

Where to get Modern Thermodynamic Data

Compilations:

NIST-JANAF thermochemical tables. Malcolm W. Chase, Jr. 4th ed. A critically evaluated data set containing recommended temperature dependent values for chemical thermodynamic properties of inorganic and C1 and C2 organic substances. Includes heat capacity, entropy, Gibbs energy function, enthalpy, enthalpy of formation, Gibbs energy of formation, logarithm of equilibrium constant of formation. Has a chemical name and formula index.

The NBS tables of chemical thermodynamic properties: selected values for inorganic and C1 and C2 organic substances in SI units. D. D. Wagman. Contains critically evaluated thermochemical property data for over 8,000 inorganic and small organic molecules in gaseous, liquid, crystalline states for solutions in water and for mixed aqueous and organic solutions. Properties include heat capacity, entropy, enthalpy, enthalpy of formation, Gibbs free energy of formation at 298.15K and 0.1 Mpa

Thermochemical data of pure substances. I. Barin. 3rd ed. VCH, 1995. Reference collection 660.29 B253t A comprehensive collection of thermodynamic properties of 2400 pure substances as a function of temperature at 100 degree intervals. Data include: heat capacity, entropy, enthalpy, Gibbs energy of formation, log of equilibrium constant of formation. Includes mainly inorganic compounds plus a selection of common hydrocarbons, carbohydrates and chlorinated hydrocarbons. Some data are derived from critically evaluated sources.

Chemical properties handbook : physical, thermodynamic, environmental, transport, safety, and health related properties for organic and inorganic chemicals. Carl L. Yaws. McGraw-Hill, c1999. Contains critical properties, heat capacity, enthalpy of vaporization, enthalpy of fusion, vapor pressure, density of liquid, surface tension, refractive index, dipole moment, radius of gyration, entropy, enthalpy of formation, gibbs energy of formation, solubility, Henry's law constant, adsorption on activated carbon, soil sorption coefficient, viscosity, thermal conductivity, flash point, exposure limits, coefficient of thermal expansion.

Other text sources:

Combustion texts: Kuo, Glassman, Turns, Kanury, etc. These will have some equilibrium constants also.

Thermodynamics texts: Howel & Buckius, Moron & Shapiro, etc. Some have limited data on combustion species.

Physical Chemistry texts: Atkins, Castellan, Levine, etc. Typically have polynomial fits & some other data.

Web resources

NIST web book. <http://webbook.nist.gov/chemistry/> No polynomial fits, but a large library of data with tabular c_p data with detailed references.

GRI mechanism data. http://www.me.berkeley.edu/gri_mech/data/thermo_table.html Thermodynamic data for the species in the GRI mechanism for methane/air combustion.

Burcat database. <http://garfield.chem.elte.hu/Burcat/burcat.html> Very comprehensive data for almost all species of interest in NASA and CHEMKIN formats.

ME 501 website. <http://mechse.uiuc.edu/research/glumac/me501/index.html> Has links to the three sites above, plus links to programs for solving equilibrium properties and compositions. These programs are:

- 1) **GASEQ** – simple and powerful Windows interface program for chemical equilibrium. Some problems with higher order functions like transport properties and shock calculations, but generally very useful.
- 2) **Chemeq** – command prompt program that solves chemical equilibrium using the Cantera (freeware) package. Not as polished as GASEQ, but more versatile for chemical equilibrium calculations.
- 3) **Gordon McBride Equilibrium Solver** – another command prompt application. The most powerful of all the solvers. Somewhat complex to run, but not all that bad. Can do condensed phases, which other programs don't do as well or at all. Widely cited.
- 4) **Colorado State Web-based Solvers** – simple programs that run on the internet. Nice for running one or two quick calculations. Use CHEMKIN software and GRI databases.

Ideal Gas Thermodynamic Properties in Chemkin Format

Thermodynamic properties for ideal gases are tabulated in a variety of locations in Chemkin format. This format involves two sets of seven constants a_1 through a_7 . These constants are fits to specific heat, enthalpy, and entropy data (or calculations) according to the following formulae:

$$\frac{\hat{c}_p}{R_u} = \frac{c_p}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \quad (1)$$

$$\frac{\hat{h}}{R_uT} = \frac{h}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T} \quad (2)$$

$$\frac{\hat{s}^\circ}{R_u} = \frac{s^\circ}{R} = a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7 \quad (3)$$

Note that all the parameters on the left hand side of equations (1) through (3) are dimensionless.

Three temperatures are given on the first line of the data, T_{low} , T_{high} , and T_{mid} . Usually, these values are 300, 5000, and 1000 K respectively. The first set of parameters a_1 through a_7 applies for the high temperature range (T_{mid} through T_{high}), while the second set applies for the low temperature range (T_{low} through T_{mid}).

Sample Data in Chemkin Format for Nitrogen (N₂)

N2	121286N	2	G	0300.00	5000.00	1000.00	1
0.02926640E+02	0.14879768E-02	-0.05684760E-05		0.10097038E-09	-0.06753351E-13		2
-0.09227977E+04	0.05980528E+02	0.03298677E+02		0.14082404E-02	-0.03963222E-04		3
0.05641515E-07	-0.024444854E-10	-0.10208999E+04		0.03950372E+02			4

Format:

Symbol	Identifier	#atoms	Phase	T_{low}	T_{high}	T_{mid}	
a_1 (hi range)	a_2 (hi range)		a_3 (hi range)	a_4 (hi range)		a_5 (hi range)	2
a_6 (hi range)	a_7 (hi range)		a_1 (lo range)	a_2 (lo range)		a_3 (lo range)	3
a_4 (lo range)	a_5 (lo range)		a_6 (lo range)	a_7 (lo range)			4

Bond Strengths

Average bond energies, H at 25

Diatomic Molecules			Polyatomic Molecules		
	kcal/mol	kJ/mol		kcal/mol	kJ/mol
H—H	104.2	436	C—H	99	414
F—F	37.5	157	C—C	83	347
Cl—Cl	58.0	243	C=C	146	610
Br—Br	46.3	194	C≡C	200	836
I—I	36.5	153	C—O	86	359
H—F	135.9	568	C=O ¹	192	803
H—Cl	103.1	432	C=O ²	166	694
H—Br	87.4	366	C=O ³	176	736
H—I	71.4	299	C=O ⁴	179	748
O=O	119.1	498	C—N	73	305
N≡N	225.9	945	C=N	147	615
			C≡N	213	890
			C—F	116	485
			C—Cl	81	339
			C—Br	68	284
			C—I	51	213
			O—H	111	464
			O—O	35	146
			O—Cl	52	217
			O—Br	48	201
			N—H	93	389
			N—N	39	163
			N—O	53	221
			N=N	100	418
			N=O	145	606
			S—H	83	339
			S—S	54	226

Enthalpy of Formation for Several Substances at 1 Atmosphere and Specified Temperature*

Substance	Formula	State	Enthalpy of formation kcal/gm-mole	Te
Carbon monoxide	CO	g	-26.42	
Carbon dioxide	CO ₂	g	-94.05	
Methane	CH ₄	g	-17.89	
Acetylene	C ₂ H ₂	g	54.23	
Ethylene	C ₂ H ₄	g	12.56	
Benzene	C ₆ H ₆	g	19.82	
Benzene	C ₆ H ₆	l	11.72	
Octane	C ₈ H ₁₈	g	-49.82	
n-Octane	C ₈ H ₁₈	l	-59.74	
n-Octane	C ₈ H ₁₈	g	-49.82	
Calcium oxide	CaO	Crystalline	-151.80	
Calcium carbonate	CaCO ₃	Crystalline	-289.50	
Oxygen	O ₂	g	0	
Nitrogen	N ₂	g	0	
Carbon (graphite)	C	Crystalline	0	
Carbon (diamond)	C	Crystalline	0.45	
Water	H ₂ O	g	-57.80	
Water	H ₂ O	l	-68.32	
Ethane	C ₂ H ₆	g	-20.24	
Propane	C ₃ H ₈	g	-24.82	
n-Butane	C ₄ H ₁₀	g	-29.81	
i-Butane	C ₄ H ₁₀	g	-31.45	
n-Pentane	C ₅ H ₁₂	g	-35.00	
n-Hexane	C ₆ H ₁₄	g	-39.96	
n-Heptane	C ₇ H ₁₆	g	-44.89	
Propylene	C ₃ H ₆	g	4.88	
Formaldehyde	CH ₂ O	g	-27.70	
Acetaldehyde	C ₂ H ₄ O	g	-39.76	
Methanol	CH ₃ OH	l	-57.02	
Ethanol	C ₂ H ₆ O	l	-66.36	
Formic acid	CH ₂ O ₂	l	-97.80	
Acetic acid	C ₂ H ₄ O ₂	l	-116.40	
Oxalic acid	C ₂ H ₂ O ₄	s	-197.60	
Carbon tetrachloride	CCl ₄	l	-33.30	
Glycine	C ₂ H ₅ O ₂ N	s	-126.33	
Ammonia	NH ₃	g	-11.00	
Hydrogen bromide	HBr	g	-8.60	
Hydrogen iodide	HI	g	6.00	

* Abstracted from NBS Circular 500.

1=Carbon dioxide, 2=Formaldehyde, 3=Aldehydes, 4=Ketones

Sample Problem Using Multiple Reactions

For a mixture of 1 mole of CO and 1 mole of O₂, it is desired to know the equilibrium composition at 3000 K. Consider CO, CO₂, O₂, and O as the possible species.

- Choose an appropriate set of reactions and calculate K_p for each reaction at 3000 K from tabulated data.
- Obtain K_p from another source for the chosen reactions (e.g. a thermo book, a combustion book, published papers, etc.) and compare results.
- Calculate the equilibrium composition of a mixture of 1 mole CO and 1 mole O₂ at 3000 K and 1 atm. Give your results in the form of mole fractions for each species.
- Repeat part c) for $P = 0.1$ atm.

Solution

For parts a) and b) the answers depend on what set of reactions that were chosen. For each reaction, $K_p = \exp(-\Delta G^\circ/\hat{R}T)$. $\Delta G^\circ = \sum_i \nu_i \hat{\mu}_i^\circ$, where $\hat{\mu}_i^\circ = \hat{u}_i(T, P_0) + \hat{R}T - T\hat{s}_i(T, P_0)$. The superscript '°' denotes that those quantities are evaluated at the reference pressure, which is typically 1 atmosphere.

Even though there are 4 species, we can only write two linearly independent reactions. For example:



I call the advancement for the first reaction ξ_1 and that for the second reaction ξ_2 . Then I can write the relations:

$$N_{\text{CO}} = 1 - \xi_1 \quad N_{\text{CO}_2} = \xi_1 \quad N_{\text{O}} = \xi_2 - \xi_1 \quad N_{\text{O}_2} = 1 - \xi_2/2 \quad (2)$$

Also, we note that the total number of moles is the sum over all the species or $N_T = 2 - \xi_1 + \xi_2/2$. These relations tell us that ξ_1 is between 0 and 1 and that ξ_2 is between ξ_1 and 2. Next, we write the expression for the equilibrium constants for these reactions. For the first reaction, $K_{p,1} = 27.16$ and for the second, $K_{p,2} = .1125$ at 3000 K (from an undergraduate thermodynamics text).

$$K_{p,1} = \frac{P_{\text{CO}_2}/P_0}{P_{\text{CO}}P_{\text{O}}/P_0^2} = \frac{X_{\text{CO}_2}}{X_{\text{CO}}X_{\text{O}}} \left(\frac{P_0}{P}\right) = \frac{N_T N_{\text{CO}_2}}{N_{\text{CO}}N_{\text{O}}} \left(\frac{P_0}{P}\right) \quad (3)$$

Where we have used the fact that $X_i = N_i/N_T$. Plugging in our relations for the N 's gives us:

$$K_{p,1} = \frac{(2 - \xi_1 + \xi_2/2)\xi_1}{(1 - \xi_1)(\xi_2 - \xi_1)} \left(\frac{P_0}{P}\right) \quad (4)$$

Similarly for $K_{p,2}$ we get:

$$K_{p,2} = \frac{\xi_2 - \xi_1}{(2 - \xi_1 + \xi_2/2)^{1/2}(1 - \xi_2/2)^{1/2}} \left(\frac{P}{P_0}\right)^{1/2} \quad (5)$$

Now we have two equations for two unknowns, ξ_1 and ξ_2 . Unfortunately, we can't isolate either variable, so we have to do a systematic search. I chose a value of ξ_1 , and then solved for ξ_2 in $K_{p,2}$ using a Newton-Raphson method on a calculator. Then I plugged these values into $K_{p,1}$ and used the agreement there as a barometer for convergence. For the $P = 1$ atm case, I got $\xi_1 = .646$ and $\xi_2 = .763$. This gives me mole fractions as follows:

$$X_{\text{CO}} = .204 \quad X_{\text{CO}_2} = .372 \quad X_{\text{O}} = .067 \quad X_{\text{O}_2} = .357 \quad (6)$$

These values agree excellently with those obtained by a canned software routine which solves for equilibrium composition. For the low pressure case, $(P/P_0) = 0.1$, and I get $\xi_1 = .349$ and $\xi_2 = .749$ leading to the following mole fractions:

$$X_{\text{CO}} = .321 \quad X_{\text{CO}_2} = .172 \quad X_{\text{O}} = .198 \quad X_{\text{O}_2} = .309 \quad (7)$$

Note that the reduced pressure has increased N_T as expected due to Le Chatlier's principle.