Copy

MRC-DA-577

A THEORETICAL STUDY OF PCB EMISSIONS FROM STATIONARY SOURCES

FINAL REPORT

By
Herman Knieriem, Jr.

Contract No. 68-02-1320
Task No. 26

September 1976

For

U. S. Environmental Protection Agency
Research Triangle Park
North Carolina 27711

RECEIVED
SEP 29 1976
EPA
DAYTON

MONSANTO RESEARCH CORPORATION
A SUBSIDIARY OF MONSANTO COMPANY

DAYTON LABORATORY

DAYTON, OHIO 45407

MONS 202466

A THEORETICAL STUDY OF PCB EMISSIONS FROM STATIONARY SOURCES

FINAL REPORT

by

Herman Knieriem, Jr.

MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
Dayton, Ohio 45407

Contract No. 68-02-1320

Task No. 26

Project Officer

Robert E. Hall
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

Prepared for

U.S. Environmental Protection Agency
Research Triangle Park
North Carolina 27711

September 1976

MONS 202467

ABSTRACT

This study was done because polychlorinated biphenyl (PCB) isomers were tentatively identified in ash and flyash from a utility steam generating boiler, causing concern. Theoretical assessment of PCB formation and destruction in conventional fossil fuel-fired sources suggests a small but finite possibility that PCB isomers may be found in their emissions.

Conclusions from this theoretical consideration are:

1) PCB emissions are more likely from coal or residual oil combustion than from refined oil or natural gas since the former have much higher chlorine contents.

2) PCB isomers with four or more chlorine atoms per molecule are more of an environmental hazard than those with three or less.

3) The probability of forming PCB isomers with four or more atoms of chlorine per molecule during combustion is restricted by the short residence times and low concentrations of chlorine available in many fossil fuels.

4) The amount of PCB emissions, if any, may be related to polynuclear aromatic hydrocarbon (PAH) emissions.

5) Based on the above, inefficient combustion control is more likely to produce PCB emission that optimum conditions.

6) The highest priority for field sampling and analysis of PCB from combustion sources should be for small and medium-sized, hand- and underfeed-stoked coal furnaces.

MONS 202468

CONTENTS

Abstract		iii
1.	INTRODUCTION	1
2.	CONCLUSIONS	3
3.	RECOMMENDATIONS	5
4.	THERMODYNAMIC CALCULATIONS	6
	A. PCB Formation	6
	B. PCB Destruction	9
5.	KINETIC AND RELATED CONSIDERATIONS	10
	A. The Fossil Fuels	11
	B. The Combustion Conditions	12
	C. "Unconventional" Fossil Fuel Combustion	15
	D. PCB Contamination As An Emission Source	15
	E. Environmental Persistence And Impact	15
References		20
Appendices		
	A. Reaction Thermodynamics, Formation	24
	B. Reaction Thermodynamics, Oxidation	27
	C. Biphenyl Thermodynamics	30

MONS 202469

TABLES

Number		Page
1	Estimated Benzo(a)Pyrene Emissions in United States, 1972	10
A-1	Reaction Thermodynamics, Formation	24
A-2	Reaction Thermodynamics, Formation	25
A-3	Reaction Thermodynamics, Formation	26
B-1	Reaction Thermodynamics, Oxidation	27
B-2	Reaction Thermodynamics, Oxidation	28
B-3	Reaction Thermodynamics, Oxidation	29
C-1	Biphenyl Thermodynamics	30
C-2	4-Chlorobiphenyl Thermodynamics	31
C-3	4,4-Dichlorobiphenyl Thermodynamics	32
C-4	2,2,4,4-Tetrachlorobenzene Thermodynamics	33
C-5	Hydrogen Chloride Thermodynamics	34
C-6	Chlorine Thermodynamics	35
C-7	Carbon Dioxide Thermodynamics	36
C-8	Water Thermodynamics	37
C-9	Oxygen Thermodynamics	38

MONS 202470

SECTION 1

INTRODUCTION

A report[1] prepared for EPA in 1975 tentatively identified the presence of polychlorinated biphenyl (PCB) isomers in the stack gas emissions from a pulverized coal-fired utility boiler. Specifically, materials with gas chromatograph column retention times comparable to tetrachloro- and hexachloro-biphenyl isomers (and a commercial PCB standard having a similar degree of chlorination) (personal communication from Dr. Mark Marcus, Midwest Research Institute, 11 May 1976) were detected in bottom ash, superheater ash and dust collector ash from the Number 8 unit of the Tennessee Valley Authority plant at Widow's Creek, Alabama. Levels detected ranged from 0.02 to 0.16 ppm (by weight of the ash) and were too low for isolation and positive characterization by the investigators.

Some PCB isomers tend to accumulate in the environment with an impact potential not yet completely understood but of significant concern.[2] The indication, however tentative, that persistent organics of this type may be found in the effluent streams from fossil fuel fired boilers bears further study and investigation.

The present effort explores some of the theoretical aspects affecting the likelihood that PCB emissions are possible from stationary combustion sources firing conventional fossil fuels. This evaluation considers:

A. Some thermodynamics for the formation and destruction of PCB isomers for which data are available under controlled conditions.

B. Some of the directional influences likely to affect reaction kinetics of PCB formation and destruction in the firebox (including fuel variables and furnace variables).

---

[1]Cowherd, C., Jr., M. Marcus, C. M. Cuenther, and J. L. Spigarelli. Hazardous Emission Characterization of Utility Boilers. Contract No. 68-02-1324, Task No. 27, U.S. Environmental Protection Agency, 23 June 1975. 185 pp.

[2]Interdepartment Task Force on PCBs. Polychlorinated Biphenyls and the Environment. COM-72-10419, Washington, D.C., May 1972. 181 pp.

MONS 202471

C. Peripheral issues which bear on the conclusions and recommendations including:

1. Potential PCB sources other than conventional fossil fuel fired furnaces.

2. Potential sources of PCB contamination.

3. Variability of PCB biodegradation rate and consequent environmental accumulation as a function of degree of chlorination.

SECTION 2

CONCLUSIONS

Thermodynamic analyses indicate that the reaction of some precursors to form polychlorinated biphenyls (PCBs) in conventional fossil fuel fired sources is theoretically possible. The presence of some precursors (biphenyl and reactive chlorine species) has been deduced from the structure of known stack gas effluent contaminants but has not been proven. There are competing reactions within the furnace, uncertain time versus temperature conditions, highly variable reactant concentrations and other kinetic uncertainties in the combustion zone. Predictions of the degree of certainty of PCB occurrence in furnace effluents cannot be made from available data.

The best known reaction which may result in the formation of PCBs in stationary combustion sources is that between biphenyl and chlorine (or an active chlorine radical). Complex kinetics within the reaction zona and lack of thermodynamic data prevent useful consideration of other possible routes to PCBs at this time (e.g., rearrangement and chlorination of PAH fragments).

Operating conditions most likely to contribute significant quantities of PCB to the environment are tentatively judged to be similar to those which maximize polynuclear aromatic hydrocarbon (PAH) emissions if sufficient chlorine is present. This judgment is drawn from structural similarities and coincident identification of related materials in some combustion emissions.[3,4]

While readily measurable aromatic hydrocarbon precursors for PCB appear ubiquitous in fossil fuel combustion, the other reactant, chlorine, has a widely variable content in fuels. It is very low or nominally absent in some cases. Consequently, the likelihood of significant PCB formation in efficiently operated natural

---

[3]Girling, G. W., and E. C. Ormerod. Variation in Concentration of Some Constituents of Tar in Coke-Oven Gas. Benzole Producers, Limited (London), Paper 1-1963, April 1963. 13 pp.

[4]Kubota, H., W. H. Griest, and M. R. Guerin. Determination of Carcinogens in Tobacco Smoke and Coal-Derived Samples - Trace Polynuclear Aromatic Hydrocarbons. CONF 750603-3, Oak Ridge National Laboratory, Oak Ridge, Tennessee. 9 pp.

MONS 202473

gas or refined oil fired furnaces may be much lower than from those sources fired with residual oil and coal. Only field measurements demonstrating the absence of organic chlorine in the fuel can eliminate them as possible PCB sources, however.

It is possible that PCBs in furnace emissions, if proven, may have originated from contamination by commercial PCBs either before or after the combustion zone. PCBs have been shown to be ubiquitous at very low levels in the environment.

Analyses of PCB contaminated tissue are reported extensively in the literature and limited degradation studies are available. Both types of study suggest that highly chlorinated PCB isomers (four chlorines and higher) are much more likely to accumulate environmentally with potential adverse impact than trichloro (and lower) isomers.

One possible technique for reducing the potential for PCB emissions may be the practice of efficient combustion techniques. Efficient combustion is known to incinerate all organics effectively.[5] Reducing biphenyl survival in combustion will reduce PCB likelihood in the emissions.

[5]Anonymous. Solving Waste Problem Profitably. Chemical Week, 104(24):38, 1969.

MONS 202474

SECTION 3

RECOMMENDATIONS

Available analysis of stack gas effluents from conventional combustion sources has shown that hand-stoked and underfeed-stoked coal furnaces are much more likely to produce polynuclear aromatic hydrocarbon emissions than other types of coal feeds (pulverized, spreader stoker, etc.). Rigorous characterization of stack gas constituents of the former types deserves high priority in assessing possible PCB output due to this recognized PAH emissions characteristic.

Analysis of feed streams (air, fuel, auxiliaries), furnace construction details, and sampling points will help to quantify the role of commercial product contamination as a potential PCB source in emissions from fossil fuel fired furnaces.

Unsupported estimates of reaction stoichiometry seem to favor a low degree of chlorination of the PCB molecule. The thermal stability of PCB increases with each additional chlorine, however. The degree of chlorination of hypothetical PCB emissions is very speculative therefore. Every effort should be made to measure this distribution in the emission contaminants which may be analyzed.

The relative environmental impact of PCBs as a function of degree of chlorination needs further assessment and confirmation. The environmental significance of possible PCB emissions from fossil fuel combustion sources, if demonstrated, may be difficult to assess without data relevant to their rate of survival and accumulation in the environment.

The development and testing of techniques for tying up the active chlorine moieties during combustion deserves serious consideration. It may be feasible to develop washing techniques to minimize chlorine content in gaseous and liquid fossil fuels. Coal treatment probably will be more difficult because of diffusion rate limitations of mass transfer in solids.

MONS 202475

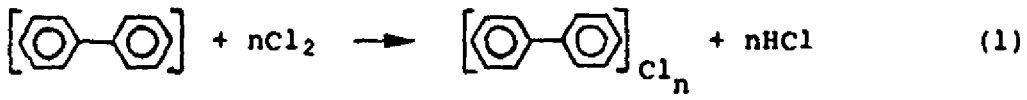
SECTION 4

THERMODYNAMIC CALCULATIONS

A. PCB FORMATION

It is possible to write many reactions of fossil fuel components or known combustion products to form polychlorinated biphenyls (PCBs). In order to consider whether any such reactions may take place, it is necessary to have data to evaluate but, for the formation of polychlorinated biphenyls, little information of this kind exists in the literature. What data are available relates to carefully controlled, bench scale reactions of known components to produce single isomers of known structure. The reaction most often considered in such experiments is given below (1). The likelihood that the reactants exist even briefly in most fossil fuel fired sources is addressed starting in the second paragraph below.

The reaction investigated is that between biphenyl and chlorine to form PCB isomers plus HCl:



(1)

When operated on a large scale to produce commercial mixtures of PCBs this reaction is induced catalytically by various metals and metal salts.[6] Temperatures within commercial reactors are much lower (150°C or less) than those typically encountered within a firebox for reasons of processing convenience.

Hot metal and metal salt surfaces which can be useful in PCB formation are readily available as catalytic surfaces in fossil fuel fired furnaces. They are present either as components of the fuels themselves or the heat exchange surfaces within the furnace or both. At the temperatures encountered, catalysis may be unnecessary.

---

[6]Kirk-Othmer. Encyclopedia of Chemical Technology. 2nd Edition, Vol. 5. Interscience Publishers, New York, NY, 1964. pp. 289 and following.

MONS 202476

Analysis of coal and oil components[7] and the structures of polynuclear aromatic hydrocarbons which have been positively identified in the stack gases of combustion sources,[8] testifies to the transient presence, at least, of benzene in most furnaces (including gas fired). The next step in the logic train considers that the commercial production of biphenyl is a relatively straightforward thermal process using only benzene as a raw material.[9] Further, biphenyl is more stable thermally than benzene[10] and has been identified in combustion effluents.[3,4] The possibility of the existence of biphenyl within the combustion zone also seems acceptable, therefore.

Little work on chlorine in fossil fuels has been published in this country because of low levels present in most domestic fossil fuels.[11,12,13] The literature cited does confirm chlorine's presence in many fossil fuels.[14] Further, there is ample evidence for the presence of HCl (at low levels) in stack gas

---

[7]Kirk-Othmer. Op. Cit., Vol. 3. pp. 367 and following.

[8]Hangebrauck, R. P., D. J. VonLehnden, and J. E. Meeker. Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat Generation and Incineration Processes. Journal of the Air Pollution Control Association, 14:267-278, July 1964.

[9]Kirk-Othmer. Op. Cit., Vol. 7. pp. 191 and following.

[10]Streitwieser, Andrew, Jr. Molecular Orbital Theory for Organic Chemists. John Wiley and Sons, Inc., New York, NY, 1961. pp. 271-243.

[11]Magee, E. M., H. J. Hall, and G. M. Varga, Jr. Potential Pollutants in Fossil Fuels. NTIS No. PB 225039, Contract No. 68-02-0629, U.S. Environmental Protection Agency, June 1973. 292 pp.

[12]Smith, W. S., and C. W. Gruber. Atmospheric Emissions from Coal Combustion - An Inventory Guide. PHS Publ. No. 999-AP-24, NTIS No. PB 170851, U.S. Department of Health, Education, and Welfare, April 1966. 112 pp.

[13]Gordon, G. E., et al. Study of Emissions from Major Air Pollution Sources and Their Atmospheric Interactions. Two-Year Progress Report, RANN Program, NSF Grant No. GE-36338X, Nov 72-Oct 74. 351 pp.

[14]Nelson, W., et al. Corrosion and Deposits in Coal- and Oil-Fired Boilers and Gas Turbines. A Review by the ASME Research Committee on Corrosion and Deposits from Combustion Gases, 1959. pp. 2-6, 13-31, 34, 38, 39, 113, 117-119.

MONS 202477

emissions.[15] HCl plus oxygen can form Cl_2 at elevated temperatures (450°C and up) via a modified Deacon process.[16]

Reactant existence and reaction conditions for Reaction 1 to take place have not been proven. An untested rationale to postulate at least their transient existence, however, has been proposed.

The equilibrium thermodynamics of Reaction 1 were calculated by S. R. Auvil of Monsanto Company for three PCB isomers over the temperature range 50°C to 1500°C (private communication from Dr. S. R. Auvil, Monsanto Co., St. Louis, Mo., May 24, 1976). The results are tabulated in Appendix A, Tables A-1, A-2, and A-3, and summarized below:

Reaction to form	Temperature (°C)	ΔF (kcal/gmole)	Ln K_p
4-MCB	50	-28.5	44.4
	1500	-27.8	7.9
4,4'-DCB	50	-57.0	88.4
	1500	-55.5	15.8
2,2',4,4'-TCB	50	-112.4	175.2
	1500	-109.5	31.1

To quote from Auvil's discussion:

> "...calculations show that the formation of the mono, di, and tetra chlorinated biphenyls by the reaction path (of Reaction 1) are very favored over the temperature range 50°C to 1500°C. Hence, if kinetic pathway exists and has a finite rate under the constraints of the reaction zone, these compounds would have a tendency to form.
>
> "...the thermodynamic properties of 4-MCB and 2,2',4,4'-TCB were estimated. It should be clear that even if the estimated free energies for these compounds were in error by ±5 kcal/gmole, which is unlikely, the reactions are still highly favored and the conclusion is unchanged."

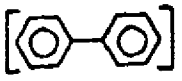
---

[15]Piper, J. D., and H. Van Vliet. Effect of Temperature Variation on Composition, Fouling Tendency, and Corrosiveness of Combustion Gas from a Pulverized-Fuel-Fired Steam Generator. Transactions of the ASME, 80;1251-63, August 1958.

[16]Kirk-Othmer. Op. Cit., Vol. II. pp. 334-36.

B. PCB DESTRUCTION

Another reaction which bears consideration in assessing possible PCB existence in effluent stack gases involves the destruction of PCB if it were formed:



$$Cl_n + [12+(10-2n)/4]O_2 \rightarrow 12CO_2 + \frac{(10-2n)}{2} H_2O + nHCl \qquad (2)$$

To quote the investigator, S. R. Auvil (private communication):

> "The following is a summary of the free energies and equilibrium constants at 50°C and 1500°C (taken from Appendix B, Tables B-1, B-2, and B-3) for the combustion of the mono, di, and tetra chlorinated biphenyls via the above equation (2):

Combustion of 1 gram mole of	Temperature (°C)	ΔF (kcal/gmole)	Ln K_p
4-MCB	50	-1435.0	2236.1
	1500	-1502.2	426.6
4,4'-DCB	50	-1397.8	2178.1
	1500	-1489.2	423.0
2,2',4,4'-TCB	50	-1325.0	2064.7
	1500	-1464.9	416.0

> Clearly each reaction is extremely favored over the 50°C to 1500°C temperature range and in a thermodynamically controlled situation, the chlorinated biphenyls would react to essentially 'extinction.'"

MONS 202479

SECTION 5

KINETIC AND RELATED CONSIDERATIONS

It has been shown in the thermodynamic calculation section that, under the conditions existing in fossil fuel combustion systems PCBs would have a tendency to form. Furthermore, once formed, it has been shown that "in a thermodynamically controlled situation the chlorinated biphenyls would react" essentially to extinction.

Another investigator[17] of PCB reactions has said,

> "...it should be pointed out that results obtained from equilibrium calculations may not immediately be applicable in practice because of kinetic conditions but can provide tendencies of practical interest."

There are inadequate data available at present to address the kinetic probability of PCB formation or destruction during combustion in conventional fossil fuel fired sources. There are, however, useful considerations to address in estimating those sources and conditions which have the highest potential for contributing PCB emissions which may have environmental impact. These considerations include (among others):

A. The specific fossil fuels burned and possible relationships between PCB and polynuclear aromatic hydrocarbon (PAH) emissions.

B. The influence of combustion parameters.

C. An estimate of the relative PCB emissions from fundamentally different kinds of stationary combustion sources.

D. The possibility of PCB contamination of the combustion system.

E. The likely environmental persistence and impact of PCB molecules which may form.

---

[17] Karlsson, L., and E. Rosen. On the Thermal Destruction of Polychlorinated Biphenyls (PCB). Some Equilibrium Considerations. Stockholm, 1(2), 1971.

MONS 202480

A. THE FOSSIL FUELS

For PCBs to be formed during fossil fuel combustion one necessary precondition assumed is the simultaneous presence of chlorine and biphenyl.

Polynuclear aromatic hydrocarbons which may include biphenyl and its precursors (see PCB/PAH discussion below) are readily formed in the combustion of all types of fossil fuels during heat generation or incineration processes.[4,8] They are more copiously emitted from inefficient coal burning sources than those using other fossil fuels (Table 1). See also PCB/PAH discussion below.

Chlorine, if detectable, is likely to be present only as chlorinated organics in natural gas, LPG, or refined oils. In coal and residual oils, however, significant quantities of inorganic chlorides may make a contribution to the availability of reactive chlorine moieties. Corrosion analyses of furnaces firing natural gas and refined oils imply that chlorine from occasional traces of chlorinated organic content in fuel gases and refined oils are at least an order of magnitude lower (or absent) than the chlorine available from chlorides in much of the domestic coals.[11,12,18]

Based on fuel constituents and corrosion analysis the likelihood that chlorine compounds will be present in sufficient quantity in the vapor phase to produce reactive chlorine moieties is judged on the average to be higher with coal than all other conventional fossil fuels.

1. PCB/PAH and Chlorine Distribution

There is a great deal of data in the literature on PAH emissions from stationary and other combustion sources and almost none on PCBs. The following discusses a possible relationship between PCB and PAH emissions.

The generally accepted definition of polynuclear aromatic hydrocarbons (PAH) includes those organic compounds in which at least two aromatic rings share a pair of carbon atoms.[19] Such rings are said to be "fused." The first member and representative compound of the PAH series so defined is naphthalene:



[18]Perry, J. H., et al. Chemical Engineers Handbook. 3rd Edition. McGraw-Hill, New York, NY, 1962. pp. 1576-78.

[19]Morrison, R. T., and R. N. Boyd. Organic Chemistry. 3rd Edition. Allyn and Bacon, Inc., Boston, MA, 1973. p. 967.

MONS 202481

Consideration of historic and present sources[7,20] of benzene and naphthalene suggests the initial presence and/or the concurrent formation of both when fossil fuels are burned. Empirical measurement of resonance energy[10] and consideration of annellation principles (primarily developed by E. Clar, University of Glasgow) indicate greater thermal stability for benzene and biphenyl than for naphthalene and related PAH. Indeed, biphenyl has been identified in some combustion source emissions.[3,4] Kirk-Othmer[6] and others[17] attest to the thermal stability of PCB which exceeds that of chlorinated PAH compounds.[21,22]

There is no experimental evidence to test the issue of a relationship between PCB and PAH emissions. However, the known correlation among PAH emission compounds,[23] the likely presence of related precursor intermediates, and the superior thermal survival of PCB versus PAH suggests some correspondence. It may be conjectured that chlorine availability limits the absolute quantity of PCB formed but that PAH indicates the likelihood of biphenyl formation and the subsequent possibility of PCB (where there is chlorine available). If valid, this theory leads to the projection that sources emitting high levels of PAH are likely PCB emitters if chlorine is present in the fuel. This projection can be tested.

The distribution of available chlorine on any organic compounds surviving combustion may be a random statistical phenomenon. Chlorine distribution may, however, be related to the thermal stability of the compounds which would tend to skew statistical projections. In any case, the degree of chlorination of possible PCB emissions bears on their relative toxicity and their environmental impact and is not a frivolous issue (see section E).

B. THE COMBUSTION CONDITIONS

Four of the combustion factors which influence both the creation and destruction of both PCB and PAH are:

---

[20]Kirk-Othmer. Op. Cit., Vol. 13. pp. 670 and following.

[21]Hurd, C. D. Pyrolysis of Carbon Compounds. American Chemical Society Monograph No. 50, 1929. pp. 143-44.

[22]Best, B. Great Lakes Carbon Corp., British 894,441, September 16, 1960.

[23]Sawicki, E., et al. Polynuclear Aromatic Hydrocarbon Composition of the Atmosphere in Some Large American Cities. Industrial Hygiene Association J., 23(2):137-144, 1962.

MONS 202482

Temperature maximums and temperature range distribution within the combustion zone.

Residence time of the fuels and combustion products in "active" temperature zones.

Mixing efficiency of fuel and air.

Particle size distribution of the fuel source introduced.

It is beyond the scope of this paper to exhaustively evaluate each of these variables for the different fuels in various stationary combustion sources. Study of selected papers[24,25] from the extensive and exhaustive literature which reports on these variables does allow postulation of useful approximations of some furnace effects on stack gas emissions and PCB/PAH structures.

Temperatures

Furnace temperatures, per se, are not separable from residence time in their influence on either production or destruction of PCB/PAH in conventional combustion sources through available literature references. There have been reports of organic chemical incinerators operating at high temperatures (about 2500°F) to ensure complete combustion of the organics.[5] There is no published data, however, which separates the impact of flame temperature and other combustion parameters in the referenced incinerator.

2. Residence Time

One of the clearest impacts of residence time on PAH formation (and PCB by prior reasoning) is reported by Cuffe and Gerstle. Their data indicate that the sudden "quenching" (temperature drop) of the combustion stream in a cyclone boiler as it passes rapidly from the cyclone burner into the convective transfer area leads to high concentrations of PAH emissions (relative to other steam boiler types). This occurs despite the very high temperatures encountered in the cyclone area (Figure 1). By contrast, a horizontally opposed (HO) wet bottom furnace (Figure 2)

[24] Cuffe, S. T., and R. W. Gerstle. Emissions from Coal-Fired Power Plants: A Comprehensive Summary. PHS Publ. No. 999-AP-35, U.S. Department of Health, Education, and Welfare, 1967. 26 pp.

[25] Perry, J. H. Op. Cit., pp. 1639-1643.

MONS 202483

yielded PAH emissions in line with dry bottom furnaces firing at lower temperatures. Presumably, the slower rate of cooling and relatively long residence time of the combustion gases in the HO furnace (relative to the cyclone) account for the lower PAH levels. Mixing efficiency and flame zone temperatures are comparable in the HO and cyclone furnaces.

3. Mixing Efficiency

The impact of this factor on PCB/PAH formation and destruction is very significant. Data from Hangebrauck et al.,[8] and EPA (Table 1)* suggest that mixing as a variable in combustion efficiency may be a major determinant in PAH and PCB emission.

These references contain data and estimates indicating that hand- and underfeed-stoked coal fired residential warm air furnaces, open burning of coal refuse and residential wood burning fireplaces are each at least an order of magnitude more severe in emissions of PAH than all the coal fired steam generating boilers in the United States combined. Of course, the three severe emitter sources cited all represent broad spectra of flame temperatures and combustion zone residence times. These worst offenders have in common, however, the poor mixing of fuel and air. This is also illustrated in Hangebrauck, et al.,[8] data on copious emissions from poorly regulated oil burners.

4. Particle Size Distribution

Obviously, this variable pertains only to liquid and solid fuels. Due to rapid convective heat transfer within the droplets, particle size of liquid fuels is probably only of significance in PCB/PAH generation when some other factor affecting combustion efficiency (temperature, residence time, mixing) is out of control. Poor particle size distribution in that circumstance can aggravate already poor combustion conditions.

In the case of solid coal particles, the internal heat transfer rate is relatively slow.[26] In a worst case situation, incomplete combustion of the central core of very large particles can be envisioned. Thus, particle size can adversely influence otherwise efficient combustion in pulverized coal (p.c.) furnaces. Well regulated p.c. burning steam power generating facilities rarely will be impacted by this factor though it has the potential to increase PCB/PAH emissions.

*While Table 1 reports benzo(a)pyrene emissions, Sawicki, et al.[23] have shown a correlation between this compound and total PAH emissions.

[26]Green, N. W. Synthetic Fuels from Coal - The Garrett Process. Clean Fuels from Coal Symposium II, Institute of Gas Technology, Chicago, June 23-27, 1975. p. 301.

MONS 202484

C. "UNCONVENTIONAL" FOSSIL FUEL COMBUSTION

As has already been shown (Table 1), sources of hydrocarbon emissions other than conventional fossil fuel fired combustion sources have the potential to generate PAH and PCB. Open burning of coal refuse may rank as the greatest non-furnace source of these compounds followed closely by poorly regulated coke production operations (the latter, strictly speaking, a pyrolysis rather than combustion process). Even rubber tire degradation in use has some major potential for PCB/PAH generation according to Table 1.

D. PCB CONTAMINATION AS AN EMISSION SOURCE

Finite levels of PCB amounting to parts per billion or more have been detected literally world-wide from penguin eggs in the Antarctic to anchovies from the Arctic circle.[2] PCBs have been used commercially in heat transfer fluids, hydraulics and lubricants, transformer fluids, capacitors, plasticizers, industrial solvents and other specialty applications. Additionally, they have been tested in semi-commercial or developmental quantities as cutting fluid additives, components of high temperature sealants and high temperature pipe caulking. They have incidental impact as infrequent components in waste oils used for dust control on coal piles and temporary corrosion protection of steel components in furnace construction.

Obviously, several of these uses could result in contamination of a furnace interior or its fuel supply with PCBs. This possibility could change the picture of PCB stack gas emissions from one of creation and survival to survival, alone. If the contaminating source is in a relatively cool section of the combustion source the PCB emission may be from continual evaporation of product until the supply is exhausted. This is likely to be only a short term phenomenon at worst.

Assessment of contamination as a source of PCB emission would require rigorous furnace study and characterization of all input streams (fuel, air, auxiliaries). The relative potential impact of contamination versus in-situ generation as a PCB emission source is unknown.

E. ENVIRONMENTAL PERSISTENCE AND IMPACT

There are a large number of references on this subject. Many are summarized and useful general conclusions are offered on both aspects (persistence and toxicity[27]) of the issue in the

---

[27]Peakall, D. B., and J. L. Lincer. Polychlorinated Biphenyls. Bioscience, 20:958-64, Sept. 1970.

MONS 202485

report of the Interdepartmental Task Force on PCBs, "Polychlorinated Biphenyls and the Environment," May 1972. The Task Force had representation from five Executive Branch departments of the Federal Government including EPA.

Among their tentative conclusions were:

1. "[PCB] Acute oral LD_{50} in mammals varies from approximately 2-10 gm/Kg. (Apparent increase in mammalian toxicity with decrease in chlorine content.)"

2. "The starting materials used in synthesis of PCBs determine to a large degree the type of impurity or contaminant in the commercial product. The contaminant variation, of course, renders some divergence in the LD 50 values or other toxicologic response of the PCBs. Fractionated samples of some PCBs of foreign manufacture have shown them to contain as contaminants the tetra- and pentachlorodibenzofurans, the hexa- and heptachloronaphthalenes.

In a report[28] prepared specifically for presentation to the Interdepartmental Task Force on PCBs, Munch presented data indicating the possibility that PCB "homologs containing less than four chlorine atoms may be degraded at rates approximately thirty times those for the five and six chlorine homologs."

There is some chance, therefore, that PCB which may show up as emissions from fossil fuel fired sources are more rapidly degraded in the environment than commercial PCB products. Section A, p. 12, discusses the possibility that potential PCB isomers in combustion stack gases have a low degree of chlorination.

---

[28] Papageorge, W. B., et al. Presentation to the Interdepartmental Task Force on PCBs. Washington, D.C., May 15, 1972. 69 pp.

MONS 202486

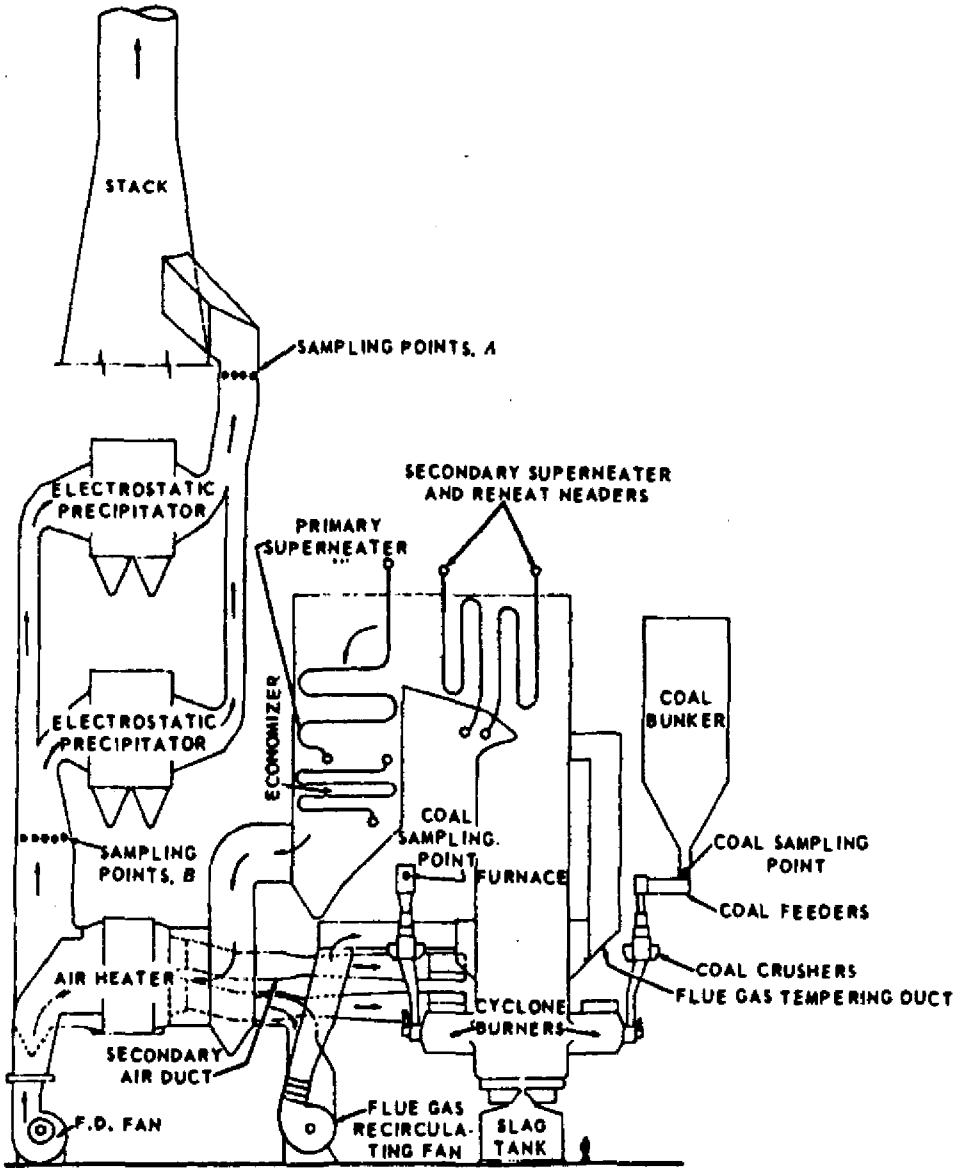


Figure 1. Boiler outline for cyclone type unit.[24]

MONS 202487

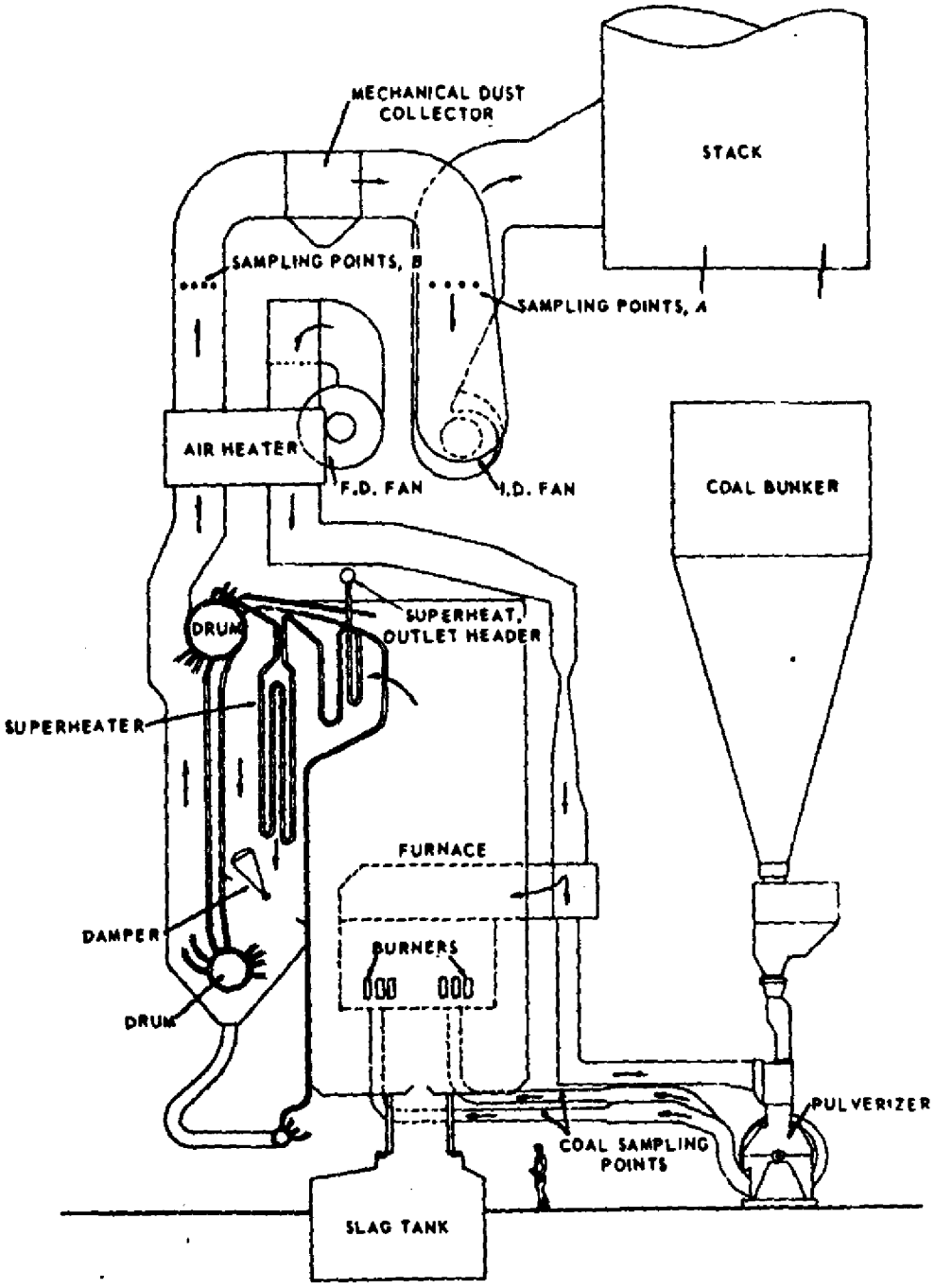


Figure 2. Boiler outline for horizontally-opposed firing unit.[24]

MONS 202488

Table 1. ESTIMATED BENZO(a)PYRENE* EMISSIONS IN UNITED STATES, 1972[a]

Source Type	Emissions, MT/yr
Stationary sources	
Coal hand-stoked and underfeed-stoked residual** furnaces	270
Coal, intermediate-size furnaces	6
Coal, steam power plants	<1
Oil, residential through steam power type	2
Gas, residential through steam power type	2
Wood, home fireplaces	23
Enclosed incineration, apartment through municipal type	3
Open burning, coal refuse	281
Open burning, vehicle disposal	5
Open burning, forest and agriculture	10
Open burning, other	9
Petroleum catalytic cracking	6
Coke production	0.05 to 153
Asphalt air-blowing	<1
Mobile sources	
Gasoline-powered, automobiles and trucks	10
Diesel-powered, trucks and buses	<1
Rubber tire degradation	10

[a]From Preferred Standards Path Report for Polycyclic Organic Matter. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Durham, N.C. October 1974. p. 27-36.

*See footnote on p. 14.

**Misprint - should read residential.

MONS 202489

REFERENCES

1. Cowherd, C., Jr., M. Marcus, C. M. Cuenther, and J. L. Spigarelli. Hazardous Emission Characterization of Utility Boilers. Contract No. 68-02-1324, Task No. 27, U.S. Environmental Protection Agency, 23 June 1975. 185 pp.

2. Interdepartmental Task Force on PCBs. Polychlorinated Biphenyls and the Environment. COM-72-10419, Washington, D.C., May 1972. 181 pp.

3. Girling, G. W., and E. C. Ormerod. Variation in Concentration of Some Constituents of Tar in Coke-Oven Gas. Benzole Producers, Limited (London), Paper 1-1963, April 1963. 13 pp.

4. Kubota, H., W. H. Griest, and M. R. Guerin. Determination of Carcinogens in Tobacco Smoke and Coal-Derived Samples - Trace Polynuclear Aromatic Hydrocarbons. CONF 750603-3, Oak Ridge National Laboratory, Oak Ridge, Tennessee. 9 pp.

5. Anonymous. Solving Waste Problem Profitably. Chemical Week, 104(24):38, 1969.

6. Kirk-Othmer. Encyclopedia of Chemical Technology. 2nd Edition, Vol. 5. Interscience Publishers, New York, NY, 1964. pp. 289 and following.

7. Op. Cit., Vol. 3. pp. 367 and following.

8. Hangebrauck, R. P., D. J. VonLehnden, and J. E. Meeker. Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat Generation and Incineration Processes. Journal of the Air Pollution Control Association, 14:267-278, July 1964.

9. Kirk-Othmer. Op. Cit., Vol. 7. pp. 191 and following.

10. Streitwieser, Andrew, Jr. Molecular Orbital Theory for Organic Chemists. John Wiley and Sons, Inc., New York, NY, 1961. pp.241-243.

11. Magee, E. M., H. J. Hall, and G. M. Varga, Jr. Potential Pollutants in Fossil Fuels. NTIS No. PB 225039, Contract No. 68-02-0629, U.S. Environmental Protection Agency, June 1973. 292 pp.

MONS 202490

12. Smith, W. S., and C. W. Gruber. Atmospheric Emissions from Coal Combustion - An Inventory Guide. PHS Publ. No. 999-AP-24, NTIS No. PB 170851, U.S. Department of Health, Education, and Welfare, April 1966. 112 pp.

13. Gordon, G. E., et al. Study of Emissions from Major Air Pollution Sources and Their Atmospheric Interactions. Two-Year Progress Report, RANN Program, NSF Grant No. GI-36338X, Nov 72-Oct 74. 351 pp.

14. Nelson, W., et al. Corrosion and Deposits in Coal- and Oil-Fired Boilers and Gas Turbines. A Review by the ASME Research Committee on Corrosion and Deposits from Combustion Gases, 1959. pp. 2-6, 13-31, 34, 38, 39, 113, 117-119.

15. Piper, J. D., and H. Van Vliet. Effect of Temperature Variation on Composition, Fouling Tendency, and Corrosiveness of Combustion Gas from a Pulverized-Fuel-Fired Steam Generator. Transactions of the ASME, 80:1251-63, August 1958.

16. Kirk-Othmer. Op. Cit., Vol. II. pp. 334-36.

17. Karlsson, L., and E. Rosen. On the Thermal Destruction of Polychlorinated Biphenyls (PCB). Some Equilibrium Considerations. Stockholm, 1(2), 1971.

18. Perry, J. H., et al. Chemical Engineers Handbook. 3rd Edition. McGraw-Hill, New York, NY, 1962. pp. 1576-78.

19. Morrison, R. T., and R. N. Boyd. Organic Chemistry. 3rd Edition. Allyn and Bacon, Inc., Boston, MA, 1973. p. 967.

20. Kirk-Othmer. Op. Cit., Vol. 13. pp. 670 and following.

21. Hurd, C. D. Pyrolysis of Carbon Compounds. American Chemical Society Monograph No. 50, 1929. pp. 143-44.

22. Best, B. Great Lakes Carbon Corp., British 894,441, September 16, 1960.

23. Sawicki, E., et al. Polynuclear Aromatic Hydrocarbon Composition of the Atmosphere in Some Large American Cities. Industrial Hygiene Association J., 23(2):137-144, 1962.

24. Cuffe, S. T., and R. W. Gerstle. Emissions from Coal-Fired Power Plants: A Comprehensive Summary. PHS Publ. No. 999-AP-35, U.S. Department of Health, Education, and Welfare, 1967. 26 pp.

25. Perry, J. H. Op. Cit., pp. 1639-1643.

MONS 202491

26. Green, N. W. Synthetic Fuels from Coal - The Garrett Process. Clean Fuels from Coal Symposium II, Institute of Gas Technology, Chicago, IL, June 23-27, 1975. p. 301.

27. Peakall, D. B., and J. L. Lincer. Polychlorinated Biphenyls. Bioscience, 20:958-64, Sept. 1970.

28. Papageorge, W. B., et al. Presentation to the Interdepartmental Task Force on PCBs. Washington, D.C., May 15, 1972. 69 pp.

MONS 202492

APPENDICES

APPENDIX A. Reaction Thermodynamics, Formation

APPENDIX B. Reaction Thermodynamics, Oxidation

APPENDIX C. Thermodynamic Data to Support Information Generated in Appendices A and B

APPENDIX A

Table A-1. REACTION THERMODYNAMICS, FORMATION

COMPOUND	STOICHIOMETERIC COEFF	STATE
4-CHLOROBIPHENYL	1	IDEAL GAS
HYDROGEN CHLORIDE	1	IDEAL GAS
BIPHENYL	-1	IDEAL GAS
CHLORINE	-1	IDEAL GAS

Biphenyl + Cl_2 ⟶ 4-MCB + HCl

TEMPERATURE (C)	DHR(T) (KCAL/GMOLE)	DSR(T) (CAL/GMOL/K)	DFR(T) (KCAL/GMOLE)	LN K
50.0	-29.344	-2.597	-28.505	44.419
100.0	-29.198	-2.175	-28.386	38.307
150.0	-29.064	-1.838	-28.286	33.661
200.0	-28.940	-1.561	-28.201	30.014
250.0	-28.826	-1.331	-28.129	27.076
300.0	-28.720	-1.138	-28.068	24.660
350.0	-28.622	-.974	-28.015	22.639
400.0	-28.531	-.834	-27.970	20.923
450.0	-28.447	-.714	-27.931	19.450
500.0	-28.370	-.610	-27.898	18.170
550.0	-28.299	-.521	-27.870	17.049
600.0	-28.233	-.443	-27.846	16.059
650.0	-28.172	-.376	-27.825	15.178
700.0	-28.116	-.317	-27.808	14.390
750.0	-28.065	-.265	-27.794	13.679
800.0	-28.017	-.219	-27.782	13.036
850.0	-27.973	-.179	-27.772	12.451
900.0	-27.932	-.143	-27.764	11.917
950.0	-27.894	-.111	-27.757	11.427
1000.0	-27.858	-.083	-27.752	10.977
1050.0	-27.825	-.057	-27.749	10.561
1100.0	-27.793	-.034	-27.747	10.175
1150.0	-27.764	-.013	-27.746	9.817
1200.0	-27.736	.006	-27.745	9.484
1250.0	-27.710	.024	-27.746	9.173
1300.0	-27.685	.040	-27.748	8.882
1350.0	-27.661	.055	-27.750	8.609
1400.0	-27.639	.069	-27.753	8.353
1450.0	-27.617	.081	-27.757	8.112
1500.0	-27.597	.093	-27.761	7.884

DEFINITIONS .....

DHR, DSR, AND DFR = HEAT, ENTROPY, AND FREE ENERGY OF THE REACTION, RESPECTIVELY.

DFR = DHR - T*DSR/1000
LN K = - DFR*1000/R/T
R = 1.98565 CAL/GMOLE/K
T = DEGREES CELSIUS + 273.15

MONS 202494

Table A-2. REACTION THERMODYNAMICS, FORMATION

COMPOUND	STOICHIOMETERIC COEFF	STATE
4,4-DICHLORBIPHENYL	1	IDEAL GAS
HYDROGEN CHLORIDE	2	IDEAL GAS
BIPHENYL	-1	IDEAL GAS
CHLORINE	-2	IDEAL GAS

Biphenyl + $2Cl_2$ ⟶ 4, 4'-DCB + 2HCl

TEMPERATURE (C)	DHR(T) (KCAL/GMOLE)	DSR(T) (CAL/GMOL/K)	DFR(T) (KCAL/GMOLE)	LN K
50.0	-58.688	-5.194	-57.010	88.838
100.0	-58.395	-4.350	-56.772	76.614
150.0	-58.127	-3.675	-56.572	67.323
200.0	-57.880	-3.121	-56.403	60.028
250.0	-57.651	-2.661	-56.250	54.152
300.0	-57.439	-2.274	-56.135	49.320
350.0	-57.243	-1.946	-56.030	45.277
400.0	-57.062	-1.666	-55.940	41.847
450.0	-56.894	-1.426	-55.863	38.900
500.0	-56.740	-1.220	-55.797	36.341
550.0	-56.597	-1.041	-55.740	34.099
600.0	-56.466	-.886	-55.692	32.119
650.0	-56.344	-.751	-55.651	30.357
700.0	-56.232	-.633	-55.617	28.779
750.0	-56.129	-.529	-55.598	27.359
800.0	-56.033	-.438	-55.564	26.073
850.0	-55.945	-.357	-55.544	24.903
900.0	-55.862	-.285	-55.528	23.835
950.0	-55.785	-.221	-55.515	22.855
1000.0	-55.713	-.163	-55.506	21.954
1050.0	-55.646	-.111	-55.499	21.122
1100.0	-55.582	-.064	-55.495	20.351
1150.0	-55.522	-.021	-55.493	19.635
1200.0	-55.465	.019	-55.493	18.969
1250.0	-55.410	.055	-55.494	18.347
1300.0	-55.358	.089	-55.498	17.765
1350.0	-55.309	.120	-55.503	17.219
1400.0	-55.261	.149	-55.510	16.707
1450.0	-55.216	.175	-55.518	16.224
1500.0	-55.172	.200	-55.527	15.769

DEFINITIONS .....

DHR, DSR, AND DFR = HEAT, ENTROPY, AND FREE ENERGY OF THE REACTION, RESPECTIVELY.

DFR = DHR - T*DSR/1000
LN K = - DFR*1000/R/T
R = 1.98585 CAL/GMOLE/K
T = DEGREES CELSIUS + 273.15

MONS 202495

Table A-3. REACTION THERMODYNAMICS, FORMATION

COMPOUND	STOICHIOMETERIC COEFF	STATE
2,2',4,4'-TETRA CB	1	IDEAL GAS
HYDROGEN CHLORIDE	4	IDEAL GAS
BIPHENYL	-1	IDEAL GAS
CHLORINE	-4	IDEAL GAS

Biphenyl + $4Cl_2$ ⟶ 2,2',4,4'-TCB + 4HCl

TEMPERATURE (C)	DHR(T) (KCAL/GMOLE)	DSR(T) (CAL/GMOL/K)	DFR(T) (KCAL/GMOLE)	LN K
50.0	-115.777	-10.388	-112.420	175.183
100.0	-115.190	-8.699	-111.944	151.068
150.0	-114.653	-7.346	-111.544	132.742
200.0	-114.157	-6.238	-111.206	118.354
250.0	-113.699	-5.317	-110.917	106.765
300.0	-113.275	-4.543	-110.671	97.235
350.0	-112.885	-3.887	-110.461	89.263
400.0	-112.521	-3.327	-110.281	82.498
450.0	-112.187	-2.848	-110.127	76.687
500.0	-111.878	-2.435	-109.995	71.641
550.0	-111.595	-2.078	-109.883	67.221
600.0	-111.331	-1.769	-109.787	63.316
650.0	-111.089	-1.499	-109.705	59.842
700.0	-110.865	-1.262	-109.636	56.732
750.0	-110.657	-1.055	-109.578	53.931
800.0	-110.465	-.671	-109.530	51.396
850.0	-110.286	-.708	-109.491	49.090
900.0	-110.119	-.562	-109.459	46.984
950.0	-109.963	-.432	-109.435	45.053
1000.0	-109.815	-.314	-109.416	43.277
1050.0	-109.676	-.206	-109.403	41.636
1100.0	-109.544	-.108	-109.395	40.117
1150.0	-109.417	-.018	-109.392	38.707
1200.0	-109.296	.066	-109.393	37.394
1250.0	-109.180	.143	-109.399	36.168
1300.0	-109.068	.216	-109.407	35.021
1350.0	-108.959	.284	-109.420	33.946
1400.0	-108.854	.347	-109.436	32.937
1450.0	-108.753	.407	-109.455	31.986
1500.0	-108.654	.464	-109.476	31.091

DEFINITIONS .....

DHR, DSR, AND DFR = HEAT, ENTROPY, AND FREE ENERGY OF THE REACTION, RESPECTIVELY.

DFR = DHR - T*DSR/1000
LN K = - DFR*1000/R/T
R = 1.98585 CAL/GMOLE/K
T = DEGREES CELSIUS + 273.15

MONS 202496

APPENDIX B

Table B-1. REACTION THERMODYNAMICS, OXIDATION

COMPOUND	STOICHIOMETERIC COEFF	STATE
CARBON DIOXIDE	12	IDEAL GAS
WATER	4	IDEAL GAS
HYDROGEN CHLORIDE	1	IDEAL GAS
4-CHLOROBIPHENYL	-1	IDEAL GAS
OXYGEN	-14	IDEAL GAS

$$4\text{-BCB} + 14O_2 \longrightarrow 12CO_2 + 4H_2O + HCl$$

TEMPERATURE (C)	DHR(T) (KCAL/GMOLE)	DSR(T) (CAL/GMOL/K)	DFR(T) (KCAL/GMOLE)	LN K
50.0	-1417.967	52.566	-1434.954	2236.080
100.0	-1417.840	52.937	-1437.593	1940.019
150.0	-1417.814	53.005	-1440.242	1713.937
200.0	-1417.695	52.830	-1442.889	1555.634
250.0	-1418.072	52.472	-1445.522	1391.401
300.0	-1418.340	51.983	-1448.134	1272.313
350.0	-1418.687	51.403	-1450.719	1172.315
400.0	-1419.101	50.765	-1453.274	1087.149
450.0	-1419.571	50.093	-1455.795	1013.737
500.0	-1420.085	49.405	-1458.283	949.799
550.0	-1420.636	48.715	-1460.736	893.606
600.0	-1421.213	48.034	-1463.154	843.830
650.0	-1421.810	47.370	-1465.539	799.427
700.0	-1422.420	46.727	-1467.892	759.570
750.0	-1423.036	46.109	-1470.212	728.593
800.0	-1423.659	45.518	-1472.503	690.954
850.0	-1424.272	44.956	-1474.765	661.209
900.0	-1424.883	44.424	-1476.999	633.937
950.0	-1425.486	43.921	-1479.208	608.980
1000.0	-1426.078	43.446	-1481.392	585.927
1050.0	-1426.657	43.000	-1483.553	564.609
1100.0	-1427.223	42.580	-1485.692	544.834
1150.0	-1427.774	42.186	-1487.811	526.442
1200.0	-1428.309	41.817	-1489.911	509.292
1250.0	-1428.826	41.470	-1491.993	493.262
1300.0	-1429.332	41.144	-1494.058	478.246
1350.0	-1429.821	40.839	-1496.106	464.149
1400.0	-1430.295	40.551	-1498.143	450.891
1450.0	-1430.754	40.280	-1500.163	438.398
1500.0	-1431.201	40.025	-1502.171	426.606

DEFINITIONS .....

DHR, DSR, AND DFR = HEAT, ENTROPY, AND FREE ENERGY OF THE REACTION, RESPECTIVELY.

DFR = DHR - T*DSR/1000
LN K = - DFR*1000/R/T
R = 1.98585 CAL/GMOLE/K
T = DEGREES CELSIUS + 273.15

MONS 202497

Table B-2. REACTION THERMODYNAMICS, OXIDATION

COMPOUND	STOICHIOMETERIC COEFF	STATE
CARBON DIOXIDE	24	IDEAL GAS
HYDROGEN CHLORIDE	4	IDEAL GAS
WATER	6	IDEAL GAS
4,4-DICHLOROBIPHENYL	-2	IDEAL GAS
OXYGEN	-27	IDEAL GAS

$2\ 4,4\text{-DCB} + 27O_2 \longrightarrow 24CO_2 + 6H_2O + 4HCl$

TEMPERATURE (C)	DHR(T) (KCAL/GMOLE)	DSR(T) (CAL/GMOL/K)	DFR(T) (KCAL/GMOLE)	LN K
50.0	-2749.840	141.336	-2795.512	4356.230
100.0	-2749.773	141.534	-2802.587	3782.066
150.0	-2749.902	141.214	-2809.657	3343.586
200.0	-2750.233	140.481	-2816.701	2997.750
250.0	-2750.791	139.442	-2823.700	2717.978
300.0	-2751.637	138.191	-2830.642	2486.962
350.0	-2752.868	136.803	-2837.517	2292.976
400.0	-2754.221	135.333	-2844.321	2127.748
450.0	-2754.273	133.826	-2851.050	1985.317
500.0	-2755.405	132.313	-2857.703	1861.259
550.0	-2756.598	130.819	-2864.281	1752.227
600.0	-2757.835	129.360	-2870.786	1655.638
650.0	-2759.102	127.949	-2877.215	1569.474
700.0	-2760.387	126.594	-2883.581	1492.128
750.0	-2761.679	125.299	-2889.879	1422.309
800.0	-2762.969	124.068	-2896.112	1358.966
850.0	-2764.249	122.902	-2902.286	1301.236
900.0	-2765.513	121.801	-2908.404	1248.403
950.0	-2766.755	120.764	-2914.468	1199.867
1000.0	-2767.973	119.788	-2920.481	1155.123
1050.0	-2769.162	118.872	-2926.447	1113.744
1100.0	-2770.320	118.013	-2932.369	1075.361
1150.0	-2771.446	117.208	-2938.250	1039.661
1200.0	-2772.538	116.453	-2944.091	1006.370
1250.0	-2773.598	115.746	-2949.896	975.254
1300.0	-2774.624	115.083	-2955.666	946.104
1350.0	-2775.617	114.461	-2961.405	918.740
1400.0	-2776.578	113.878	-2967.113	893.003
1450.0	-2777.509	113.330	-2972.793	868.751
1500.0	-2778.411	112.814	-2978.447	845.859

DEFINITIONS .....

DHR, DSR, AND DFR = HEAT, ENTROPY, AND FREE ENERGY OF THE REACTION, RESPECTIVELY.

DFR = DHR - T*DSR/1000
LN K = - DFR*1000/R/T
R = 1.98585 CAL/GMOLE/K
T = DEGREES CELSIUS + 273.15

MONS 202498

Table B-3. REACTION THERMODYNAMICS, OXIDATION

COMPOUND	STOICHIOMETERIC COEFF	STATE
CARBON DIOXIDE	24	IDEAL GAS
WATER	2	IDEAL GAS
HYDROGEN CHLORIDE	8	IDEAL GAS
2,2,4,4-TETRA CB	-2	IDEAL GAS
OXYGEN	-25	IDEAL GAS

2 2,2',4,4'-TCB + $25O_2$ ⟶ $24CO_2$ + $2H_2O$ + 8HCl

TEMPERATURE (C)	DHR(T) (KCAL/GMOLE)	DSR(T) (CAL/GMOL/K)	DFR(T) (KCAL/GMOLE)	LN K
50.0	-2580.851	213.742	-2649.922	4129.357
100.0	-2581.161	212.555	-2660.588	3590.441
150.0	-2581.655	211.619	-2671.201	3178.319
200.0	-2582.330	210.115	-2681.746	2854.121
250.0	-2583.170	208.429	-2692.210	2591.411
300.0	-2584.155	206.633	-2702.587	2374.460
350.0	-2585.260	204.787	-2712.872	2192.251
400.0	-2586.462	202.932	-2723.065	2037.041
450.0	-2587.740	201.101	-2733.166	1903.230
500.0	-2589.076	199.315	-2743.176	1786.666
550.0	-2590.451	197.591	-2753.098	1684.210
600.0	-2591.852	195.939	-2762.936	1593.440
650.0	-2593.266	194.364	-2772.694	1512.457
700.0	-2594.683	192.870	-2782.374	1439.757
750.0	-2596.092	191.458	-2791.982	1374.127
800.0	-2597.488	190.126	-2801.521	1314.580
850.0	-2598.863	188.873	-2810.996	1260.306
900.0	-2600.213	187.697	-2820.410	1210.632
950.0	-2601.534	186.594	-2829.767	1164.996
1000.0	-2602.823	185.561	-2839.071	1122.923
1050.0	-2604.079	184.594	-2848.324	1084.012
1100.0	-2605.299	183.690	-2857.531	1047.916
1150.0	-2606.483	182.841	-2866.694	1014.342
1200.0	-2607.631	182.049	-2875.816	983.032
1250.0	-2608.742	181.307	-2884.900	953.765
1300.0	-2609.816	180.613	-2893.947	926.348
1350.0	-2610.855	179.963	-2902.962	900.609
1400.0	-2611.859	179.353	-2911.945	876.399
1450.0	-2612.829	178.782	-2920.898	853.585
1500.0	-2613.766	178.246	-2929.823	832.053

DEFINITIONS .....

DHR, DSR, AND DFR = HEAT, ENTROPY, AND FREE ENERGY OF THE REACTION, RESPECTIVELY.

DFR = DHR - T*DSR/1000

LN K = - DFR*1000/R/T

R = 1.98585 CAL/GMOLE/K

T = DEGREES CELSIUS + 273.15

MONS 202499

APPENDIX C

Table C-1. BIPHENYL THERMODYNAMICS

BIPHENYL (IDEAL GAS) MOLECULAR WT. 154.200

TEMPERATURE (C)	CP (CAL/GMOL/K)	H-H(25 C) (KCAL/GMOLE)	S-S(25 C) (CAL/GMOL/K)	DHF(T) (KCAL/GMOLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/GMOLE)	LN K
50.0	42.528	1.016	3.272	43.028	-80.135	68.924	-107.404
100.0	49.306	3.320	9.889	42.119	-82.754	72.999	-98.512
150.0	55.796	5.956	16.508	41.307	-84.800	77.190	-91.859
200.0	61.465	8.890	23.056	40.565	-86.414	81.472	-86.709
250.0	66.276	12.093	29.487	39.947	-87.698	85.826	-82.612
300.0	71.182	15.539	35.775	39.395	-88.725	90.237	-79.281
350.0	75.334	19.203	41.902	38.892	-89.550	94.695	-76.522
400.0	79.077	23.065	47.862	38.462	-90.213	99.190	-74.201
450.0	82.451	27.105	53.649	38.091	-90.746	103.714	-72.221
500.0	85.492	31.305	59.264	37.772	-91.173	108.262	-70.513
550.0	88.233	35.649	64.708	37.502	-91.511	112.830	-69.024
600.0	90.704	40.124	69.984	37.277	-91.777	117.412	-67.714
650.0	92.931	44.715	75.097	37.093	-91.982	122.007	-66.553
700.0	94.939	49.413	80.053	36.947	-92.137	126.610	-65.515
750.0	96.748	54.206	84.855	36.835	-92.249	131.220	-64.582
800.0	98.379	59.085	89.510	36.755	-92.326	135.834	-63.739
850.0	99.850	64.041	94.024	36.702	-92.374	140.452	-62.971
900.0	101.175	69.067	98.402	36.674	-92.398	145.071	-62.270
950.0	102.370	74.157	102.650	36.667	-92.405	149.691	-61.627
1000.0	103.446	79.302	106.773	36.676	-92.397	154.311	-61.034
1050.0	104.417	84.499	110.777	36.697	-92.381	158.931	-60.486
1100.0	105.292	89.743	114.667	36.725	-92.360	163.549	-59.977
1150.0	106.081	95.027	118.447	36.755	-92.339	168.167	-59.504
1200.0	106.792	100.349	122.122	36.781	-92.320	172.783	-59.062
1250.0	107.432	105.705	125.697	36.797	-92.310	177.399	-58.649
1300.0	108.010	111.092	129.177	36.795	-92.311	182.015	-58.263
1350.0	108.531	116.505	132.565	36.767	-92.329	186.630	-57.900
1400.0	109.000	121.944	135.865	36.706	-92.366	191.248	-57.559
1450.0	109.423	127.405	139.081	36.601	-92.427	195.847	-57.239
1500.0	109.804	132.885	142.216	36.444	-92.517	200.491	-56.938

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE, H = ENTHALPY, S = ENTROPY, AND DHF, DSF, AND DFF ARE THE HEAT, ENTROPY, AND FREE ENERGY OF FORMATION, RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T, WHERE
R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202500

Table C-2. 4-CHLOROBIPHENYL THERMODYNAMICS

Table C-2. 4-CHLOROBIPHENYL THERMODYNAMICS

4-CHLOROBIPHENYL (IDEAL GAS) MOLECULAR WT. 188.661

TEMPERATURE (C)	CP (CAL/GMOL/K)	H-H(25 C) (KCAL/GMOLE)	S-S(25 C) (CAL/GMOL/K)	DHF(T) (KCAL/GMOLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/GMOLE)	LN K
50.0	46.458	1.125	3.622	35.761	-85.084	63.256	-98.572
100.0	53.736	3.643	10.855	35.032	-87.185	67.566	-91.179
150.0	59.907	6.487	17.999	34.392	-88.798	71.967	-85.643
200.0	65.494	9.623	24.999	33.853	-90.047	76.439	-81.353
250.0	70.413	13.022	31.823	33.350	-91.020	80.967	-77.955
300.0	74.871	16.656	38.454	32.934	-91.780	85.538	-75.152
350.0	78.872	20.501	44.885	32.579	-92.375	90.142	-72.843
400.0	82.461	24.536	51.111	32.279	-92.839	94.773	-70.897
450.0	85.682	28.741	57.135	32.028	-93.198	99.424	-69.254
500.0	88.571	33.099	62.961	31.823	-93.473	104.092	-67.796
550.0	91.164	37.594	68.593	31.658	-93.680	108.771	-66.541
600.0	93.491	42.211	74.038	31.531	-93.830	113.459	-65.434
650.0	95.579	46.939	79.303	31.438	-93.933	118.153	-64.450
700.0	97.452	51.765	84.394	31.377	-93.998	122.851	-63.570
750.0	99.133	56.681	89.319	31.344	-94.031	127.552	-62.777
800.0	100.641	61.676	94.086	31.337	-94.038	132.254	-62.059
850.0	101.994	66.742	98.700	31.352	-94.024	136.956	-61.404
900.0	103.206	71.873	103.169	31.387	-93.994	141.656	-60.804
950.0	104.297	77.061	107.499	31.438	-93.952	146.355	-60.253
1000.0	105.279	82.301	111.698	31.501	-93.901	151.051	-59.744
1050.0	106.152	87.587	115.770	31.573	-93.846	155.745	-59.273
1100.0	106.939	92.914	119.722	31.649	-93.790	160.436	-58.835
1150.0	107.643	98.279	123.560	31.722	-93.737	165.124	-58.427
1200.0	108.279	103.678	127.286	31.790	-93.690	169.809	-58.045
1250.0	108.848	109.106	130.912	31.844	-93.654	174.493	-57.688
1300.0	109.358	114.562	134.436	31.878	-93.632	179.175	-57.354
1350.0	109.815	120.041	137.865	31.885	-93.627	183.856	-57.039
1400.0	110.226	125.542	141.203	31.856	-93.645	188.538	-56.744
1450.0	110.595	131.063	144.454	31.783	-93.686	193.221	-56.466
1500.0	110.925	136.601	147.622	31.655	-93.761	197.907	-56.208

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE, H = ENTHALPY, S = ENTROPY, AND DHF, DSF, AND DFF ARE THE HEAT, ENTROPY, AND FREE ENERGY OF FORMATION, RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T, WHERE R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202501

Table C-3. 4,4-DICHLOROBIPHENYL THERMODYNAMICS

4,4-DICHLOROBIPHENYL (IDEAL GAS) MOLECULAR WT. 223.110

TEMPERATURE (C)	CP (CAL/GMOL/K)	H-H(25 C) (KCAL/GMOLE)	S-S(25 C) (CAL/GMOL/K)	DHF(T) (KCAL/GMOLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/GMOLE)	LN K
50.0	51.188	1.234	3.975	28.494	-90.034	57.589	-89.740
100.0	57.968	3.966	11.822	27.946	-91.616	62.132	-83.847
150.0	64.021	7.019	19.491	27.477	-92.796	66.744	-79.427
200.0	69.426	10.357	26.943	27.082	-93.683	71.407	-75.997
250.0	74.252	13.952	34.160	26.753	-94.341	76.108	-73.258
300.0	78.561	17.774	41.135	26.484	-94.834	80.838	-71.023
350.0	82.408	21.800	47.868	26.266	-95.199	85.589	-69.164
400.0	85.843	26.008	54.361	26.095	-95.463	90.356	-67.593
450.0	88.910	30.378	60.623	25.966	-95.649	95.134	-66.246
500.0	91.649	34.894	66.659	25.873	-95.773	99.920	-65.079
550.0	94.094	39.538	72.480	25.814	-95.848	104.711	-64.057
600.0	96.277	44.299	78.093	25.785	-95.882	109.504	-63.153
650.0	98.226	49.162	83.509	25.784	-95.883	114.298	-62.348
700.0	99.966	54.118	88.737	25.807	-95.859	119.092	-61.625
750.0	101.520	59.156	93.784	25.853	-95.813	123.884	-60.972
800.0	102.908	64.267	98.662	25.919	-95.750	128.673	-60.378
850.0	104.146	69.444	103.376	26.003	-95.674	133.459	-59.836
900.0	105.252	74.679	107.937	26.101	-95.588	138.240	-59.338
950.0	106.240	79.967	112.351	26.211	-95.497	143.017	-58.879
1000.0	107.122	85.302	116.625	26.329	-95.402	147.790	-58.455
1050.0	107.909	90.678	120.767	26.453	-95.307	152.558	-58.063
1100.0	108.612	96.091	124.783	26.576	-95.215	157.321	-57.693
1150.0	109.239	101.538	128.679	26.696	-95.129	162.079	-57.350
1200.0	109.800	107.014	132.460	26.806	-95.053	166.834	-57.028
1250.0	110.300	112.517	136.134	26.901	-94.990	171.585	-56.727
1300.0	110.747	118.043	139.704	26.973	-94.943	176.333	-56.444
1350.0	111.146	123.590	143.175	27.017	-94.916	181.079	-56.178
1400.0	111.502	129.157	146.553	27.023	-94.912	185.825	-55.927
1450.0	111.820	134.740	149.841	26.983	-94.935	190.571	-55.691
1500.0	112.104	140.338	153.043	26.888	-94.990	195.319	-55.469

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE. H = ENTHALPY. S = ENTROPY. AND DHF, DSF, AND DFF ARE THE HEAT, ENTROPY, AND FREE ENERGY OF FORMATION, RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T, WHERE R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202502

Table C-4. 2,2,4,4-TETRACHLOROBENZENE THERMODYNAMICS

2,2,4,4-TETRA CB (IDEAL GAS) MOLECULAR WT. 292.008

TEMPERATURE (C)	CP (CAL/GMOL/K)	H-H(25 C) (KCAL/GMOLE)	S-S(25 C) (CAL/GMOL/K)	DHF(T) (KCAL/GMOLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/GMOLE)	LN K
50.0	59.851	1.452	4.673	15.561	-99.932	47.854	-74.570
100.0	66.442	4.612	13.756	15.372	-100.476	52.365	-71.341
150.0	72.261	8.083	22.477	15.248	-100.790	57.897	-68.900
200.0	77.399	11.827	30.535	15.181	-100.942	62.941	-66.987
250.0	81.936	15.813	38.139	15.162	-100.980	67.990	-65.444
300.0	85.942	20.012	46.502	15.185	-100.938	73.038	-64.170
350.0	89.479	24.399	53.839	15.243	-100.842	78.083	-63.098
400.0	92.602	28.953	60.866	15.330	-100.706	83.122	-62.181
450.0	95.360	33.653	67.601	15.442	-100.547	88.153	-61.385
500.0	97.795	38.483	74.058	15.575	-100.370	93.176	-60.687
550.0	99.945	43.428	80.255	15.726	-100.180	98.190	-60.068
600.0	101.843	48.474	86.205	15.893	-99.983	103.194	-59.514
650.0	103.519	53.609	91.923	16.075	-99.782	108.188	-59.015
700.0	104.999	58.822	97.423	16.268	-99.578	113.172	-58.562
750.0	106.306	64.106	102.717	16.472	-99.373	118.146	-58.148
800.0	107.460	69.450	107.817	16.685	-99.170	123.109	-57.768
850.0	108.479	74.849	112.734	16.906	-98.969	128.063	-57.417
900.0	109.378	80.296	117.479	17.133	-98.771	133.006	-57.092
950.0	110.172	85.786	122.061	17.363	-98.579	137.940	-56.789
1000.0	110.874	91.312	126.489	17.594	-98.394	142.864	-56.506
1050.0	111.493	96.872	130.772	17.824	-98.217	147.780	-56.242
1100.0	112.040	102.460	134.918	18.048	-98.051	152.686	-55.993
1150.0	112.523	108.074	138.934	18.263	-97.897	157.585	-55.759
1200.0	112.949	113.711	142.827	18.464	-97.758	162.476	-55.539
1250.0	113.325	119.368	146.603	18.645	-97.637	167.361	-55.331
1300.0	113.658	125.043	150.269	18.801	-97.536	172.240	-55.134
1350.0	113.951	130.734	153.830	18.924	-97.459	177.115	-54.948
1400.0	114.210	136.438	157.291	19.008	-97.408	181.987	-54.772
1450.0	114.439	142.154	160.657	19.043	-97.387	186.856	-54.606
1500.0	114.641	147.881	163.934	19.021	-97.400	191.726	-54.449

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE, H = ENTHALPY, S = ENTROPY, AND DHF, DSF, AND DFF ARE THE HEAT, ENTROPY, AND FREE ENERGY OF FORMATION, RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T, WHERE
R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202503

Table C-5. HYDROGEN CHLORIDE THERMODYNAMICS

HYDROGEN CHLORIDE (IDEAL GAS) MOLECULAR WT. 36.490

TEMPERATURE (C)	CP (CAL/GMOL/K)	H-H(25 C) (KCAL/GMOLE)	S-S(25 C) (CAL/GMOL/K)	DHF(T) (KCAL/GMOLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/GMOLE)	LN K
50.0	6.957	.174	.961	-22.077	2.352	-22.837	35.587
100.0	6.946	.522	1.561	-22.111	2.256	-22.953	30.974
150.0	6.957	.869	2.435	-22.149	2.161	-23.063	27.446
200.0	6.982	1.218	3.213	-22.188	2.072	-23.169	24.658
250.0	7.016	1.567	3.916	-22.229	1.991	-23.270	22.399
300.0	7.058	1.919	4.555	-22.269	1.918	-23.368	20.531
350.0	7.105	2.273	5.150	-22.309	1.851	-23.462	18.960
400.0	7.156	2.630	5.701	-22.347	1.792	-23.553	17.619
450.0	7.210	2.989	6.215	-22.384	1.738	-23.641	16.463
500.0	7.267	3.351	6.699	-22.420	1.690	-23.727	15.454
550.0	7.327	3.716	7.156	-22.454	1.645	-23.811	14.566
600.0	7.387	4.084	7.590	-22.487	1.609	-23.892	13.779
650.0	7.449	4.454	8.003	-22.518	1.575	-23.972	13.076
700.0	7.512	4.829	8.398	-22.546	1.545	-24.050	12.445
750.0	7.575	5.206	8.776	-22.574	1.517	-24.126	11.874
800.0	7.639	5.586	9.139	-22.599	1.493	-24.201	11.356
850.0	7.702	5.970	9.488	-22.623	1.472	-24.276	10.884
900.0	7.765	6.356	9.825	-22.644	1.453	-24.349	10.451
950.0	7.827	6.746	10.150	-22.665	1.436	-24.421	10.054
1000.0	7.888	7.139	10.465	-22.683	1.421	-24.492	9.687
1050.0	7.948	7.535	10.770	-22.701	1.407	-24.563	9.348
1100.0	8.006	7.934	11.066	-22.717	1.396	-24.633	9.033
1150.0	8.063	8.335	11.353	-22.731	1.385	-24.702	8.741
1200.0	8.117	8.740	11.633	-22.745	1.376	-24.772	8.468
1250.0	8.169	9.147	11.904	-22.757	1.368	-24.840	8.212
1300.0	8.218	9.557	12.169	-22.768	1.360	-24.908	7.973
1350.0	8.264	9.969	12.427	-22.779	1.354	-24.976	7.749
1400.0	8.308	10.383	12.678	-22.789	1.347	-25.044	7.537
1450.0	8.348	10.800	12.924	-22.799	1.342	-25.111	7.338
1500.0	8.384	11.218	13.163	-22.808	1.337	-25.178	7.158

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE. H = ENTHALPY. S = ENTROPY.
AND DHF. DSF. AND DFF ARE THE HEAT. ENTROPY. AND FREE ENERGY OF FORMATION. RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T. WHERE
R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202504

Table C-6. CHLORINE THERMODYNAMICS

CHLORINE (IDEAL GAS) MOLECULAR WT. 70.910

TEMPERATURE (C)	CP (CAL/GMOL/K)	H-H(25 C) (KCAL/GMOLE)	S-S(25 C) (CAL/GMOL/K)	DHF(T) (KCAL/GMOLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/GMOLE)	LN K
50.0	8.216	.204	.657	0.000	0.000	0.000	0.000
100.0	8.378	.619	1.851	0.000	0.000	0.000	0.000
150.0	8.495	1.041	2.912	0.000	0.000	0.000	0.000
200.0	8.584	1.468	3.865	0.000	0.000	0.000	0.000
250.0	8.653	1.899	4.732	0.000	0.000	0.000	0.000
300.0	8.710	2.333	5.525	0.000	0.000	0.000	0.000
350.0	8.757	2.770	6.255	0.000	0.000	0.000	0.000
400.0	8.797	3.209	6.933	0.000	0.000	0.000	0.000
450.0	8.832	3.650	7.564	0.000	0.000	0.000	0.000
500.0	8.862	4.092	8.156	0.000	0.000	0.000	0.000
550.0	8.888	4.535	8.712	0.000	0.000	0.000	0.000
600.0	8.912	4.981	9.237	0.000	0.000	0.000	0.000
650.0	8.932	5.427	9.733	0.000	0.000	0.000	0.000
700.0	8.951	5.874	10.205	0.000	0.000	0.000	0.000
750.0	8.967	6.322	10.654	0.000	0.000	0.000	0.000
800.0	8.982	6.771	11.082	0.000	0.000	0.000	0.000
850.0	8.996	7.220	11.492	0.000	0.000	0.000	0.000
900.0	9.008	7.670	11.884	0.000	0.000	0.000	0.000
950.0	9.019	8.121	12.260	0.000	0.000	0.000	0.000
1000.0	9.029	8.572	12.621	0.000	0.000	0.000	0.000
1050.0	9.039	9.024	12.969	0.000	0.000	0.000	0.000
1100.0	9.047	9.476	13.305	0.000	0.000	0.000	0.000
1150.0	9.056	9.929	13.629	0.000	0.000	0.000	0.000
1200.0	9.064	10.382	13.941	0.000	0.000	0.000	0.000
1250.0	9.071	10.835	14.244	0.000	0.000	0.000	0.000
1300.0	9.079	11.289	14.537	0.000	0.000	0.000	0.000
1350.0	9.086	11.743	14.821	0.000	0.000	0.000	0.000
1400.0	9.094	12.197	15.097	0.000	0.000	0.000	0.000
1450.0	9.101	12.652	15.365	0.000	0.000	0.000	0.000
1500.0	9.109	13.107	15.625	0.000	0.000	0.000	0.000

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE, H = ENTHALPY, S = ENTROPY, AND DHF, DSF, AND DFF ARE THE HEAT, ENTROPY, AND FREE ENERGY OF FORMATION, RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T, WHERE
R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202505

Table C-7. CARBON DIOXIDE THERMODYNAMICS

CARBON DIOXIDE (IDEAL GAS) MOLECULAR WT. 44.010

TEMPERATURE (C)	CP (CAL/GMOL/K)	H-H(25 C) (KCAL/GMOLE)	S-S(25 C) (CAL/GMOL/K)	DHF(T) (KCAL/GMOLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/GMOLE)	LN K
50.0	9.150	.225	.726	-94.058	.694	-94.283	146.920
100.0	9.643	.695	2.078	-94.066	.673	-94.317	127.250
150.0	10.078	1.189	3.517	-94.074	.652	-94.350	112.279
200.0	10.468	1.703	4.965	-94.085	.628	-94.382	100.448
250.0	10.822	2.235	5.534	-94.098	.601	-94.413	90.878
300.0	11.144	2.784	6.537	-94.115	.571	-94.442	82.975
350.0	11.439	3.349	7.481	-94.134	.539	-94.470	76.340
400.0	11.708	3.928	8.374	-94.155	.506	-94.496	70.689
450.0	11.955	4.519	9.222	-94.178	.473	-94.520	65.819
500.0	12.181	5.123	10.029	-94.202	.441	-94.543	61.577
550.0	12.388	5.737	10.799	-94.223	.409	-94.564	57.850
600.0	12.576	6.361	11.535	-94.254	.378	-94.584	54.548
650.0	12.749	6.995	12.240	-94.281	.348	-94.602	51.604
700.0	12.906	7.636	12.917	-94.307	.320	-94.619	48.961
750.0	13.049	8.285	13.567	-94.333	.294	-94.634	46.576
800.0	13.180	8.941	14.193	-94.359	.269	-94.648	44.413
850.0	13.300	9.603	14.796	-94.385	.246	-94.661	42.441
900.0	13.409	10.270	15.377	-94.409	.225	-94.673	40.637
950.0	13.510	10.943	15.939	-94.433	.205	-94.684	38.981
1000.0	13.603	11.621	16.482	-94.457	.186	-94.693	37.454
1050.0	13.689	12.304	17.008	-94.480	.168	-94.702	36.042
1100.0	13.770	12.990	17.517	-94.502	.151	-94.710	34.732
1150.0	13.846	13.681	18.011	-94.525	.135	-94.717	33.514
1200.0	13.920	14.375	18.490	-94.548	.119	-94.724	32.379
1250.0	13.991	15.072	18.956	-94.571	.104	-94.729	31.318
1300.0	14.062	15.774	19.409	-94.596	.088	-94.734	30.324
1350.0	14.133	16.479	19.850	-94.622	.072	-94.738	29.391
1400.0	14.205	17.187	20.280	-94.650	.054	-94.741	28.514
1450.0	14.280	17.899	20.699	-94.681	.036	-94.743	27.687
1500.0	14.359	18.615	21.109	-94.716	.016	-94.745	26.907

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE, H = ENTHALPY, S = ENTROPY, AND DHF, DSF, AND DFF ARE THE HEAT, ENTROPY, AND FREE ENERGY OF FORMATION, RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T, WHERE
R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202506

Table C-8. WATER THERMODYNAMICS

WATER (IDEAL GAS) MOLECULAR WT. 18.020

TEMPERATURE (C)	CP (CAL/GMOL/K)	H-H(25 C) (KCAL/GMOLE)	S-S(25 C) (CAL/GMOL/K)	DHF(T) (KCAL/GMOLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/GMOLE)	LN K
50.0	8.059	.201	.647	-57.858	-10.890	-54.367	84.720
100.0	8.136	.606	1.812	-57.977	-11.144	-53.819	72.628
150.0	8.286	1.015	2.841	-58.096	-11.443	-53.254	63.374
200.0	8.449	1.430	3.767	-58.213	-11.705	-52.675	56.061
250.0	8.472	1.850	4.611	-58.328	-11.936	-52.084	50.134
300.0	8.601	2.277	5.390	-58.440	-12.141	-51.482	45.231
350.0	8.737	2.710	6.115	-58.549	-12.323	-50.870	41.108
400.0	8.877	3.151	6.795	-58.654	-12.486	-50.250	37.590
450.0	9.021	3.598	7.436	-58.756	-12.631	-49.622	34.554
500.0	9.168	4.053	8.044	-58.854	-12.762	-48.987	31.906
550.0	9.317	4.515	8.623	-58.947	-12.879	-48.346	29.576
600.0	9.467	4.984	9.177	-59.037	-12.985	-47.699	27.509
650.0	9.618	5.462	9.708	-59.122	-13.079	-47.048	25.664
700.0	9.770	5.946	10.220	-59.203	-13.165	-46.391	24.006
750.0	9.921	6.439	10.713	-59.280	-13.242	-45.731	22.507
800.0	10.071	6.938	11.190	-59.352	-13.311	-45.067	21.147
850.0	10.219	7.446	11.652	-59.421	-13.374	-44.400	19.907
900.0	10.365	7.960	12.100	-59.485	-13.430	-43.730	18.771
950.0	10.509	8.482	12.536	-59.546	-13.481	-43.057	17.726
1000.0	10.649	9.011	12.960	-59.603	-13.527	-42.382	16.763
1050.0	10.786	9.547	13.372	-59.657	-13.568	-41.705	15.872
1100.0	10.919	10.090	13.775	-59.708	-13.605	-41.025	15.045
1150.0	11.047	10.639	14.168	-59.755	-13.640	-40.344	14.275
1200.0	11.169	11.194	14.551	-59.800	-13.671	-39.661	13.557
1250.0	11.286	11.756	14.926	-59.843	-13.699	-38.977	12.886
1300.0	11.396	12.323	15.292	-59.884	-13.726	-38.292	12.257
1350.0	11.500	12.895	15.651	-59.923	-13.750	-37.605	11.666
1400.0	11.596	13.473	16.001	-59.961	-13.773	-36.917	11.111
1450.0	11.684	14.055	16.344	-59.999	-13.795	-36.227	10.587
1500.0	11.764	14.641	16.679	-60.036	-13.817	-35.537	10.092

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE. H = ENTHALPY. S = ENTROPY. AND DHF, DSF, AND DFF ARE THE HEAT, ENTROPY, AND FREE ENERGY OF FORMATION, RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T. WHERE
R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202507

Table C-9. OXYGEN THERMODYNAMICS

OXYGEN (IDEAL GAS) MOLECULAR WT. 32.000

TEMPERATURE (C)	CP (CAL/G*OL/K)	H-H(25 C) (KCAL/G*OLE)	S-S(25 C) (CAL/G*OL/K)	DHF(T) (KCAL/G*OLE)	DSF(T) (CAL/GMOL/K)	DFF(T) (KCAL/G*OLE)	LN K
50.0	7.048	.176	.566	0.000	0.000	0.000	0.000
100.0	7.136	.530	1.586	0.000	0.000	0.000	0.000
150.0	7.248	.890	2.590	0.000	0.000	0.000	0.000
200.0	7.369	1.255	3.506	0.000	0.000	0.000	0.000
250.0	7.490	1.627	4.052	0.000	0.000	0.000	0.000
300.0	7.609	2.004	4.741	0.000	0.000	0.000	0.000
350.0	7.721	2.387	5.383	0.000	0.000	0.000	0.000
400.0	7.827	2.776	5.983	0.000	0.000	0.000	0.000
450.0	7.925	3.170	6.547	0.000	0.000	0.000	0.000
500.0	8.016	3.569	7.080	0.000	0.000	0.000	0.000
550.0	8.099	3.971	7.585	0.000	0.000	0.000	0.000
600.0	8.175	4.378	8.064	0.000	0.000	0.000	0.000
650.0	8.244	4.789	8.522	0.000	0.000	0.000	0.000
700.0	8.306	5.203	8.958	0.000	0.000	0.000	0.000
750.0	8.363	5.619	9.376	0.000	0.000	0.000	0.000
800.0	8.415	6.039	9.776	0.000	0.000	0.000	0.000
850.0	8.462	6.461	10.160	0.000	0.000	0.000	0.000
900.0	8.506	6.885	10.530	0.000	0.000	0.000	0.000
950.0	8.546	7.311	10.886	0.000	0.000	0.000	0.000
1000.0	8.583	7.740	11.229	0.000	0.000	0.000	0.000
1050.0	8.619	8.170	11.560	0.000	0.000	0.000	0.000
1100.0	8.653	8.601	11.880	0.000	0.000	0.000	0.000
1150.0	8.687	9.035	12.191	0.000	0.000	0.000	0.000
1200.0	8.721	9.470	12.491	0.000	0.000	0.000	0.000
1250.0	8.757	9.907	12.783	0.000	0.000	0.000	0.000
1300.0	8.794	10.346	13.066	0.000	0.000	0.000	0.000
1350.0	8.833	10.786	13.342	0.000	0.000	0.000	0.000
1400.0	8.876	11.229	13.611	0.000	0.000	0.000	0.000
1450.0	8.922	11.674	13.873	0.000	0.000	0.000	0.000
1500.0	8.973	12.121	14.128	0.000	0.000	0.000	0.000

DEFINITIONS ..... CP = HEAT CAPACITY AT CONSTANT PRESSURE, H = ENTHALPY, S = ENTROPY, AND DHF, DSF, AND DFF ARE THE HEAT, ENTROPY, AND FREE ENERGY OF FORMATION, RESPECTIVELY.

DFF = DHF - T*DSF/1000 AND LN K = - DFF*1000/R/T, WHERE
R = 1.98585 CAL/GMOLE/K ... AND ... T = DEGREES CELSIUS + 273.15

MONS 202508