

FLAMMABILITY OF R134a, R22, & R123 IN CHLORINE

by

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Presented at the Chlorine Institute
CFC Refrigerant Alternatives Seminar

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OUTLINE

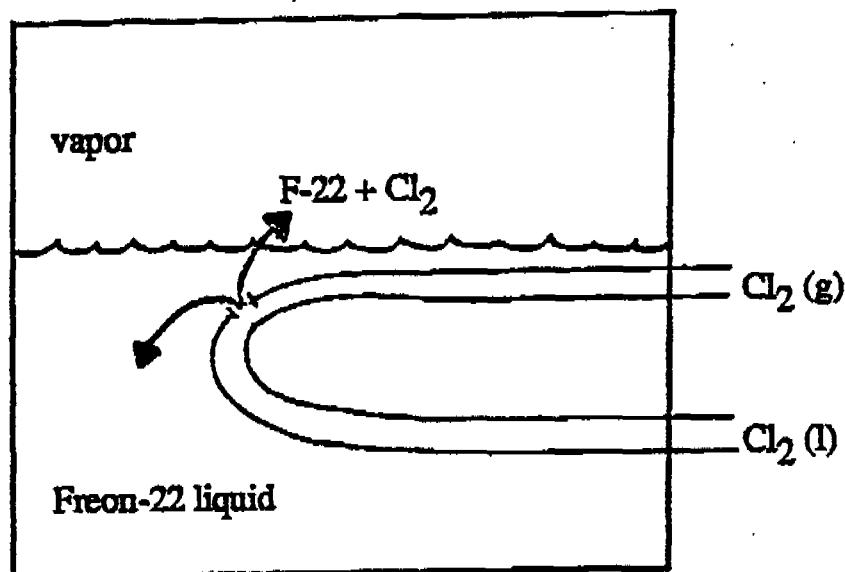
- R22 + CL2 FLAMMABILITY PROJECT
- CALCULATIONAL TOOLS
- R22, 123, 134a CALCS & PLOTS
- EXPERIMENTAL RESULTS
- INTERPRETATION & CONCLUSIONS

DO 073059
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R22 + CL2

FLAMMABILITY PROJECT

- IS R22 FLAMMABLE IN CL2 ?



Cl₂ + organic oil = heat

heat + Cl₂ + R22 ⇒ **PROPAGATION ?**

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CALCULATIONAL TOOLS

CALCULATED FLAME TEMPS @ THE LFL

FUEL		Tf (K) CALCULATED	
Name	Formula	Air or O2	Cl2
Acetylene	C2H2	1300	712
Methane	CH4	1440	824
Ethane	C2H6	1530	909
Chloroethane	C2H5CL	1630	1027
Dichloroethane	1,2-C2H4CL2	1673	1137
Chloroform	CHCL3	-	705
F22 (PREDICTED)	CHCLF2	-	890

- NASA-CET calcs predict Tf, Pm, & Reaction Products
- Tf @ LFL are ~600° lower in CL₂ than in AIR or O₂

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R22 + CL2 FLAMMABILITY CALCS & PREDICTIONS

R22 + CL₂ @ 100°C & 13.6 ATM
CALCS PREDICTED THE FOLLOWING:

- LFL-UFL OF 25-85 VOL%
- Pm/Pi ~ 3.3
- Kg ~ 10 - 100
- MIE < 1 JOULE

EXPERIMENTAL CHALLENGES:

- SAFETY OF CL2 HANDLING
- NEUT/CLEAN HCL, CL2, HF, C ...
- TEST @ 100°C & 13.6 ATM
50/50 R22/CL2 (VP, Tc)

KEY PURPOSE OF DATA:

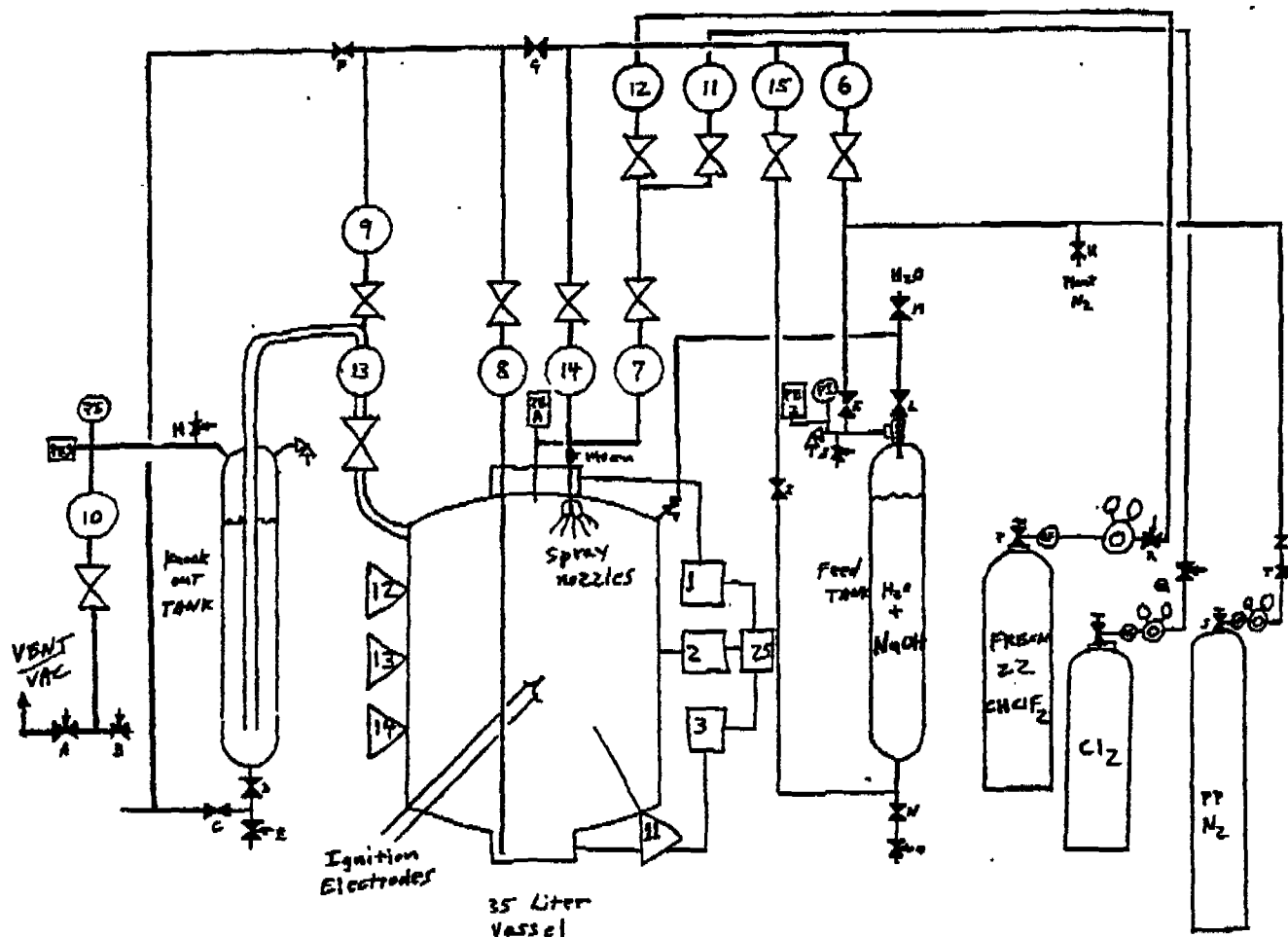
- ANSWER ? OF PROPAGATION
- CONFIRMATION OF CALC
Pm/Pi, Kg, & MIE

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MODIFIED 35 L SYSTEM

FOR FREON 22 + CL2



- CONFORMS TO ASTM E-918-83, Calls for 1 lit r

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EXPERIMENTAL RESULTS

R22 + CL2 DEFLAGRATIONS

RUN DATA

RUN	R22	CL2	T _i	P _i	P _m	P _m /P _i	T _m	dP/dt _m	COMMENTS
#	%	%	°C	psia	psia	ratio	°C	psi/s	
1	unk	unk	113	>62	>100	>1.0	>200	>0	ign on R22 int CL2 wall hot spot ~180°C
2	48	52	107	208	653	3.1	>400	431	fuse wire ign
3	78	22	107	208	208	1.0	107	-	fuse wire ign
4	100	0	109	200	200	1.0	109	-	chem ign 10 Kjoules
5	trc	bal	115	>60	>60	>1.0	>250	>0	chem ign + CL2 rxn
6	68	32	111	200	200	1.0	111	-	fuse wire ign
7	51	49	27	66	208	3.2	>200	317	fuse wire + M103

- HOT SPOT OR STATIC COULD IGNITE

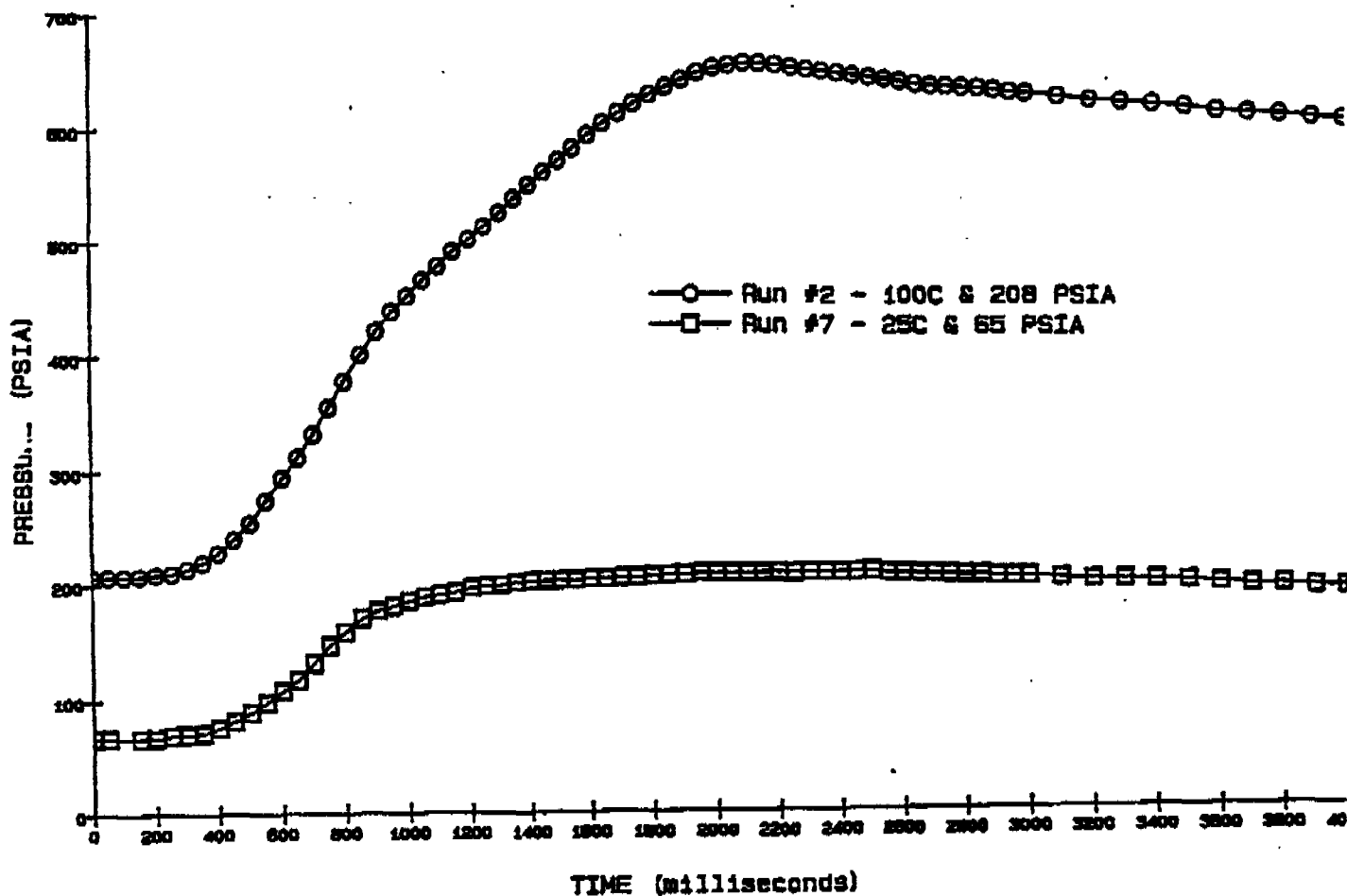
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EXPERIMENTAL RESULTS

50/50 R22 + CL2 DEFLAGRATIONS

PRES VS TIME AFTER IGN



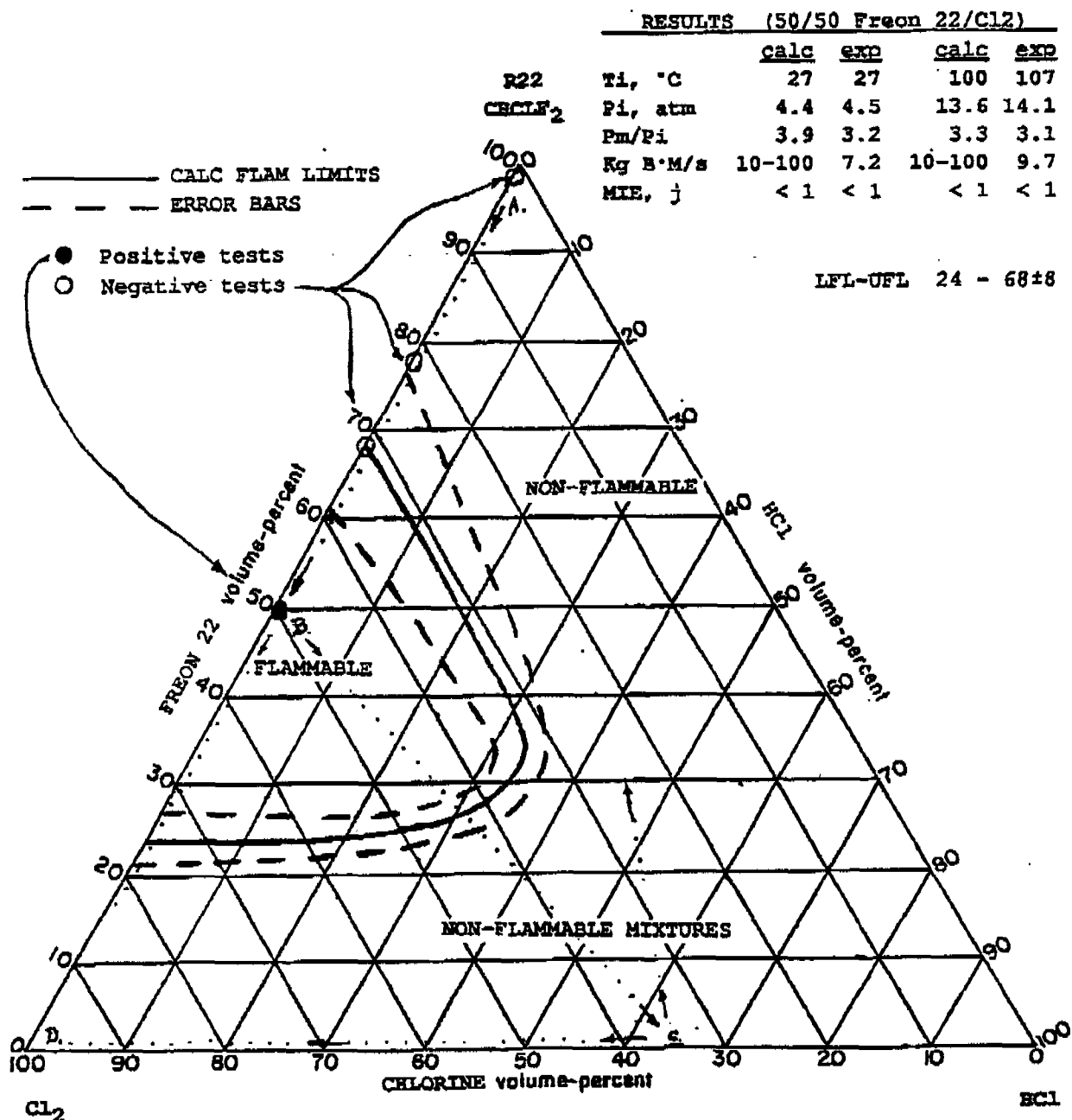
- VERY SLOW FLAME SPEEDS

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CALC & EXP RESULTS

FLAMMABILITY DIAGRAM FOR R22, CL2, & HCL @ 100°C & 13.6 ATM



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NASA-CET CALCULATIONS

OF FREONS IN CL2 @ 100°C & 13.6 ATM

FREON 22 (CHCLF2) + CL2

CHCLF2 + CL2	→	CCL4	HCL	CF4	CL2	HF	C	CCL2F2	CCLF3	CCL3F	TOT GAS	Tf	Pf	Pf/Pi
moles	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol	moles	K	atm	ratio
100	0	0.0	75.2	40.2	9.5	24.8	54.7	0.6	4.5	0.1	154.7	1106	62.4	4.6
90	10	0.1	72.1	36.1	15.1	17.9	47.6	0.9	5.3	0.1	147.6	1104	59.4	4.4
80	20	0.1	67.4	31.8	21.6	12.6	40.8	1.2	5.8	0.2	140.8	1092	56.1	4.1
70	30	0.3	61.5	27.4	28.4	8.5	34.2	1.6	6.1	0.4	134.2	1072	52.5	3.9
60	40	0.6	54.6	22.9	35.5	5.4	27.7	2.0	6.2	0.6	127.7	1044	48.6	3.6
50	50	1.3	46.8	18.3	42.2	3.2	21.1	2.4	5.9	1.0	121.1	1008	44.5	3.3
40	60	2.6	38.2	13.8	48.0	1.8	14.0	2.8	5.3	1.4	114.0	971	40.4	3.0
30	70	5.1	29.1	9.5	52.3	0.9	6.2	2.9	4.4	1.9	106.2	936	36.2	2.7
20	80	6.9	19.6	6.2	60.0	0.4	0	2.2	2.9	1.8	100.0	869	31.7	2.3
10	90	4.2	9.9	3.9	80.0	0.1	0	0.5	0.9	0.5	100.0	664	24.2	1.8

FREON 123 (C2HCL2F3) + CL2

C2HCL2F3 + CL2	→	CCL4	HCL	CF4	CL2	HF	C	CCL2F2	CCLF3	CCL3F	TOT GAS	Tf	Pf	Pf/Pi
moles	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol	moles	K	atm	ratio
100	0	6.5	98.0	62.4	24.1	2.0	112	4.6	12.4	2.1	212.0	772	59.6	4.4
90	10	7.6	88.3	55.1	26.4	1.7	98.2	4.8	11.9	2.4	198.2	777	56.1	4.1
80	20	8.8	78.5	48.0	28.7	1.5	84.3	4.9	11.3	2.6	184.3	782	52.5	3.9
70	30	10.0	68.8	41.0	31.2	1.2	70.6	5.0	10.6	2.8	170.6	789	49.1	3.6
60	40	11.2	59.0	34.2	33.8	1.0	56.9	5.0	9.8	3.0	156.9	796	45.5	3.5
50	50	12.4	49.2	27.5	36.6	0.8	43.3	4.9	8.7	3.2	143.3	805	42.0	3.2
40	60	13.6	39.3	21.0	39.7	0.6	29.9	4.6	7.5	3.3	129.9	815	38.6	2.9
30	70	14.8	29.5	14.8	43.2	0.5	16.6	4.2	6.1	3.4	116.6	826	35.1	2.7
20	80	16.0	19.7	9.0	47.2	0.3	3.6	3.6	4.4	3.3	103.6	840	31.7	2.4
18	82	16.3	17.7	7.8	48.1	0.3	1.0	3.4	4.1	3.3	101.0	843	31.0	2.4
17	83	16.3	16.8	7.3	49.0	0.2	0	3.3	3.8	3.2	100.	842	30.7	2.3
10	90	10.5	9.9	5.2	70.0	0.1	0	1.2	1.7	1.2	100.	706	25.7	2.0

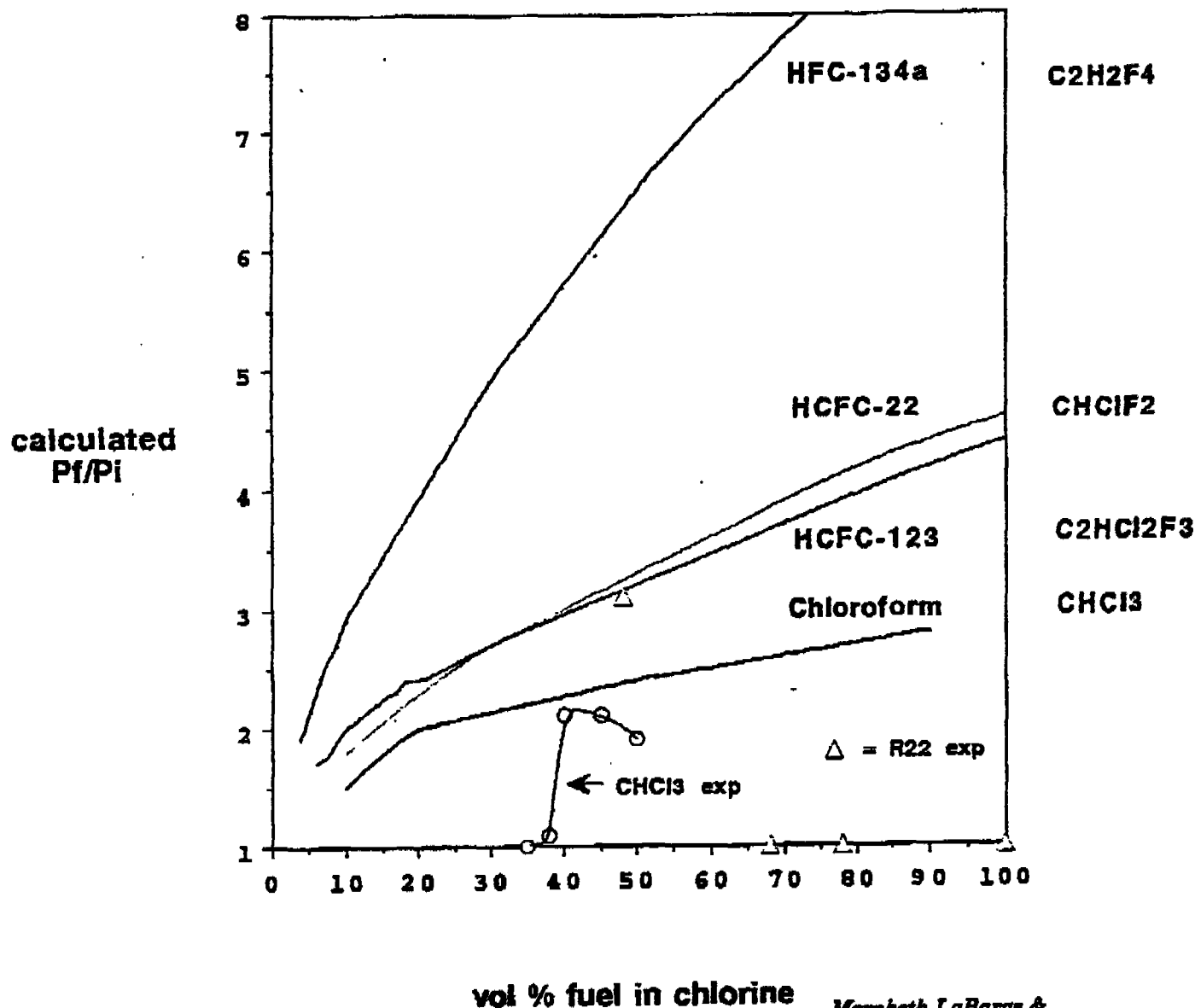
FREON 134a (C2H2F4) + CL2

C2H2F4 + CL2	→	CCL4	HCL	CF4	CL2	HF	C	CCL2F2	CCLF3	CCL3F	TOT GAS	Tf	Pf	Pf/Pi
moles	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol	moles	K	atm	ratio
100	0	0	0	50.0	0	200	150	0	0	0	250.0	1351	123	9.4
90	10	0	18.9	49.3	0.2	161	130	0	0.6	0	230.1	1396	117	8.9
80	20	0	35.2	47.6	1.5	125	111	0	1.6	0	210.8	1437	110	8.4
70	30	0	46.6	44.4	4.9	93.4	92.6	0.1	2.8	0	192.7	1464	103	7.8
60	40	0.0	52.4	39.9	11.1	67.6	75.7	0.3	4.0	0.	176.0	1469	94.2	7.2
50	50	0.0	53.6	34.4	19.8	46.4	60.0	0.6	4.9	0.1	160.3	1452	84.8	6.5
40	60	0.0	51.0	28.2	30.4	29.0	45.3	0.9	5.4	0.1	145.6	1409	74.8	5.7
30	70	0.1	44.9	21.4	42.7	15.1	31.4	1.3	5.5	0.3	131.6	1331	63.8	4.9
20	80	0.4	34.8	13.9	56.4	5.2	18.2	1.8	5.0	0.6	118.3	1195	51.5	3.9
10	90	4.1	19.3	5.8	65.7	0.7	2.8	2.4	3.3	1.7	102.8	998	37.4	2.9
9	91	5.0	17.4	5.0	65.6	0.5	0.8	2.3	3.0	1.8	100.8	980	36.0	2.7
8	92	5.2	15.6	4.5	68.0	0.4	0	2.0	2.6	1.7	100.	942	34.3	2.6
6	94	4.3	11.8	3.9	76.0	0.2	0	1.2	1.6	1.0	100.	829	30.2	2.3

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CALCULATED PRESSURE RISE RATIOS OF FREONS AND CHLOROFORM IN CL2



Marabeth LaBarge &
Dan O'Shaughnessy
DOW CHEMICAL
January 28, 1991

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R22, 134a, & 123 EXPERIMENTAL RESULTS

FREONS IN CHLORINE @ 38°C & 6.6 ATM (unless noted)

RUN #	R22 t	Pm		Pm/Pi		dP/dtm psi/s	Tm °C	COMMENTS
		psia	sec	meas	calc			
calc	10				1.966			
calc	20				2.645			
130	29.3	93	20	1.01	3.008	2	38	M
135	35.2	248	11.2	2.46	3.225	68	245	M
140	41.2	344	3.8	3.38	3.437	184		M
146B4	44.1	338	2.57	3.40	3.544	387	>40	MF, Ti=19
145	45.2	351	2.24	3.48	3.584	274	273	MF
146B5	45.9	354	1.3	3.51	3.610	383	291	MF, Ti=30 sampled
146	46.7	365	2.15	3.63	3.639	378	289	F
147E	47.7	344	2.09	3.42	3.676	205	259	MF
147A	48.0	361	2.36	3.62	3.687	377	263	F
148	48	>244		>2.44	3.7	>50	>200	pre-ign
149	49.0	345	3.05	3.39	3.723	286	>240	F
150	50.9	247	12	2.43	3.771	50	242	M
160	59.7	99	20	1.0	4.110	0	39	M
162	60.0	100	20	1.0	4.121	0	37	MF
147B	46.9	178	1.72	3.42	3.7	147	186	Pi=52.0, Ti=19
147C	46.8	106	1.48	3.35	3.7	125	152	Pi=31.5, Ti=21
147D	47.8	29	1.47	2.42	2.7	50	61	Pi=12.0, Ti=21

R134a &

calc	10				3.119			
210	14.0	75	20	1.0	3.625	0	38	F
225	25.6	472	2.72	4.67	4.983	308	202	MF
227A	28.0	508	1.96	5.08	5.239	353	356	MF
228E	28.7	440	1.57	4.40	5.314	563	320	MF
229	29.2	501	2.11	4.96	5.367	400	377	MF
227B	30.1	432	3.34	4.15	5.463	300	341	MF
230	30.4	328	6.75	3.29	5.491	200	282	MF
228F	30.6	>460		>4.4			365	MF, sampled
235	35.6	141	1.66	1.39	5.985	73	48	MF
240	40.0	100	10	1.0	6.403	0	38	F
245	44.7	100	10	1.0	6.817	0	41	F
250	50.3	102	10	1.0	7.306	0	38	F
calc	60				8.064			
228C	28.5	12	1.27	2.18	2.7	11	31	Pi=5.5, Ti=19

R123 &

310	9.9	59.4	0.17	1.01	2.1	2	33.9	Pi=59.0, Ti=33.3
315	15.1	59.8	0.21	1.01	2.4	3	37.3	Pi=59.2, Ti=36.8
318	20.2	91.0	20	1.0	2.6	0	81.0	Pi=91.0, Ti=81.0
320	22.2	92.3	20	1.0	2.7	0	86.5	Pi=92.3, Ti=86.5
322	31.2	71.2	20	1.0	2.9	0	86.3	Pi=71.2, Ti=86.3
340	34.8	72.6	0.05	1.003	3.0	4	63.7	Pi=72.4, Ti=63.3
350	49.9	63.6	0.06	1.003	3.5	3	62.2	Pi=63.4, Ti=62.2

- R123 + CL₂ IS NON-FLAMMABLE @ PROCESS CONDITIONS

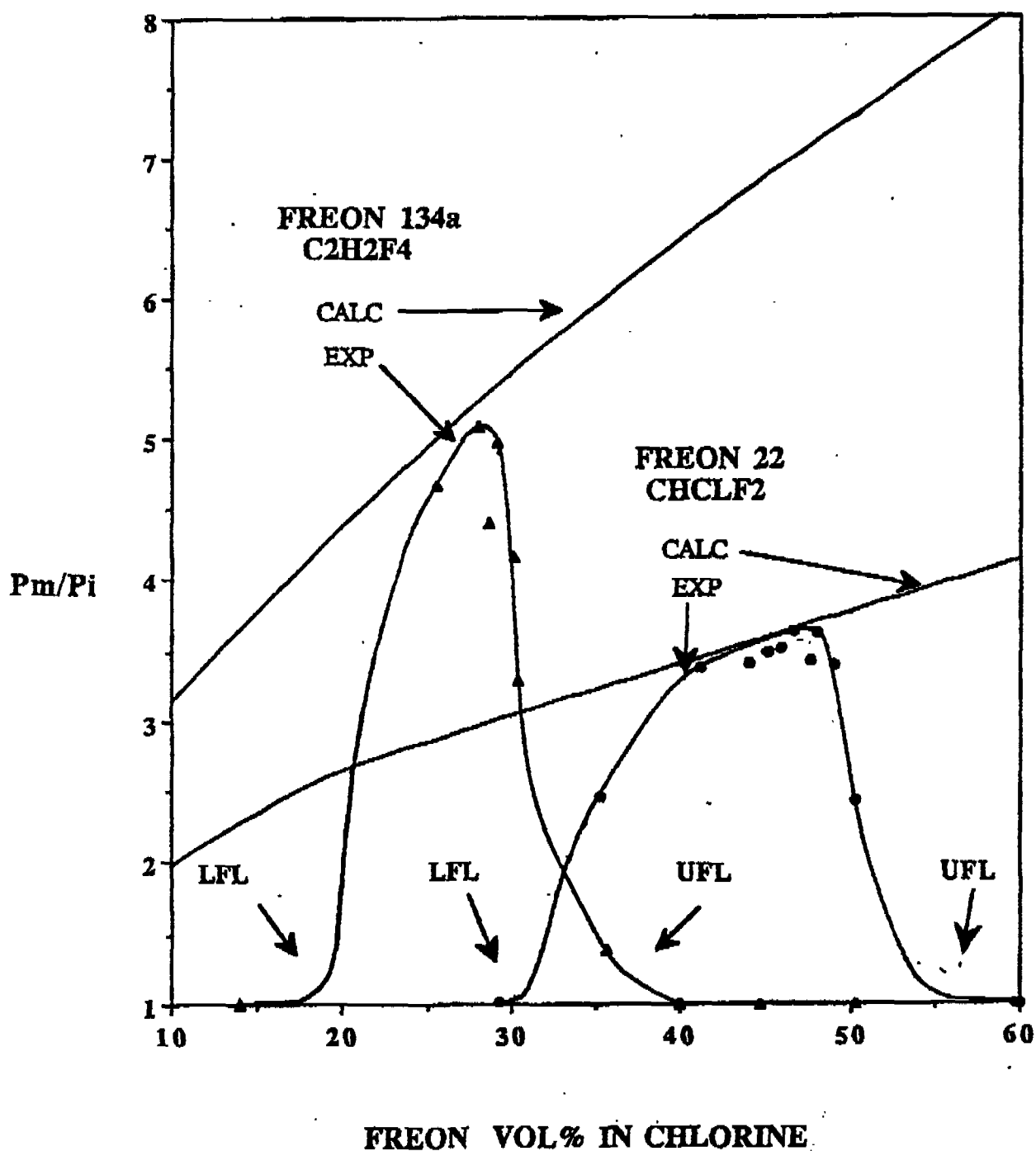
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COMPRESSION RATIOS (P_m/P_i) vs. FREON IN Cl_2 @ 38°C & 6.8 ATM

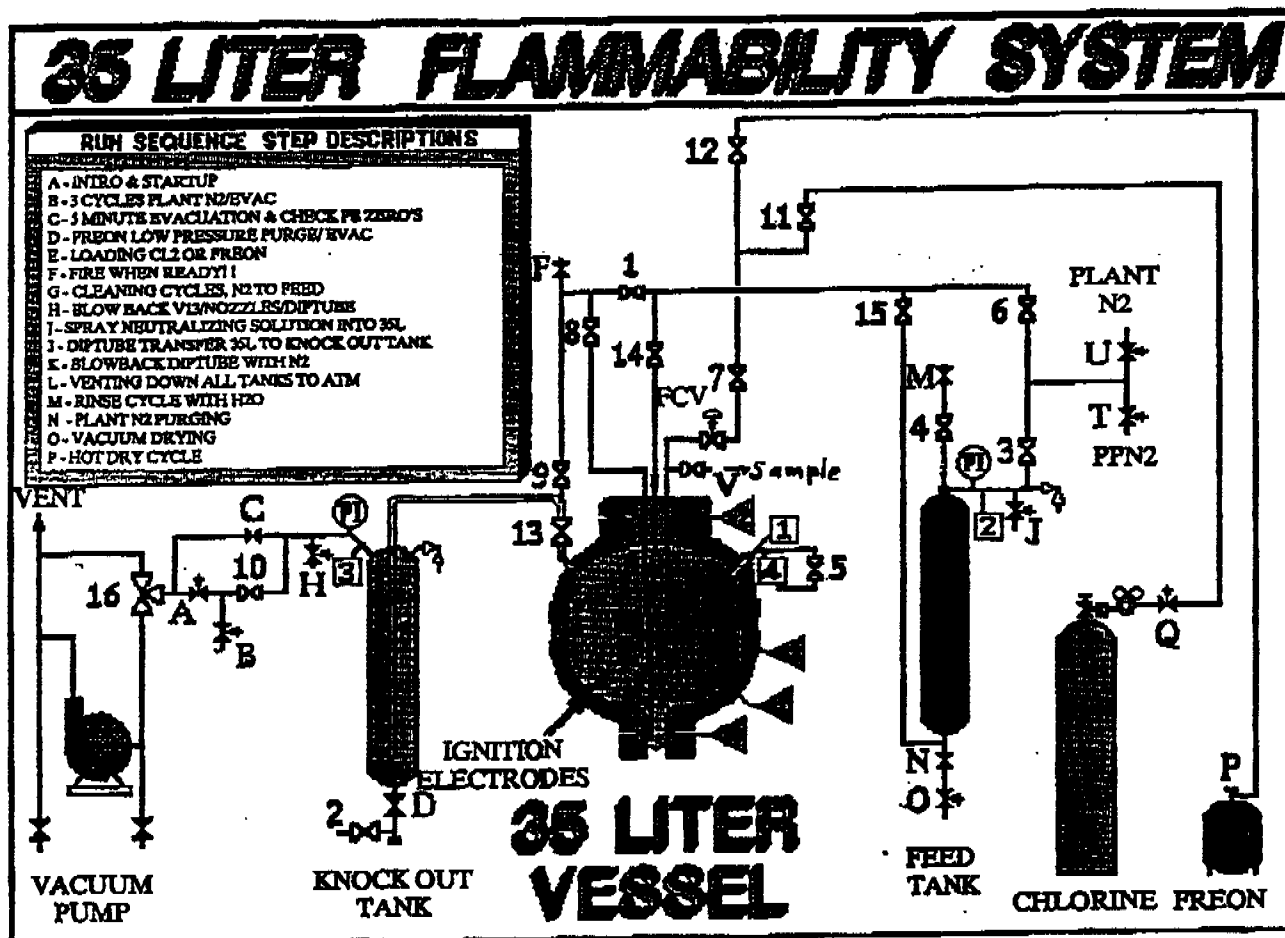


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35 LITER FLAMMABILITY SYSTEM

MODIFIED FOR R22, 123, & 134a



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INTERPRETATION & CONCLUSIONS

- PHYSICAL PROPERTIES CAN LIMIT FLAMMABILITY
- PEAK PRESSURES ASSUME HOMOGENOUS MIXTURES
- STATIC OR HOT SPOT COULD IGNITE
- COMBUSTION PRODUCTS AID INERTING
- R123 + CL_2 NON-FLAMMABLE @ PROCESS CONDITIONS
- NASA-CET CALCS PREDICT LFL & Pm/Pi

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NASA-CET CALCULATIONS

OF CHLOROFORM IN CL2 @ 100°C & 6.1 ATM

CHCL3 + CL2	⇒	CCL4 + HCL + CL2	+ C	TOTAL GAS	Tf	Pf	Pf/Pi	Pf/Pi exp	
<u>moles</u>		<u>mol</u>	<u>mol</u>	<u>mol</u>	<u>moles</u>	<u>K</u>	<u>atm</u>	<u>ratio</u>	<u>ratio</u>
90	10	36.1	90.0	27.8	53.9	153.9	681	17.1	2.8
80	20	34.5	80.0	30.9	45.4	145.4	694	16.5	2.7
70	30	32.9	70.0	34.2	37.1	137.1	708	15.9	2.6
60	40	31.2	60.0	37.7	28.8	128.8	722	15.2	2.5
50	50	29.3	50.0	41.3	20.7	120.7	737	14.5	2.4
45	55								1.9
40	60	27.4	40.0	45.2	12.6	112.6	753	13.9	2.3
38	62								2.1
35	65								1.1
30	70	25.3	30.0	49.4	4.7	104.7	770	13.2	2.2
20	80	20.0	20.0	60.0	0.0	100.0	730	11.9	2.0
10	90	10.0	10.0	80.0	0.0	100.0	578	9.5	1.5
									1.0
									LFL

SEE GRAPHICAL PLOTS OF:

CALCULATED FLAME TEMPERATURES
OF FREONS AND CHLOROFORM IN CL2

CALCULATED PRESSURE RISE RATIOS
OF FREONS AND CHLOROFORM IN CL2

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NASA-CET CALCULATIONS

OF FREONS IN CL2 @ 38°C & 6.8 ATM

FREON 22 (CHCLF2) + CL2

CHCLF2 + CL2	=	CCl4	+ HCL	+ CF4	+ CL2	+ HF	+ C	+ CCL2F2	+ CCLF3	+ CCL3F	TOT GAS	Tf	Pf	Pf/Pi
moles		mol	mol	mol	mol	mol	mol	mol	mol	mol	moles	K	atm	ratio
100	0	0.0	75.8	40.8	9.6	24.2	54.8	0.4	3.9	0.0	154.8	1068	36.1	5.3
90	10	0.0	72.7	36.8	15.4	17.3	47.7	0.7	4.6	0.1	147.7	1065	34.4	5.1
80	20	0.1	67.9	32.6	22.0	12.1	41.0	1.0	5.2	0.2	141.0	1052	32.4	4.8
70	30	0.2	62.0	28.2	29.1	8.0	34.5	1.3	5.5	0.3	134.5	1030	30.3	4.5
60	40	0.5	55.0	23.6	36.3	5.0	28.2	1.7	5.5	0.5	128.2	999	28.0	4.1
50	50	1.1	47.2	19.0	43.2	2.8	21.6	2.0	5.4	0.8	121.6	961	25.5	3.8
40	60	2.5	38.5	14.5	49.1	1.5	14.5	2.4	4.9	1.2	114.5	921	23.1	3.4
30	70	5.1	29.3	10.1	53.1	0.7	6.6	2.5	4.1	1.7	106.6	885	20.6	3.0
20	80	7.2	19.7	6.5	60.0	0.3	0.0	1.9	2.7	1.6	100.0	822	18.0	2.6
10	90	4.4	10.0	4.1	80.0	0.0	0.0	0.4	0.8	0.3	100.0	611	13.3	2.0

FREON 123 (C2HCL2F3) + CL2

C2HCL2F3 + CL2	=	CCl4	+ HCL	+ CF4	+ CL2	+ HF	+ C	+ CCL2F2	+ CCLF3	+ CCL3F	TOT GAS	Tf	Pf	Pf/Pi
moles		mol	mol	mol	mol	mol	mol	mol	mol	mol	moles	K	atm	ratio
100	0	7.3	98.5	63.7	23.6	1.5	112.	4.1	11.2	1.9	211.8	728	35.7	5.0
90	10	8.5	88.7	56.5	25.9	1.3	98.	4.2	10.8	2.1	197.9	733	31.7	4.7
80	20	9.7	78.9	49.3	28.2	1.1	84.	4.3	10.3	2.3	184.1	739	29.7	4.4
70	30	10.9	69.1	42.2	30.7	0.9	70.	4.4	9.6	2.5	170.4	745	27.8	4.1
60	40	12.1	59.2	35.3	33.4	0.8	57.	4.4	8.9	2.7	156.7	753	25.8	3.8
50	50	13.3	49.4	28.5	36.2	0.6	43.	4.3	8.0	2.9	143.1	761	23.8	3.5
40	60	14.4	39.5	21.9	39.4	0.5	30.	4.1	6.9	3.0	129.7	771	21.8	3.2
30	70	15.6	29.6	15.6	42.9	0.4	16.	3.7	5.6	3.0	116.5	782	19.9	2.9
20	80	16.7	19.8	9.5	47.0	0.2	4.	3.2	4.1	3.0	103.5	795	18.0	2.6
10	90	10.9	10.0	5.6	70.0	0.0	0.	1.0	1.5	1.0	100.	655	14.3	2.1

FREON 134a (C2H2F4) + CL2

C2H2F4 + CL2	=	CCl4	+ HCL	+ CF4	+ CL2	+ HF	+ C	+ CCL2F2	+ CCLF3	+ CCL3F	TOT GAS	Tf	Pf	Pf/Pi
moles		mol	mol	mol	mol	mol	mol	mol	mol	mol	moles	K	atm	ratio
100	0	0	0	50.0	0	200	150	0	0	0	250.	1312	71.7	10.5
90	10	0	18.9	49.3	0.2	161	130	0	0.5	0	230.	1357	68.2	10.0
80	20	0	35.1	47.7	1.6	125	111	0	1.4	0	211.	1397	64.4	9.5
70	30	0	46.2	44.6	5.3	94	93	0.1	2.5	0	193.	1421	60.0	8.8
60	40	0	51.9	40.2	11.7	68	76	0.3	3.5	0	176.	1424	54.8	8.0
50	50	0	53.1	34.8	20.5	47	60	0.5	4.3	0	161.	1406	49.5	7.3
40	60	0	50.7	28.7	31.1	29	46	0.7	4.7	0	146.	1363	43.5	6.4
30	70	0.1	44.9	22.0	43.5	13	32	1.0	4.9	0.2	132.	1284	37.0	5.5
20	80	0.3	35.1	14.5	57.3	5	19	1.5	4.5	0.5	119.	1145	29.8	4.4
10	90	1.5	19.4	6.2	66.6	1	3	2.1	3.0	1.5	103.	941	21.2	3.1

Dan O'Shaughnessy
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