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**AP-42 Section Number:** 1.3

**Reference Number:** 35

**Title:** A Theoretical Study of PCB Emissions from Stationary Sources

Knierien, H., EPA-600/7-76-028

US EPA

September 1976

EPA U.S. Environmental Protection Agency
Office of Research and Development

Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

EPA-600/7-76-028
October 1976

# PCB EMISSIONS FROM STATIONARY SOURCES: A Theoretical Study

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EPA-600/7-76-028
October 1976

# PCB EMISSIONS FROM STATIONARY SOURCES A THEORETICAL STUDY

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Contract No. 68-02-1320, Task 26
Program Element No. EHE624A

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

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## 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).

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[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.

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 zone 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

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[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.

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.

## 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.

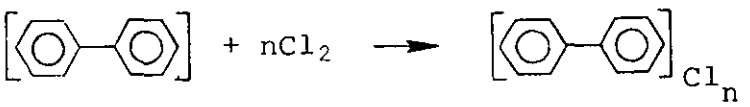
## SECTION 4

## 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 <u>any</u> 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.

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

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

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[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.

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:

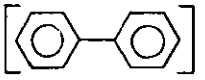
> "...calculations show that the formation of the mono, di, and tetra chlorinated biphenyls by the reaction path (of Reaction 1) are very favored over the temperature range 50°C to 1500°C. Hence, if kinetic pathway exists and has a finite rate under the constraints of the reaction zone, these compounds 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.'"

## 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.

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

## 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.

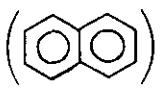
Chlorine, if detectable, is likely to be present only as chlorinated organics in natural gas, LPG, or refined oils. In coal and residual oils, however, significant quantities of inorganic chlorides may make a contribution to the availability of reactive chlorine moieties. Corrosion analyses of furnaces 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.

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:

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[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.

1. Temperature maximums and temperature range distribution within the combustion zone.

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

3. Mixing efficiency of fuel and air.

4. 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.

1. 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 3500°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)

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[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.

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.

## 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 <u>in-situ</u> 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

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

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.

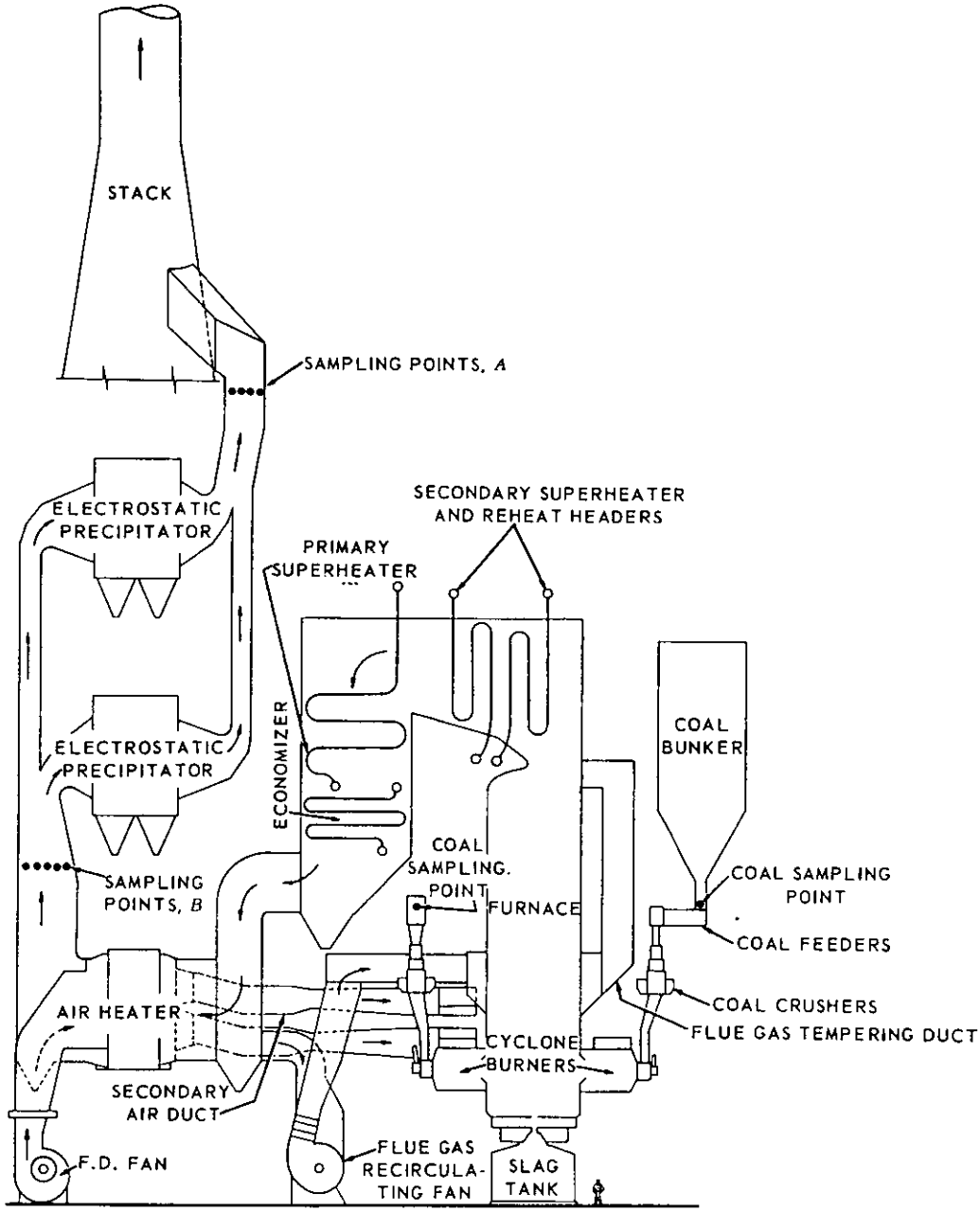


Figure 1. Boiler outline for cyclone type unit.[24]

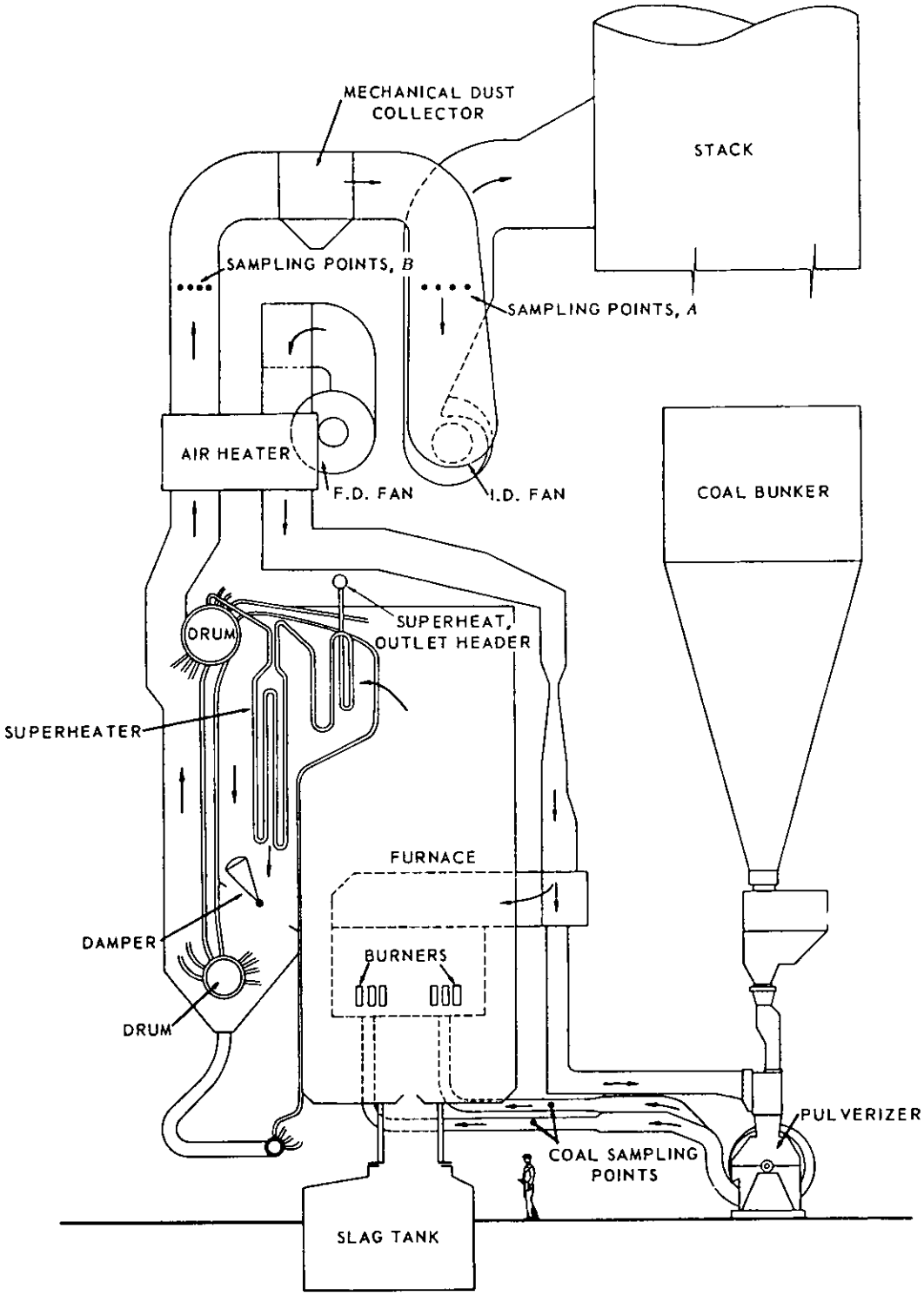


Figure 2. Boiler outline for horizontally-opposed firing unit.[24]

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.

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# 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 |

$$\text{Biphenyl} + Cl_2 \longrightarrow \text{4-MCB} + HCl$$

| 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 = 1.98585 CAL/GMOLE/K
T = DEGREES CELSIUS + 273.15

Table A-2. REACTION THERMODYNAMICS, FORMATION

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

$$\text{Biphenyl} + 2Cl_2 \longrightarrow 4,4'\text{-DCB} + 2HCl$$

| 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 | -56.258 | 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 | -55.588 | 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

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 | -112.883 | -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 | -111.593 | -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 | -.871 | -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

## 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-CHLORCBIPHENYL | -1 | IDEAL GAS |
| OXYGEN | -14 | IDEAL GAS |

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

| 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 | -1417.893 | 52.830 | -1442.889 | 1535.634 |
| 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 | 723.593 |
| 800.0 | -1423.655 | 45.518 | -1472.503 | 690.954 |
| 850.0 | -1424.272 | 44.956 | -1474.765 | 661.209 |
| 900.0 | -1424.883 | 44.424 | -1476.999 | 633.987 |
| 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 | -1428.828 | 41.470 | -1491.993 | 493.262 |
| 1300.0 | -1429.332 | 41.144 | -1494.058 | 478.246 |
| 1350.0 | -1429.821 | 40.839 | -1496.108 | 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

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 |

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

| 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 | -2750.751 | 139.442 | -2823.700 | 2717.978 |
| 300.0 | -2751.437 | 138.191 | -2830.642 | 2486.968 |
| 350.0 | -2752.268 | 136.803 | -2837.517 | 2292.976 |
| 400.0 | -2753.221 | 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 | -2877.218 | 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

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 |

$$2\ 2,2',4,4'\text{-TCB} + 25O_2 \longrightarrow 24CO_2 + 2H_2O + 8HCl$$

| 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 | 212.655 | -2660.588 | 3590.441 |
| 150.0 | -2581.655 | 211.619 | -2671.201 | 3178.819 |
| 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 | 183.688 | -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 | 832.050 |

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

# 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 | 49.506 | 3.320 | 9.889 | 42.119 | -82.754 | 72.099 | -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 | 40.585 | -86.414 | 81.472 | -86.709 |
| 250.0 | 66.576 | 12.093 | 29.487 | 39.947 | -87.698 | 85.626 | -82.612 |
| 300.0 | 71.182 | 15.539 | 35.775 | 39.385 | -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 | 195.867 | -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

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 | 46.858 | 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 | 65.444 | 9.623 | 24.999 | 33.833 | -90.047 | 76.439 | -81.353 |
| 250.0 | 70.413 | 13.022 | 31.823 | 33.350 | -91.020 | 80.967 | -77.935 |
| 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 | -69.234 |
| 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 | 103.208 | 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 | 105.275 | 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 | 31.648 | -93.790 | 160.436 | -58.835 |
| 1150.0 | 107.645 | 98.279 | 123.560 | 31.722 | -93.737 | 165.124 | -58.427 |
| 1200.0 | 108.279 | 103.678 | 127.288 | 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 | -93.688 | 193.221 | -56.466 |
| 1500.0 | 110.925 | 136.601 | 147.622 | 31.655 | -93.761 | 197.907 | -56.204 |

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

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 | 3.973 | 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 | -93.680 | 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 | 25.765 | -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 | 90.676 | 120.767 | 26.453 | -95.307 | 152.556 | -58.060 |
| 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

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 | 52.865 | -71.341 |
| 150.0 | 72.261 | 8.083 | 22.477 | 15.248 | -100.790 | 57.897 | -68.900 |
| 200.0 | 77.399 | 11.827 | 30.835 | 15.181 | -100.942 | 62.941 | -66.987 |
| 250.0 | 81.936 | 15.813 | 38.839 | 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 | -100.708 | 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

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 | .561 | -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 | 4.558 | -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 | 1.648 | -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 | 7.150 |

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

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 | 3.866 | 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 | 4.536 | 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

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 | 127.280 |
| 150.0 | 10.078 | 1.189 | 3.317 | -94.074 | .652 | -94.350 | 112.279 |
| 200.0 | 10.468 | 1.703 | 4.465 | -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 | -94.228 | .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

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 | 8.055 | .201 | .647 | -57.858 | -10.800 | -54.367 | 84.720 |
| 100.0 | 8.136 | .606 | 1.812 | -57.977 | -11.144 | -53.819 | 72.628 |
| 150.0 | 8.236 | 1.015 | 2.841 | -58.096 | -11.443 | -53.254 | 63.374 |
| 200.0 | 8.349 | 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

Table C-9. OXYGEN THERMODYNAMICS

OXYGEN ( IDEAL GAS ) MOLECULAR WT. 32.000

| 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 | 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 | 2.490 | 0.000 | 0.000 | 0.000 | 0.000 |
| 200.0 | 7.369 | 1.255 | 3.306 | 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

TECHNICAL REPORT DATA
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| | | |
|---|---|---|
| 1. REPORT NO. EPA-600/7-76-028 | 2. | 3. RECIPIENT'S ACCESSION NO. |
| 4. TITLE AND SUBTITLE PCB Emissions from Stationary Sources: A Theoretical Study | | 5. REPORT DATE October 1976 |
| | | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) Herman Knieriem, Jr. | | 8. PERFORMING ORGANIZATION REPORT NO. MRC-DA-577 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation Dayton Laboratory Dayton, Ohio 45407 | | 10. PROGRAM ELEMENT NO. EHE624A |
| | | 11. CONTRACT/GRANT NO. 68-02-1320, Task 26 |
| 12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711 | | 13. TYPE OF REPORT AND PERIOD COVERED Final; 3-6/76 |
| | | 14. SPONSORING AGENCY CODE EPA-ORD |

15. SUPPLEMENTARY NOTES IERL-RTP task officer for this report is R. E. Hall, 919/549-8411 Ext 2477, Mail Drop 65.

16. ABSTRACT The report gives results of a theoretical assessment of polychlorinated biphenyl (PCB) formation and destruction in conventional fossil fuel fired sources. Results suggest a small but finite possibility that PCB isomers may be found in their emissions. The study was the result of concern caused by tentative identification of PCB isomers in ash and flyash from a utility steam generating boiler. The theoretical assessment concluded that: (1) PCB emissions are more likely from higher-chlorine content coal or residual oil combustion than from refined oil or natural gas; (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 emissions; (5) based on the above, inefficient combustion control is more likely to produce PCB emissions than optimum conditions; and (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.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|---|
| Air Pollution | Coal | Air Pollution Control | 13B |
| Combustion | Fuel Oil | Stationary Sources | 21B |
| Fossil Fuels | Natural Gas | Polychlorinated Biphenyl Isomers | 21D |
| Polycyclic Compounds | Boilers | | 07C 13A |
| Aromatic Polycyclic Hydrocarbons | Stokers | Stoker Fired Boilers | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT Unlimited | 19. SECURITY CLASS *(This Report)* Unclassified | 21. NO. OF PAGES 43 |
| | 20. SECURITY CLASS *(This page)* Unclassified | 22. PRICE |

EPA Form 2220-1 (9-73)

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