugacity

The logarithm of the fugacity coefficient

$$\ln \varphi = \int_0^{p_r} \frac{Z-1}{p_r} dp_r \quad (28)$$

One can analytically integrate along an isotherm in every pressure interval. Replacing Z by Eq. (4), applying Eqs (1)-(7) and denoting the beginnings of

the pressure intervals by p_{ro}

$$\begin{aligned} \ln \varphi = & \sum_{p_r < p_{ro}} \ln \varphi + a \ln \frac{p_r}{p_{ro}} + b(p_r - p_{ro}) + c(p_r^2 - p_{ro}^2) + d(p_r^3 - p_{ro}^3) + \\ & + e(p_r^4 - p_{ro}^4) + f(p_r^5 - p_{ro}^5) + g(p_r^6 - p_{ro}^6) + h(p_r^7 - p_{ro}^7) + \\ & + i(p_r^8 + p_{ro}^8) \end{aligned} \quad (29)$$

where the sum adds the integrals calculated for the intervals belonging to lower pressures than the given one. The coefficients are

$$a = A_o - 1 + A_d(A_p + A_r T_r + A_s T_r^2) \quad (30a)$$

$$b = B_o + A_d(B_p + B_r T_r + B_s T_r^2) + B_d(A_p + A_r T_r + A_s T_r^2) \quad (30b)$$

$$\begin{aligned} c = & \frac{1}{2} [C_o + A_d(C_p + C_r T_r + C_s T_r^2) + B_d(B_p + B_r T_r + B_s T_r^2) + \\ & + C_d(A_p + A_r T_r + A_s T_r^2)] \end{aligned} \quad (30c)$$

$$\begin{aligned} d = & \frac{1}{3} [D_o + A_d(D_p + D_r T_r + D_s T_r^2) + B_d(C_p + C_r T_r + C_s T_r^2) + \\ & + C_d(B_p + B_r T_r + B_s T_r^2) + D_d(A_p + A_r T_r + A_s T_r^2)] \end{aligned} \quad (30d)$$

$$\begin{aligned} e = & \frac{1}{4} [E_o + A_d(E_p + E_r T_r + E_s T_r^2) + B_d(D_p + D_r T_r + D_s T_r^2) + \\ & + C_d(C_p + C_r T_r + C_s T_r^2) + D_d(B_p + B_r T_r + B_s T_r^2) + \\ & + E_d(A_p + A_r T_r + A_s T_r^2)] \end{aligned} \quad (30e)$$

$$\begin{aligned} f = & \frac{1}{5} [B_d(E_p + E_r T_r + E_s T_r^2) + C_d(D_p + D_r T_r + D_s T_r^2) + \\ & + D_d(C_p + C_r T_r + C_s T_r^2) + E_d(B_p + B_r T_r + B_s T_r^2)] \end{aligned} \quad (30f)$$

$$\begin{aligned} g = & \frac{1}{6} [C_d(E_p + E_r T_r + E_s T_r^2) + D_d(D_p + D_r T_r + D_s T_r^2) + \\ & + E_d(C_p + C_r T_r + C_s T_r^2)] \end{aligned} \quad (30g)$$

$$h = \frac{1}{7} [D_d(E_p + E_r T_r + E_s T_r^2) + E_d(D_p + D_r T_r + D_s T_r^2)] \quad (30h)$$

$$i = \frac{1}{8} E_d(E_p + E_r T_r + E_s T_r^2) \quad (30i)$$

In the first pressure interval one has to integrate from 0. In Eq. (29) the coefficient of the unintegrable logarithmic term is a . Of, however, the lower limit of the pressure interval is 0 then A_o equals to 1 and A_d to 0 so that $a=0$.

Calculation of pressure dependence of enthalpy

The pressure dependence of the enthalpy for gases and fluids is given by the expression

$$\frac{H^\square - H}{RT_c} = T_r^2 \int_0^{p_r} \left(\frac{\partial Z}{\partial T_r} \right)_{p_r} d \ln p_r \quad (31)$$

where H^\square stands for the molar enthalpy of the perfect gas at the given temperature. By taken into consideration Eq. (4)

$$\frac{H^\square - H}{RT_c} = T_r^2 \int_0^{p_r} \left(\frac{\partial q}{\partial T_r} \right)_{p_r} \Delta Z d \ln p_r \quad (32)$$

Applying formulae (1)–(7)

$$\begin{aligned} \frac{H^\square - H}{RT_c} = T_r^2 & \left[\sum_{p_r < p_{ro}} \frac{H^\square - H}{RT_c} + \right. \\ & a' \ln \frac{p_r}{p_{ro}} + b'(p_r - p_{ro}) + c'(p_r^2 - p_{ro}^2) + \\ & + d'(p_r^3 - p_{ro}^3) + e'(p_r^4 - p_{ro}^4) + f'(p_r^5 + p_{ro}^5) + \\ & \left. + g'(p_r^6 - p_{ro}^6) + h'(p_r^7 - p_{ro}^7) + i'(p_r^8 - p_{ro}^8) \right] \end{aligned} \quad (33)$$

The coefficients are the following

$$a' = A_d(A_r + 2A_s T_r) \quad (34a)$$

$$b' = A_d(B_r + 2B_s T_r) + B_d(A_r + 2A_s T_r) \quad (34b)$$

$$c' = \frac{1}{2} [A_d(C_r + 2C_s T_r) + B_d(B_r + 2B_s T_r) + C_d(A_r + 2A_s T_r)] \quad (34c)$$

$$\begin{aligned} d' = \frac{1}{3} & [A_d(D_r + 2D_s T_r) + B_d(C_r + 2C_s T_r) + C_d(B_r + 2B_s T_r) + \\ & + D_d(A_r + 2A_s T_r)] \end{aligned} \quad (34d)$$

$$\begin{aligned} e' = \frac{1}{4} & [A_d(E_r + 2E_s T_r) + B_d(D_r + 2D_s T_r) + C_d(C_r + 2C_s T_r) + \\ & + D_d(B_r + 2B_s T_r) + E_d(A_r + 2A_s T_r)] \end{aligned} \quad (34e)$$

$$f' = \frac{1}{5} [B_d(E_r + 2E_s T_r) + C_d(D_r + 2D_s T_r) + D_d(C_r + 2C_s T_r) + E_d(B_r + 2B_s T_r)] \quad (34f)$$

$$g' = \frac{1}{6} [C_d(E_r + 2E_s T_r) + D_d(D_r + 2D_s T_r) + E_d(C_r + 2C_s T_r)] \quad (34g)$$

$$h' = \frac{1}{7} [D_d(E_r + 2E_s T_r) + E_d(D_r + 2D_s T_r)] \quad (34h)$$

$$i' = \frac{1}{8} E_d(E_r + 2E_s T_r) \quad (34i)$$

Computer program for calculation of Z , φ and H

Two programs have been constructed, one for calculation of Z and another for φ and H . The selection of the programs was straightforward because when φ and H are calculated one has to omit the ranges in which the substance is liquid. Input data for the first program are: p_c , T_c , Z_c , T , S (if $T < T_c$), u and or p or V . For liquids $S=1$, for gases it is 2. If p is an input parameter $u=1$ whereas when V is an input datum $u=2$. In the latter case the program searches the point of intersection between the isotherm and the straight line $Z = Z_c p_r V_r / T_r$ by successive approximation. Formulae (1)–(7) have been calculated for four fluids of different critical compressibility coefficients namely for $Z_c = 0.244, 0.278, 0.290$ and 0.302 . In the latest case compressibility coefficients of helium have been used. The program (if it finds enough data) calculates the compressibility coefficients for all four types (Z_1, Z_2, Z_3 and Z_4). If, however, $Z_c < 0.278$ Z_4 is not calculated but the program interpolates between the first three types. For this interpolation again a quadratic function has been applied. In lack of many data, however, the coefficients have not been determined by the least square method but the quadratic function has been laid on three fix points

$$k = m(Z_c - Z_{c1}) + n(Z_c - Z_{c1})^2 \quad (35)$$

where $k = (Z - Z_1)/(Z_3 - Z_1)$. It follows from this definition that

$$m(Z_{c3} - Z_{c1}) + n(Z_{c3} - Z_{c1})^2 = 1.$$

Hence

$$m = \frac{1}{\Delta Z_c} - n \Delta Z_c \quad (36)$$

Substituting into Eq. (35)

$$k = \zeta + n(Z_c - Z_{c1})(Z_c - Z_{c1} - Z_{c3} + Z_{c1}) \quad (37)$$

where $\zeta = (Z_c - Z_{c1})/4Z_c$. Substituting into Eq. (37) Z_2 calculated for a fluid of critical compressibility coefficient Z_{c2} n can be expressed

$$n = \frac{\zeta_2 - k_2}{(Z_{c2} - Z_{c1})(Z_{c3} - Z_{c2})} \quad (38)$$

It follows from the nature of the compressibility isotherms that at higher pressures the ratio of the compressibility coefficients of fluids with different Z_c values depends no more on pressure. This has allowed the extrapolation of Eq. (38) for higher pressures also in the lack of data for Z_2 . Obviously the ratio of compressibility coefficients determined for identical reduced pressure and temperature varies with the temperature. This change can be described by a linear function. Thus, for these regions n has been obtained as a linear function of the temperature. As an example the interpolation formula relating to the field marked by an asterisk in Fig. 2 is given

$$\begin{aligned} Z = Z_1 + & [181.9 - 192.4 T_r + (1425 T_r - 1362) Z_c + \\ & +(2526 - 2610 T_r) Z_c^2] (Z_4 - Z_1) \end{aligned} \quad (39)$$

The second program calculates φ and H . Its input data are: p_c , T_c , Z_c , p , T and u . If we are interested only in the fugacity coefficient $u=1$, if only in the enthalpy $u=2$ and if both are interesting $u=3$. The program calculates formulae (29)–(30) or (33)–(34) for the four types of fluids. The interpolation between these relies on the same ground, evidently the coefficients in the formulae are different (like in the first program, the coefficients depend on the value of u (1 or 2)).

Acknowledgement

The author is grateful to Mrs. K. Réé for transferring programs on computer.

Literature

1. VARSÁNYI, Gy.: A Revised Reduced Compressibility Chart and Fugacity Diagram for Fluids. Periodica Polytechnica 32, 4, 277 (1988).
2. International Thermodynamic Tables of the Fluid State. Vol 4. Series CDS. Edited and compiled by Angus, S., de Reuck, K. M. and Armstrong, B. Pergamon Press 1977 London, New York.

Prof. Dr. György VARSÁNYI H-1521 Budapest