

Correlation constants for chemical compounds

Procedures to speed calculations for:

- Heat capacities
- Heats of formation
- Free energies of formation
- Heats of vaporization

Carl L. Yaws, Lamar University, and others*

□ Correlation constants in an easy-to-use tabular format are especially applicable for rapid engineering usage with the hand calculator or computer. The constants are based on extensive documentation and scores of experimental data. Margins of statistical accuracy are noted for each chemical listed.

For gas-phase properties, extrapolation to lower (200 K) and higher (1,500 K) temperatures provides

reliable results. Extrapolation for liquid-phase properties is not required in most cases because the temperature range covers melting point to critical point.

The tabulated constants may be used in various activities associated with the chemical process industries, such as chemical-reaction engineering, thermodynamics, fluid flow, heat transfer, mass transfer and process design.

HEAT CAPACITIES OF GAS

Robin W. Borreson, Gordon R. Schorr and Carl L. Yaws

The heat capacity of major chemicals is important for engineering design in the chemical process industries. For example, in gas-phase chemical reactions, heat capacities for the gas are required to determine the energy (heat) necessary to bring the chemical compound up to reaction temperature. Additional usage includes heat-exchanger and energy-balance design calculations. The heat capacity of mixtures may be determined from the heat capacities of the individual components contained in the mixtures.

Correlation constants—Table 22—1

The correlation for heat capacity of the ideal gas at low pressure is a series expansion in temperature:

$$C_p^\circ = A + BT + CT^2 + DT^3 \quad (22-1)$$

where C_p° = heat capacity of ideal gas at low pressure, cal/(g-mol)(°K); A , B , C and D = characteristic constants for the chemical compound; and T = temperature, °K.

The correlation constants (A , B , C and D) were determined from a least-squares fit of the available data. The numerous data points were processed with a generalized least-squares computer program for minimizing the deviation.

A comparison of calculated and data values is shown in Fig. 22-1 for a representative chemical. In most cases, average deviations between correlation and data results are less than 0.5%.

Example 22-1—Let us estimate the heat capacity of

*For author biographies, see p. 87.

Correlation constants: heat capacity of ideal gas

Table 22-1

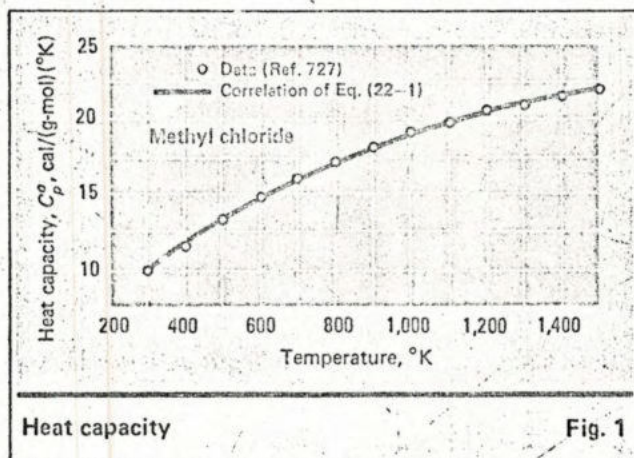
$$C_p^0 = A + BT + CT^2 + DT^3$$

Compound	A	B x 10 ³	C x 10 ⁶	D x 10 ⁹	C _p ⁰ at 298 K, cal/(g-mol)(°K)	Range, °K	Average error, %	Data points, no.	References
Halogens									
Fluorine, F ₂	5.89	6.94	-5.48	1.52	7.51	298-1,500	0.225	59	7,15, 6,18,20
Chlorine, Cl ₂	7.00	5.05	-4.39	1.30	8.15	298-1,500	0.234	60	7,15, 6,18,20
Bromine, Br ₂	8.11	2.32	-2.04	0.62	8.64	298-1,500	0.131	60	7,15, 16,19,20
Iodine, I ₂	8.57	1.13	-0.91	0.27	8.83	298-1,500	0.059	51	7,15, 16,18,20
Sulfur oxides									
Sulfur dioxide, SO ₂	5.85	15.4	-11.1	2.91	9.52	298-1,500	0.33	46	7,15, 17, 546
Sulfur trioxide, SO ₃	3.96	34.6	-26.8	6.96	12.06	298-1,500	2.03	22	7,15
Nitrogen oxides									
Nitrous oxide, N ₂ O	5.64	14.8	-9.68	2.33	9.25	298-1,500	0.142	13	7,15
Nitric oxide, NO	6.93	-0.065	2.23	-0.98	7.08	298-1,500	0.339	13	7,15
Nitrogen dioxide, NO ₂	5.53	13.2	-7.96	1.71	8.80	298-1,500	0.131	13	7,15
Carbon oxides									
Carbon monoxide, CO	6.92	-0.65	2.80	-1.14	6.94	298-1,500	0.244	21	7,15
Carbon dioxide, CO ₂	5.14	15.4	-9.94	2.42	8.91	298-1,500	0.155	21	7,15
Hydrogen halides									
Hydrogen fluoride, HF	7.16	-1.01	1.34	-0.28	6.96	298-1,500	0.093	39	7,11, 15, 34
Hydrogen chloride, HCl	7.24	-1.76	3.07	-1.00	6.96	298-1,500	0.066	47	7,11, 15, 34
Hydrogen bromide, HBr	7.15	-1.52	3.21	-1.13	6.95	298-1,500	0.132	26	7,15, 34
Hydrogen iodide, HI	6.95	-0.76	2.81	-1.09	6.94	298-1,500	0.223	26	7,15, 34
Nitrogen hydrides									
Ammonia, NH ₃	6.07	8.23	-0.16	-0.66	8.49	298-1,500	0.189	28	7,15
Hydrazine, N ₂ H ₄	3.87	35.7	-23.0	5.98	12.63	298-1,500	1.17	47	7,15, 189, 218
Hydrogen oxides									
Water, H ₂ O	8.10	-0.72	3.63	-1.16	8.18	298-1,500	0.438	79	7,15, 18, 646
Hydrogen peroxide, H ₂ O ₂	5.52	19.8	-13.9	3.74	10.28	298-1,500	1.082	63	7,15, 18, 241, 245, 251
Diatomic gases									
Hydrogen, H ₂	6.88	-0.022	0.21	0.13	6.90	298-1,500	0.454	100	7,15, 16, 19, 646
Nitrogen, N ₂	7.07	-1.32	3.31	-1.26	6.94	298-1,500	0.167	100	7,15, 16, 19, 646
Oxygen, O ₂	6.22	2.71	-0.37	-0.22	6.99	298-1,500	0.28	100	7,15, 16, 19, 646
Inert gases									
Helium, He	4.97	-	-	-	4.97	298-1,500	-	-	16, 18
Neon, Ne	4.97	-	-	-	4.97	298-1,500	-	-	16, 18
Argon, Ar	4.97	-	-	-	4.97	298-1,500	-	-	16, 18
Olefins									
Ethylene, C ₂ H ₄	0.934	36.9	-19.3	4.01	10.32	298-1,500	0.415	34	7,11, 15
Propylene, C ₃ H ₆	0.68	56.8	-28.6	5.6	15.26	298-1,500	0.150	17	15, 637
1-Butene, C ₄ H ₈	-0.515	83.1	-45.5	9.8	20.48	298-1,500	0.100	22	15, 646
Alkanes									
Methane, CH ₄	5.04	9.32	8.87	-5.37	8.53	298-1,500	1.635	37	15, 461, 646
Ethane, C ₂ H ₆	2.46	36.1	-7.0	-0.46	12.57	298-1,500	1.010	44	15, 461, 646
Propane, C ₃ H ₈	-0.58	69.9	-32.9	6.54	17.50	298-1,500	0.649	44	15, 461, 646
Xylenes									
<i>o</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	-3.69	142.0	-82.1	19.2	31.85	298-1,500	0.108	22	15, 646
<i>m</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	-6.67	149.0	-87.6	19.55	30.48	298-1,500	0.121	22	15, 646
<i>p</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	-6.3	146.0	-84.4	18.6	30.32	298-1,500	0.136	32	15, 637, 646
Aromatics									
Benzene, C ₆ H ₆	-8.79	116.0	-76.1	18.9	19.50	298-1,500	0.333	91	3, 15, 18, 19, 484
Naphthalene, C ₁₀ H ₈	-13.02	185.0	-126.0	31.9	32.05	298-1,500	0.240	25	3, 15, 637
Alkyl aromatics									
Toluene, C ₆ H ₅ CH ₃	-9.34	138.5	-87.2	20.6	24.73	298-1,500	0.505	21	15, 417
Ethylbenzene, C ₆ H ₅ C ₂ H ₅	-8.42	159.0	-99.5	23.7	30.75	298-1,500	0.186	21	15, 417
Cumene, C ₆ H ₅ CH(CH ₃) ₂	-9.38	165.7	-117.0	28.1	36.26	298-1,500	0.198	35	15, 417, 646
Benzene derivatives									
Chlorobenzene, C ₆ H ₅ Cl	-5.97	123.0	-88.9	24.1	23.43	298-1,000	0.137	10	15, 416
Aniline, C ₆ H ₅ NH ₂	-8.11	143.4	-107.0	30.7	25.93	298-1,000	0.149	10	15, 416
Phenol, C ₆ H ₅ OH	-5.68	126.0	-85.4	20.5	24.82	298-1,000	0.236	10	15, 416, 418
Cycloalkanes									
Cyclopropane, C ₃ H ₆	-6.20	79.8	-50.5	12.2	13.36	298-1,000	0.197	18	5, 416, 637
Cyclobutane, C ₄ H ₈	-9.0	105.0	-62.9	14.5	17.25	298-1,500	0.153	19	5, 416, 637
Cyclopentane, C ₅ H ₁₀	-13.4	132.5	-76.09	16.8	19.82	298-1,500	0.206	24	15, 416, 646
Cyclohexane, C ₆ H ₁₂	-16.2	165.0	-91.3	18.8	25.41	298-1,500	0.294	24	15, 416, 646
Olefin monomers									
Isobutylene, C ₄ H ₈	1.22	79.5	-43.2	9.35	21.31	298-1,500	0.315	22	15, 646
Styrene, C ₆ H ₅ CH=CH ₂	-7.22	150.0	-99.9	25.2	29.17	298-1,500	0.134	26	15, 611, 637

Correlation constants: heat capacity of ideal gas (continued)

Table 22-1

Compound	$C_p^o = A + BT + CT^2 + DT^3$				C_p^o at 298 K, cal/(g-mol)(°K)	Range, °K	Average error, %	Data points, no.	References
	A	$B \times 10^3$	$C \times 10^6$	$D \times 10^9$					
Diolefins									
1,3 Butadiene, C_4H_6	-0.56	81.1	-53.5	13.6	19.21	298-1,500	0.434	34	15,417,636
Isoprene, C_5H_8	0.63	100.5	-64.0	15.8	25.31	298-1,500	0.395	34	15,417,636
Chloroprene, C_4H_5Cl	2.93	75.6	-48.3	11.8	21.5			est.	
Organic oxides									
Ethylene oxide, C_2H_4O	-2.06	54.4	-32.1	7.31	11.53	298-1,500	0.182	28	7,15,637
Propylene oxide, C_3H_6O	-3.57	86.4	-61.6	18.5	17.20	298-1,000	0.314	24	15,649,654
Butylene oxide, C_4H_8O	-2.81	97.9	-48.6	6.1	22.2			est.	
Primary alcohols									
Methanol, CH_3OH	3.62	24.9	-7.05		10.49	298-1,000	0.429	35	15,416,418,637,692
Ethanol, C_2H_5OH	0.239	62.3	-38.06	9.47	15.64	298-1,500	1.357	33	15,418,637,692
<i>n</i> -Propanol, C_3H_7OH	2.71	68.6	-27.0	1.51	20.82	298-1,000	0.137	28	15,416,418,692
<i>n</i> -Butanol, C_4H_9OH	2.51	91.1	-39.6	4.09	26.29	298-1,000	0.131	26	15,418,692
Chloromethanes									
Methyl chloride, CH_3Cl	2.96	26.2	-12.6	2.35	9.74	298-1,500	0.127	49	7,15,418,727
Methylene chloride, CH_2Cl_2	4.3	32.7	-21.6	5.4	12.13	298-1,500	0.274	49	7,15,418,727
Chloroform, $CHCl_3$	7.71	34.3	-26.4	7.29	15.78	298-1,500	0.394	34	15,418,727
Carbon tetrachloride, CCl_4	12.6	33.2	-29.3	8.58	20.12	298-1,500	0.618	34	15,418,727



methane (CH_4) as a low-pressure gas at 25 C (298.16 K).

We obtain the correlation constants (A , B , C , D) for methane from Table 22-I and substitute them into Eq. (22-1) at a temperature of 298.16 K to get:

$$C_p^o = 5.04 + 9.3 \times 10^{-3}(298.16) + 8.87 \times 10^{-6}(298.16)^2 - 5.4 \times 10^{-9}(298.16)^3$$

$$C_p^o = 8.46 \text{ cal/(g-mol)(°K)}$$

The calculated and data values compare favorably (8.46 vs. 8.53).

Example 22-2—Let us now calculate the energy required to heat chlorine (Cl_2) from 25 C to 225 C at low pressure.

From thermodynamics, we recall that the change in enthalpy, ΔH , at constant pressure is:

$$\Delta H = \int_{T_1}^{T_2} C_p^o dT$$

$$\Delta H = \int_{T_1}^{T_2} (A + BT + CT^2 + DT^3) dT$$

$$\Delta H = \left[AT + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4 \right]_{T_1}^{T_2}$$

By substituting the correlation constants (A , B , C , D) for chlorine from Table 22-I and the temperature limits, ($T_2 = 498.16$ K) and ($T_1 = 298.16$ K) into the equation, we obtain:

$$\begin{aligned} \Delta H = & 7.00[498.16 - 298.16] + \\ & \frac{5.05 \times 10^{-2}}{2}[(498.16)^2 - (298.16)^2] - \\ & \frac{4.39 \times 10^{-9}}{3}[(498.16)^3 - (298.16)^3] + \\ & \frac{1.30 \times 10^{-9}}{4}[(498.16)^4 - (298.16)^4] \end{aligned}$$

$$\Delta H = 1,667.5 \text{ cal/g-mol}$$

HEATS OF FORMATION

L. David Hood and Carl L. Yaws

Heats of formation for individual chemicals in chemical reactions are required to determine the heat of reaction, ΔH_r^o , and associated heating and cooling requirements. If $\Delta H_r^o < 0$, then the chemical reaction is

exothermic and cooling is needed. If $\Delta H_r^o > 0$, the reaction is endothermic and heating is required. Agreement of calculated and data values for this procedure is very good.

Correlation constants: heat of formation of ideal gas

Table 22-11

Compound	$\Delta H_f^\circ = A + BT + CT^2$			ΔH_f° at 298 K, kcal/mol	Range, °K	Average error (absolute), kcal/mol	Data points, no.	References
	A	B x 10 ³	C x 10 ⁶					
Sulfur oxides								
Sulfur dioxide, SO ₂	-69.6	-5.29	-	-70.95	298-717	0.135	14	7,15
	-86.9	0.32	-	-86.6 @ 800K	717-1,500	0.008	11	7,15
Sulfur trioxide, SO ₃	-93.1	-5.34	-	-94.6	298-717	0.146	14	7,15
	-110.5	0.80	-	-110.1 @ 800	717-1,500	0.199	11	7,15
Nitrogen oxides								
Nitrous oxide, N ₂ O	13.1	0.803	-	19.5	298-1,500	0.114	23	7,15
Nitric oxide, NO	21.6	0.0036	-	21.6	298-1,500	0.010	23	7,15
Nitrogen dioxide, NO ₂	7.94	-0.178	-	8.00	298-1,500	0.097	23	7,15
Carbon oxides								
Carbon monoxide, CO	-26.5	0.84	-1.05	-26.4	298-1,500	0.040	23	7,15
Carbon dioxide, CO ₂	-93.9	-0.43	-	-94.05	298-1,500	0.019	23	7,15
Hydrogen halides								
Hydrogen fluoride, HF	-64.6	-0.801	-	-64.9	298-1,500	0.160	37	7,15
Hydrogen chloride, HCl	-21.9	-0.610	-	-22.05	298-1,500	0.031	37	7,15
Hydrogen bromide, HBr	-8.13	20.1	-73.4	-8.69	100-331	0.017	6	7,15
	-12.0	-1.35	0.45	-12.5 @ 400	331-1,500	0.016	19	7,15
Hydrogen iodide, HI	7.02	-2.42	-	6.3	299-386	0.011	6	7,15
	7.12	-7.67	-	4.06 @ 400	386-457	0.005	4	7,15
	-0.85	-1.24	0.45	-1.55 @ 800	457-1,500	0.005	17	7,15
Nitrogen hydrides								
Ammonia, NH ₃	-9.34	-6.20	2.36	-10.9	298-1,500	0.036	22	7,15
Hydrazine, N ₂ H ₄	24.7	-8.01	4.02	22.8	298-1,500	0.124	37	7,15,218
Hydrogen oxides								
Water, H ₂ O	-57.4	-1.79	-	-57.8	298-1,500	0.0822	23	7,15
Hydrogen peroxide, H ₂ O ₂	-31.8	-3.04	1.19	-32.5	298-1,500	0.043	37	7,15,245
Olefins								
Ethylene, C ₂ H ₄	14.8	-8.81	3.15	12.53	298-1,500	0.051	51	7,11,15,417,637
Propylene, C ₃ H ₆	8.44	-13.8	5.31	4.86	298-1,500	0.076	37	15,417,637
1-Butene, C ₄ H ₈	4.53	-17.5	7.22	-0.03	298-1,500	0.305	37	15,417,637
Alkanes								
Methane, CH ₄	-15.4	-9.59	3.50	-17.9	298-1,500	0.042	36	15,461,637
Ethane, C ₂ H ₆	-16.4	-14.8	6.13	-20.1	298-1,500	0.35	48	15,461,447,637
Propane, C ₃ H ₈	-20.0	-19.1	8.15	-24.9	298-1,500	0.17	49	15,447,401,637
Xylenes								
<i>o</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	10.5	-23.4	9.95	4.54	298-1,500	0.102	22	15,417
<i>m</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	10.4	-24.6	10.5	4.12	298-1,500	0.118	22	15,417
<i>p</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	10.7	-25.1	10.6	4.29	298-1,500	0.115	22	15,417
Aromatics								
Benzene, C ₆ H ₆	23.7	-15.3	6.27	19.8	298-1,500	0.092	22	15,417,637
Naphthalene, C ₁₀ H ₈	41.5	-21.1	10.1	36.1	298-1,000	0.135	18	15,502
Alkyl aromatics								
Toluene, C ₆ H ₅ CH ₃	16.8	-19.0	7.84	11.95	298-1,500	0.166	22	15,417
Ethylbenzene, C ₆ H ₅ C ₂ H ₅	13.1	-23.5	10.2	7.12	298-1,500	0.129	22	15,417
Cumene, C ₆ H ₅ CH(CH ₃) ₂	7.80	-27.2	12.1	0.940	298-1,500	0.162	22	15,417
Benzene derivatives								
Chlorobenzene, C ₆ H ₅ Cl	15.7	-13.0	6.40	12.39	298-1,000	0.028	9	15
Aniline, C ₆ H ₅ NH ₂	25.2	-17.6	8.98	20.76	298-1,000	0.046	9	15
Phenol, C ₆ H ₅ OH	-19.3	-14.6	7.18	-23.0	298-1,000	0.036	9	15
Cycloalkanes								
Cyclopropane, C ₃ H ₆	16.9	-16.7	7.90	12.74	298-1,000	0.064	18	15,637
Cyclobutane, C ₄ H ₈	12.6	-24.8	12.4	6.37	298-1,000	0.042	9	15
Cyclopentane, C ₅ H ₁₀	-11.5	-27.8	12.3	-18.47	298-1,500	0.226	50	15,531,417,637
Cyclohexane, C ₆ H ₁₂	-21.6	-32.0	15.8	-29.43	298-1,500	0.328	37	15,417,637
Olefin monomers								
Isobutylene, C ₄ H ₈	0.560	-17.9	7.41	-4.04	298-1,500	0.058	22	15,417
Styrene, C ₆ H ₅ CH=CH ₂	39.6	-17.2	7.32	35.22	298-1,500	0.097	22	15,417
Diolefins								
1,3-Butadiene, C ₄ H ₆	29.0	-10.1	4.13	26.5	298-1,500	0.234	48	15,417,630,636
Isoprene, C ₅ H ₈	21.8	-14.4	6.16	18.1	298-1,500	0.079	35	15,417,636
Chloroprene, C ₄ H ₅ Cl	27.8	-12.1	3.78	21.02	298-1,500	-	-	Estimated
Organic oxides								
Ethylene oxide, C ₂ H ₄ O	-9.29	-12.9	6.12	-12.59	298-1,000	0.022	9	15
Propylene oxide, C ₃ H ₆ O	-17.7	-17.3	6.40	-22.1	298-1,000	0.099	27	15,449,654
Butylene oxide, C ₄ H ₈ O	-22.1	-19.5	8.29	-27.4	298-1,500	-	-	Estimated

Compound	$\Delta H_f^\circ = A + BT + CT^2$			ΔH_f° at 298 K, kcal/mol	Range, °K	Average error (absolute), kcal/mol	Data points, no.	References
	A	B x 10 ³	C x 10 ⁶					
Primary alcohols								
Methanol, CH ₃ OH	-44.96	-11.9	4.98	-48.08	298-1,000	0.015	35	15,418,692
Ethanol C ₂ H ₅ OH	-51.8	-16.6	7.59	-56.12	298-1,000	0.043	27	15,418,692
n-Propanol, C ₃ H ₇ OH	-55.7	-22.3	10.5	-61.55	298-1,000	0.110	27	15,418,692
n-Butanol, C ₄ H ₉ OH	-59.8	-26.9	12.8	-65.59	298-1,000	0.0365	27	15,418,692
Chloromethanes								
Methyl chloride, CH ₃ Cl	-19.9	-2.57	-	-20.2	298-1,500	0.549	51	7,15,418,727
Methylene chloride, CH ₂ Cl ₂	-21.5	-5.13	2.15	-22.8	298-1,500	0.048	51	7,15,418,727
Chloroform, CHCl ₃	-24.7	0.0334	-	-24.5	298-1,500	0.179	37	15,418,727
Carbon tetrachloride, CCl ₄	-24.0	2.42	-	-23.5	298-1,500	0.358	37	15,418,727

Correlation constants—Table 22-II

The correlation for heat of formation of the ideal gas at low pressure is based on a series expansion in temperature:

$$\Delta H_f^\circ = A + BT + CT^2 \quad (22-2)$$

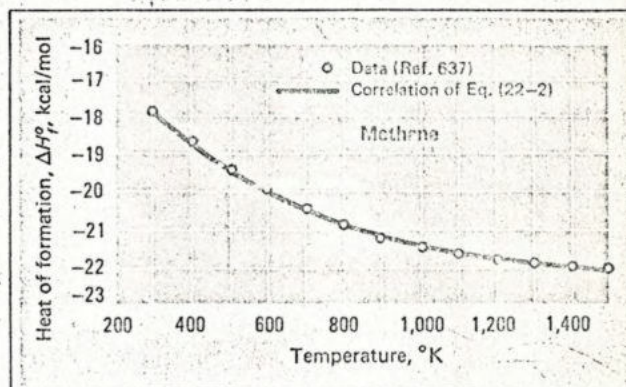
where ΔH_f° = heat of formation of ideal gas at low pressure, kcal/g-mol; A , B , C = correlation constants characteristic for the chemical compound; and T = temperature, °K.

A least squares regression analysis of the available data was used to determine the constants A , B and C . A generalized least-squares regression computer program for minimizing deviation was used to process the numerous data points.

Correlation and data values are compared in Fig. 22-2 for a representative chemical compound. The agreement is quite good. In most cases, the average absolute deviations of correlation and data are less than 0.2 kcal/g-mol.

Example 22-3—Let us estimate the heat of formation of ethylene (C₂H₄) as an ideal gas at 400 K.

Substituting the values of the correlation constants A , B and C for ethylene from Table 22-II and tempera-



Heat of formation

Fig. 2

ture $T = 400$ K into Eq. 22-2 yields:

$$\Delta H_f^\circ = 14.8 + (-8.81 \times 10^{-3})(400) + 3.15 \times 10^{-6}(400)^2$$

$$\Delta H_f^\circ = 11.78 \text{ kcal/g-mol}$$

The calculated value compares favorably with the data results (11.78 vs. 11.79).

FREE ENERGIES OF FORMATION

Cecil E. Gorin II and Carl L. Yaws

Gibbs free energy of formation is important in chemical-reaction engineering. (Two notations are used to denote Gibbs free energy of formation: ΔF_f° and ΔG_f° . Usage of ΔG_f° is increasing and is adopted here.) Values for the free energy of formation for individual chemicals are required to determine the free energy of reaction, ΔG_r° , and the accompanying chemical thermodynamic equilibrium for the reaction.

In addition, the following criteria are generally true for screening the feasibility of chemical reactions:

Reaction promising:

$$\Delta G_r^\circ < 0 \text{ kcal/g-mol}$$

Reaction possibly promising:

$$0 < \Delta G_r^\circ < 10 \text{ kcal/g-mol}$$

Reaction not promising:

$$\Delta G_r^\circ > 10 \text{ kcal/g-mol}$$

Correlation constants—Table 22-III

Correlation constants for Gibbs free energy of formation of the ideal gas at low pressure were based on a linear relationship in temperature:

$$\Delta G_f^\circ = A + BT \quad (22-3)$$

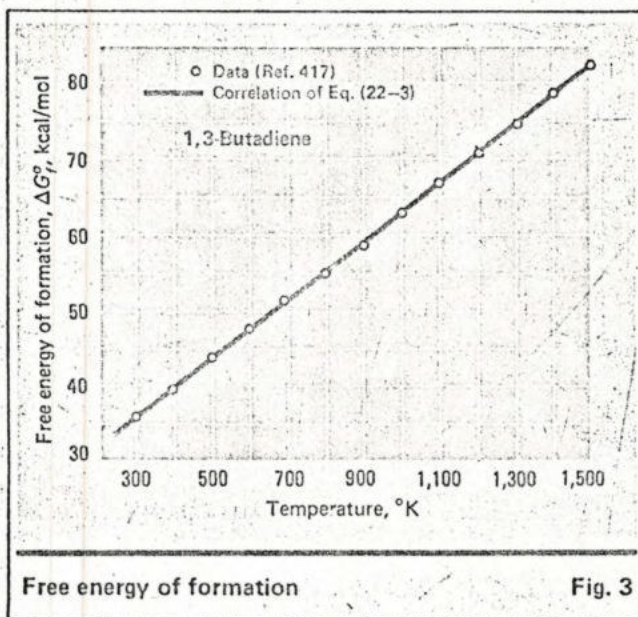
where ΔG_f° = free energy of formation of ideal gas at

Correlation constants: free energy of formation of ideal gas

Table 22-III

Compound	$\Delta G_f^\circ = A + BT$		ΔG_f° at 298 K, kcal/mol	Range, °K	Average error (absolute), kcal/mol	Data points, no.	References
	A	B x 10 ³					
Sulfur oxides							
Sulfur dioxide, SO ₂	-71.9	0.25	-71.7	298-717	0.107	13	7,15
	-86.8	17.7	-72.6 @ 800	717-1,500	0.193	12	7,15
Sulfur trioxide, SO ₃	-95.6	23.1	-88.6	298-717	0.118	13	7,15
	-110.	39.7	-78.2 @ 800	717-1,500	0.104	12	7,15
Nitrogen oxides							
Nitrous oxide, N ₂ O	19.6	17.7	24.9	298-1,500	0.065	23	7,15
Nitric oxide, NO	21.6	-3.02	20.7	298-1,500	0.008	23	7,15
Nitrogen dioxide, NO ₂	7.82	15.1	12.3	298-1,500	0.069	23	7,15
Carbon oxides							
Carbon monoxide, CO	-26.5	-21.3	-32.8	298-1,500	0.074	23	7,15
Carbon dioxide, CO ₂	-94.2	-0.42	-94.3	298-1,500	0.029	23	7,15
Hydrogen halides							
Hydrogen fluoride, HF	-65.2	-1.25	-65.5	298-1,500	0.151	23	7,15
Hydrogen chloride, HCl	-22.3	-1.72	-22.8	298-1,500	0.047	23	7,15
Hydrogen bromide, HBr	-5.02	-25.9	-12.8	298-331	0.023	5	7,15
	-12.7	-1.76	-13.4 @ 400	331-1,500	0.036	20	7,15
Hydrogen iodide, HI	5.72	-17.9	0.38	298-586	0.001	5	7,15
	2.05	-9.04	-1.53 @ 400	386-457	0.035	4	7,15
	-1.56	-1.78	-2.41 @ 500	457-1,500	0.014	18	7,15
Nitrogen hydrides							
Ammonia, NH ₃	-12.3	27.2	-3.89	298-1,500	0.178	23	7,15
Hydrazine, N ₂ H ₄	21.3	54.9	38.0	298-1,500	0.223	37	7,15,218
Hydrogen oxides							
Water, H ₂ O	-58.6	12.7	-54.6	298-1,500	0.138	23	7,15
Hydrogen peroxide, H ₂ O ₂	-33.2	26.4	-25.2	298-1,500	0.101	37	7,15,245
Olefins							
Ethylene, C ₂ H ₄	10.4	18.1	16.3	298-1,500	0.291	51	7,11,15,417,637
Propylene, C ₃ H ₆	1.80	41.9	15.0	298-1,500	0.401	37	15,417,637
1-Butene, C ₄ H ₈	-3.43	66.5	17.1	298-1,500	0.414	37	15,417,637
Alkanes							
Methane, CH ₄	-20.1	24.9	-12.2	298-1,500	0.298	37	15,461,637
Ethane, C ₂ H ₆	-23.3	49.7	-7.83	298-1,500	0.388	51	15,447,461,637
Propane, C ₃ H ₈	-28.8	74.7	-5.68	298-1,500	0.467	51	15,447,461,637
Xylenes							
<i>o</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	-0.12	94.9	29.2	298-1,500	0.565	23	15,417
<i>m</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	-0.79	94.4	28.4	298-1,500	0.609	23	15,417
<i>p</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	-0.74	95.9	29.0	298-1,500	0.630	23	15,417
Aromatics							
Benzene, C ₆ H ₆	16.7	45.9	31.0	298-1,500	0.409	38	15,417,637
Naphthalene, C ₁₀ H ₈	33.3	66.4	53.5	298-1,000	0.327	18	15,502
Alkyl aromatics							
Toluene, C ₆ H ₅ CH ₃	7.80	68.7	29.2	298-1,500	0.557	23	15,417
Ethylbenzene, C ₆ H ₅ C ₂ H ₅	2.67	93.0	31.2	298-1,500	0.648	23	15,417
Cumene, C ₆ H ₅ CH(CH ₃) ₂	-4.32	121.	32.7	298-1,500	0.619	23	15,417
Benzene derivatives							
Chlorobenzene, C ₆ H ₅ Cl	10.7	42.9	23.7	298-1,000	0.192	9	15
Aniline, C ₆ H ₅ NH ₂	18.5	70.6	39.8	298-1,000	0.248	9	15
Phenol, C ₆ H ₅ OH	-25.0	56.5	-7.86	298-1,000	0.219	9	15
Cycloalkanes							
Cyclopropane, C ₃ H ₆	10.3	47.7	24.9	298-1,000	0.260	14	15,637
Cyclobutane, C ₄ H ₈	3.09	76.2	26.3	298-1,000	0.366	9	15
Cyclopentane, C ₅ H ₁₀	-24.1	108.	9.23	298-1,500	0.617	51	15,591,417,637
Cyclohexane, C ₆ H ₁₂	-35.1	139.	7.59	298-1,500	0.532	37	15,417,637
Olefin monomers							
Isobutylene, C ₄ H ₈	-7.68	69.6	13.9	298-1,500	0.465	23	15,417
Styrene, C ₆ H ₅ CH=CH ₂	32.0	62.4	51.1	298-1,500	0.729	22	15,417
Diolefins							
1,3-Butadiene, C ₄ H ₆	24.2	38.6	36.2	298-1,500	0.325	51	15,417,637,636
Isoprene, C ₅ H ₈	15.2	63.8	34.9	298-1,500	0.348	23	15,417,636
Chloroprene, C ₄ H ₅ Cl	19.1	39.6	31.1	298-1,500	0.488	4	Estimated
Organic oxides							
Ethylene oxide, C ₂ H ₄ O	-14.4	36.8	-3.13	298-1,000	0.203	9	15
Propylene oxide, C ₃ H ₆ O	-24.5	60.4	-6.17	298-1,000	0.267	10	15,634
Butylene oxide, C ₄ H ₈ O	-31.6	88.5	-4.92	298-1,500	0.255	4	Estimated

Compound	$\Delta G_f^\circ = A + BT$		ΔG_f° at 298 K, kcal/mol	Range, °K	Average error (absolute), kcal/mol	Data points, no.	References
	A	B x 10 ³					
Primary alcohols							
Methanol, CH ₃ OH	-50.2	36.5	-38.8	298-1,000	0.292	35	15,418,637,692
Ethanol, C ₂ H ₅ OH	-58.3	59.7	-40.1	298-1,000	0.341	27	15,418,692
<i>n</i> -Propanol, C ₃ H ₇ OH	-64.5	84.8	-38.8	298-1,000	0.368	27	15,418,692
<i>n</i> -Butanol, C ₄ H ₉ OH	-69.4	110.	-36.0	298-1,000	0.420	27	15,418,692
Chloromethanes							
Methyl chloride, CH ₃ Cl	-22.0	23.7	-14.5	298-1,500	0.545	51	7,15,418,727
Methylene chloride, CH ₂ Cl ₂	-23.9	24.2	-16.5	298-1,500	0.132	51	7,15,418,727
Chloroform, CHCl ₃	-24.8	26.9	-16.7	298-1,500	0.158	37	15,418,727
Carbon tetrachloride, CCl ₄	-22.6	32.1	-12.8	298-1,500	0.422	37	15,418,727



low pressure, kcal/g-mol; A , B = correlation constants characteristic of the chemical compound; and T = temperature, °K.

The correlation constants, A and B , were ascertained from a least-squares regression analysis of the available data. The regression analysis was done with a generalized least-squares computer program for minimizing deviation.

Correlation and data values for free energy of formation compare favorably, as illustrated in Fig. 22-3 for a representative chemical.

Average absolute deviations between correlation and data values are less than 0.6 kcal/g-mol in most cases.

Example 22-4—Let us now estimate the free energy of formation of methanol (CH₃OH) as an ideal gas at 400 K.

Substituting values for the correlation constants, A and B , for methanol from Table 22-III, and the temperature of 400 K into Eq. (22-3), yields:

$$\Delta G_f^\circ = -20.1 + 0.0249(400)$$

$$\Delta G_f^\circ = -10.14 \text{ kcal/g-mol}$$

HEATS OF VAPORIZATION

Shailesh B. Thakore, Joseph W. Miller, Jr. and Carl L. Yaws

Heat-of-vaporization data are important in process engineering design. In distillation, heat-of-vaporization values are needed to determine the heat requirements for the reboiler. Such values are also needed to establish cooling requirements for the condenser handling the overhead fraction from the distillation. Additional usage includes process-energy requirements for unit operations involving saturated-liquid and vapor phases.

Correlation constants—Table 22-IV

Heats of vaporization at any temperature are based on the original Watson correlation:

$$\Delta H_v = \Delta H_{v1} \left[\frac{T_c - T}{T_c - T_1} \right]^n \quad (22-4)$$

where ΔH_v = heat of vaporization at any temperature, cal/g; ΔH_{v1} = heat of vaporization at T_1 , cal/g; T_c = critical temperature, °K; T = temperature, °K; T_1 = temperature for ΔH_{v1} , °K; and n = characteristic constant for the chemical (in most cases, $n = 0.38$).

Values for the correlation constants (ΔH_{v1} , T_1 and n) are given in Table 22-IV. Results for ΔH_{v1} at T_1 are based on extensive screening of the literature and selection of recommended values from the experimental investigations. The temperature range over which the correlation constants are usable is also given. In most cases, the usable range covers the entire saturated-liquid state, from the melting point to the critical point.

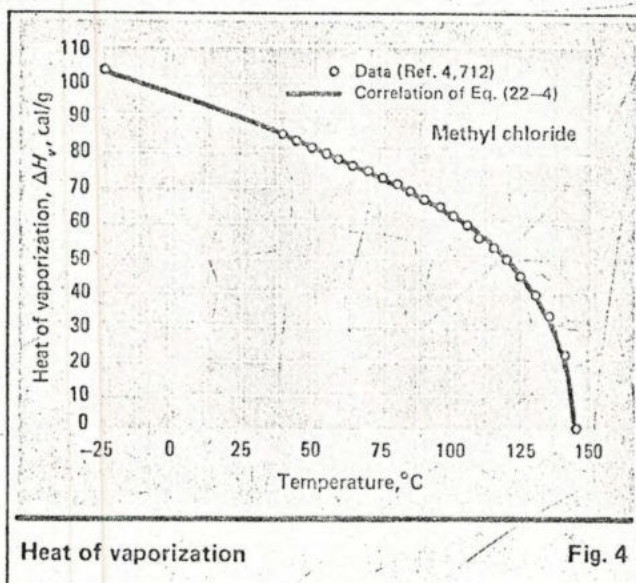
Calculated and data values are compared in Fig. 22-4 for a representative chemical. The average devi-

Correlation constants: heat of vaporization

Table 22-IV

Compound	ΔH_{v1} , cal/g	T_1 , °C	T_c , °C	n	Range, °C	References	$\Delta H_v = \Delta H_{v1} \left[\frac{T_c - T}{T_c - T_1} \right]^n$
Halogens							
Fluorine, F ₂	41.1	-188.1	-129.0	0.38	-219.6 to -129.0	1,4,9,10,14,43,70	
Chlorine, Cl ₂	69.6	-34.06	144.0	0.38	-101.0 to 144.0	1,9,14,30,43,70	
Bromine, Br ₂	44.8	58.78	315.0	0.38	-7.2 to 315.0	1,4,9,14,43,70	
Iodine, I ₂	39.3	184.4	546.0	0.38	112.6 to 546.0	1,4,9,43,62,70	
Sulfur oxides							
Sulfur dioxide, SO ₂	93.0	-10.0	157.6	0.38	-72.7 to 157.6	10,12,13,73,81,90	
Sulfur trioxide, SO ₃	128.0	44.8	218.3	0.38	16.8 to 218.3	13,85,91	
Nitrogen oxides							
Nitrous oxide, N ₂ O	89.9	-89.5	36.5	0.38	-90.8 to 36.5	1,9,10,12,14,118	
Nitric oxide, NO	110.0	-151.8	-93.1	0.38	-163.8 to -93.1	1,9,10,12,14	
Nitrogen dioxide, NO ₂	99.0	21.2	158.0	0.38	-11.2 to 158.0	1,10,4,14	
Carbon oxides							
Carbon monoxide, CO	51.6	-191.5	-140.1	0.38	-205.0 to -140.1	9,10,13,14,115	
Carbon dioxide, CO ₂	56.1	0	31.1	0.38	-56.5 to 31.1	9,10,13,14,115,157	
Hydrogen halides							
Hydrogen fluoride, HF		(Equation not valid for HF)				4,10,183,184,185	
Hydrogen chloride, HCl	105.8	-85.03	51.5	0.38	-114.2 to 51.5	1,4,6,10,12,30,167,174	
Hydrogen bromide, HBr	52.0	-66.8	90.0	0.38	-86.9 to 90.0	4,6,10,12,167	
Hydrogen iodide, HI	36.9	-35.5	151.0	0.38	-50.8 to 151.0	1,6,10,12,167,174	
Nitrogen hydrides							
Ammonia, NH ₃	327.4	-33.43	132.4	0.38	-77.74 to 132.4	2,6,9,10,13,14,194	
Hydrazine, N ₂ H ₄	302	113.5	380	0.38	2.0 to 380	14,189,195,206,218	
Hydrogen oxides							
Water, H ₂ O	538.7	100	374.2	0.38	0 to 374.2	9,12,239,246	
Hydrogen peroxide, H ₂ O ₂	321.9	150.2	455	0.38	-0.43 to 455	4,210,242,256,257,260	
Diatomic gases							
Hydrogen, H ₂	107	-252.8	-240.2	0.237	-259.4 to -240.2	10,284,293,302,306,307,309,335	
Nitrogen, N ₂	47.5	-195.8	-146.8	0.38	-209.9 to -146.8	10,43,45,47,277,300,306,317	
Oxygen, O ₂	50.9	-183.0	-119.5	0.38	-218.4 to -119.5	10,43,45,47,296,300,306,309,317	
Inert gases							
Helium, He	5.2	-268.9	-268.0	0.38	-269.9 to -268.0	10,43,311,322,345,387	
Neon, Ne	20.52	-246.0	-228.7	0.38	-248.7 to -228.7	10,43,47,345	
Argon, Ar	38.99	-185.9	-122.4	0.38	-189.3 to -122.4	10,43,47,345	
Olefins							
Ethylene, C ₂ H ₄	115.4	-103.7	9.9	0.38	-169.2 to 9.9	3,10,246,414,415,419,440	
Propylene, C ₃ H ₆	104.6	-47.7	91.9	0.38	-185.3 to 91.9	3,10,246,414,415,419,440	
1-Butene, C ₄ H ₈	93.4	-6.3	146.2	0.38	-185.4 to 146.2	3,10,246,414,415,419	
Alkenes							
Methane, CH ₄	121.7	-161.5	-82.6	0.38	-182.6 to -82.6	3,10,47,246,417,419,454	
Ethane, C ₂ H ₆	116.7	-89.2	32.3	0.38	-163.2 to 32.3	3,10,246,417,419,453	
Propane, C ₃ H ₈	101.8	-42.1	96.7	0.38	-187.7 to 96.7	3,10,246,417,419,453	
Xylenes							
<i>o</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	82.9	144.4	357.8	0.38	-25.2 to 357.8	2,4,9,417,419,484	
<i>m</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	81.9	139.1	343.8	0.38	-47.9 to 343.8	2,4,9,417,419,484	
<i>p</i> -Xylene, C ₆ H ₄ (CH ₃) ₂	81.0	138.4	344.0	0.38	13.3 to 344.0	2,4,9,417,419,472,484	
Aromatics							
Benzene, C ₆ H ₆	94.1	80.10	288.94	0.38	5.53 to 288.94	3,4,15,309,415,417,419	
Naphthalene, C ₁₀ H ₈	80.7	218.00	475.02	0.38	80.55 to 475.02	3,6,419	
Alkyl aromatics							
Toluene, C ₆ H ₅ CH ₃	86.1	110.6	318.8	0.38	-95.0 to 318.8	4,413,415,417,419,516	
Ethylbenzene, C ₆ H ₅ C ₂ H ₅	80.0	136.2	344	0.38	-95.0 to 344	413,415,417,419,516	
Cumene, C ₆ H ₅ CH(CH ₃) ₂	74.6	152.4	350	0.38	-96.0 to 350	4,413,415,417,419,516	
Benzene derivatives							
Chlorobenzene, C ₆ H ₅ Cl	76.0	131.7	359.2	0.38	-45.2 to 359.2	3,4,413,574	
Aniline, C ₆ H ₅ NH ₂	112.4	184.4	426.0	0.38	-6.15 to 426.0	3,4,413,574	
Phenol, C ₆ H ₅ OH	116.1	181.8	420.0	0.38	40.75 to 420.0	3,547,563	
Cycloalkanes							
Cyclopropane, C ₃ H ₆	113.8	-32.80	124.9	0.33	-127.42 to 124.9	15,417,609,605	
Cyclobutane, C ₄ H ₈	103.0	12.51	190.4	0.38	-90.73 to 190.4	15,417,604	
Cyclopentane, C ₅ H ₁₀	93.0	49.26	238.5	0.38	-93.83 to 238.5	15,413,417,419,591	
Cyclohexane, C ₆ H ₁₂	85.1	80.74	260.3	0.38	6.55 to 260.3	15,413,417,419,577,582	
Olefin monomers							
Isobutylene, C ₄ H ₈	84.22	-6.9	144.7	0.38	-140.35 to 144.7	3,10,417,607,611,619,620	
Styrene, C ₆ H ₅ CH=CH ₂	84.69	145.0	369.0	0.33	-30.6 to 369.0	3,611,623,622	
Diolenes							
1,3-Butadiene, C ₄ H ₆	100.2	-4.41	152.0	0.33	-106.9 to 152.0	10,419,620,609,640	
Isoprene, C ₅ H ₈	91.5	34.67	210.2	0.38	-146.0 to 210.2	419,620	
Chloroprene, C ₄ H ₆ Cl	72.3	60.0	261.7	0.38	-101.0 to 261.7	4,620	

Compound	ΔH_{v1} , cal/g	T_1 , °C	T_c , °C	n	Range, °C	References
Organic oxides						
Ethylene oxide, C ₂ H ₄ O	138.5	10.55	195.8	0.466	-112.5 to 195.8	4,10,15,309,574,657,658,659,660
Propylene oxide, C ₃ H ₇ O	114.8	25.0	209.1	0.466	-112.0 to 209.1	4,656,657,658
Butylene oxide, C ₄ H ₈ O	100.5	63.2	252.6	0.466	-150.0 to 252.6	4,657
Primary alcohols						
Methanol, CH ₃ OH	260.1	64.7*	239.4	0.40	-97.6 to 239.4	4,9,15,413,646,692
Ethanol, C ₂ H ₅ OH	202.6	78.3*	243.1	0.40	-114.1 to 243.1	4,9,15,413,646,692
<i>n</i> -Propanol, C ₃ H ₇ OH	162.3	97.2*	263.6	0.40	-126.2 to 263.6	4,9,15,413,646,670,672,678,691,692
<i>n</i> -Butanol, C ₄ H ₉ OH	140.5	117.7*	289.6	0.40	-89.3 to 289.8	4,9,15,413,646,692
Chloromethanes						
Methyl chloride, CH ₃ Cl	102.2	-23.8	143.1	0.38	-97.7 to 143.1	4,9,15,574,708,712,718,725
Methylene chloride, CH ₂ Cl ₂	78.7	39.8	241.0	0.38	-96.7 to 241.0	4,9,15,574,708,718,721
Chloroform, CHCl ₃	58.9	61.3	263.4	0.38	-63.2 to 263.4	4,9,15,574,708,718,721
Carbon tetrachloride, CCl ₄	46.55	76.7	283.2	0.38	-22.9 to 283.2	4,9,15,574,708,718,721



ations between correlation and data values are in most cases less than 1 to 5%.

Example 22-5—Let us estimate the heat of vaporization of methyl chloride (CH₃Cl) at 40°C.

From Table 22-IV, we obtain the correlation constants for methyl chloride as:

$$\begin{aligned} T &= 40 \text{ C} = 313.2 \text{ K} \\ T_c &= 143.1 \text{ C} = 416.3 \text{ K} \\ T_1 &= -23.8 \text{ C} = 249.4 \text{ K} \\ \Delta H_{v1} &= 102.2 \text{ cal/g} \end{aligned}$$

By substituting these values into Eq. (22-4); we obtain:

$$\Delta H_v = 102.2 \left[\frac{416.3 - 313.2}{416.3 - 249.4} \right]^{0.38}$$

$$\Delta H_v = 85.10 \text{ cal/g}$$

The calculated and data values compare favorably (85.10 vs. 83.84).

References

The reference citations listed in this article appeared in Parts 1 through 21 of this series. References 1-72, Part 1, June 10, 1974, p. 78; 73-93, Part 2, July 8, 1974, p. 92; 94-134, Part 3, Aug. 19, 1974, p. 106; 135-157, Part 4, Sept. 30, 1974, p. 122; 158-187, Part 5, Oct. 28, 1974, p. 122; 188-235, Part 6, Nov. 25, 1974, p. 100; 236-262, Part 7, Dec. 23, 1974, p. 74; 263-336, Part 8, Jan. 20, 1975, p. 106; 337-408, Part 9, Feb. 17, 1975, p. 94; 409-443, Part 10, Mar. 31, 1975, p. 109; 444-469, Part 11, May 12, 1975, p. 97; 470-490, Part 12, July 21, 1975, p. 122; 491-515, Part 13, Sept. 1, 1975, p. 115; 516-546, Part 14, Sept. 29, 1975, p. 81; 547-574, Part 15, Oct. 27, 1975, p. 127; 575-606, Part 16, Dec. 8, 1975, p. 128; 607-629, Part 17, Jan. 19, 1976, p. 115; 630-646, Part 18, Mar. 1, 1976, p. 115; 647-665, Part 19, Apr. 12, 1976, p. 137; 666-704, Part 20, June 7, 1976, p. 127; 705-734, Part 21, July 5, 1976, p. 89.

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