Table II. Density Measurements

Eutectic Melt	α, G./Cc.	$\beta \times 10^4$, G./Cc./°C.	Std. Dev. of $\rho \times 10^3$, G./Cc.	Temp., Range, °C.
63.2 mole % LiI-KI	3.350	9.863	1.4	303.6–499.1
60.0 mole % LiBr-KBr	2.860	8.084	2.5	399.1–761.9

tion is 63.2 mole % lithium iodide, and the eutectic temperature is 286.4° C. When the iodide melts are free from moisture, they are stable and can be kept in borosilicate glass or quartz containers. If a trace of moisture is present, hydrogen iodide is evolved, and the alkaline residues attack borosilicate glass and quartz quickly. The composition of the lithium bromide–potassium bromide eutectic is 60.0 mole % lithium bromide (*1*).

The density data were fitted to the equation $\rho = \alpha - \beta t$ by the method of least squares, where ρ is the density, α and β are constants, and t is the temperature in °C. The results are presented in Table II. Measurements were made at 12 and nine different temperatures for the bromide and iodide melts, respectively.

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Vapor Pressures and Heats of Sublimation of Cobalt Dihalides

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The vapor pressures of CoF_2, $CoCl_2$, $CoBr_2$, and CoI_2 were measured by the Knudsen-effusion and torsion-effusion techniques. The results were analyzed by computer, and the uncertainties shown are the standard deviation of the least squares fit to the curves. Standard heats of sublimation are those determined using free energy functions calculated from estimated parameters. Derived heats of sublimation were corrected for partial dimerization where mass spectrometric data were available, and second-law and third-law values of sublimation energies were compared.

ACCURATE THERMODYNAMIC constants for many of the metal dihalides are lacking, although Brewer *et al.* (*1*) have estimated values for most of them. This study is the first product of a systematic attempt by the Bureau of Mines to characterize these vaporization processes more completely and establish more accurate thermodynamic data. The cobalt dihalides were the first of this series to be investigated by the Knudsen-effusion (*7*) and torsion-effusion (*13*) methods simultaneously. There are apparently no experimental data available on CoI_2, and the data on $CoBr_2$ and CoF_2 are limited. Kana'an, Besenbruch, and Margrave (*6*) studied CoF_2 by the Knudsen and Langmuir techniques, and mass spectrometric studies were made on $CoCl_2$ and $CoBr_2$ by Schoonmaker, Friedman, and Porter (*12*). Maier (*8*) and Schaefer (*10*) studied the vapor pressure of $CoCl_2$ at higher temperatures.

Data reported here were obtained by both Knudsen-effusion and torsion-effusion measurements on purified samples. Commercial cobalt difluoride and cobalt dichloride were purified by vacuum dehydration. Cobalt dibromide was prepared by the reaction of cobalt carbonate powder and hydrobromic acid. The solution was evaporated on a steam bath until purple crystals of cobalt bromide hexahydrate formed. The sample was then treated by vacuum dehydration at 450° C. until an ultimate pressure of 1×10^{-5} mm. of Hg was attained. Analyses of the final products are shown in Table I.

Cobalt iodide was prepared by direct combination of the elements in a sealed tube. High purity cobalt metal in the form of machine turnings was placed in a borosilicate glass tube with a slight excess of iodine. The end of the tube containing the reactants was cooled in liquid nitrogen while the tube was evacuated to less than 10^{-5} mm. of Hg and then sealed. After iodine was sublimed away from the cobalt metal to the opposite end of the tube, the tube was placed in a two-zone furnace and the end containing the iodine was heated to 200° C. to provide approximately 1-atm. pressure of iodine. The end containing the cobalt was heated to 400° C. and the reaction was allowed to proceed. Excess iodine was removed from the CoI_2 by subliming it to the other end of the tube. The tube was broken open in an inert atmosphere glove box and the CoI_2 removed. The average chemical analyses of several samples is shown in Table I.

Table I. Analyses of Cobalt Dihalides

Compound	Metal-Halogen Ratio	
	Chemical analyses[a]	Theoretical
CoF_2	1.506 ± 0.014	1.551
$CoCl_2$	0.838 ± 0.010	0.831
$CoBr_2$	0.367 ± 0.004	0.369
CoI_2	0.232 ± 0.002	0.232

	Spectrographic Impurity Analysis		
	Fe, %	Mn, %	Ni, %
CoF_2	0.003–0.03	0.003–0.03	0.40[b]
$CoCl_2$	0.003–0.03	0.003–0.03	0.44[b]
CoBr	0.003–0.03	0.003–0.03	0.01–0.1
CoI_2	0.03 –0.3	0.01 –0.1	0.03–0.3

[a] Uncertainties shown are standard deviations of analyses of six samples. [b] Wet chemical analysis.

EXPERIMENTAL

Knudsen Effusion. Knudsen weight-loss effusion experiments and calibration of the apparatus have been described in detail (*5*). Briefly, a constant-temperature fluidized sand bath heater surrounded a glass vacuum tube containing the platinum-10% rhodium effusion cell. The cell hung from a continuous-recording semimicrobalance. A 28-gage platinum-platinum-10% rhodium thermocouple in a glass thermowell positioned adjacent to the suspended effusion cell was used to measure the sample temperature. A schematic diagram is shown in Figure 1.

The vapor pressure at each temperature was calculated from the well known Knudsen equation for molecular flow:

$$P_K = 17.14 \frac{\Delta W}{KAt} \left(\frac{T}{M}\right)^{1/2} \qquad (1)$$

Torsion Effusion. The torsion-effusion apparatus used was similar in design to one used by Pratt and Aldred (*9*). It consists essentially of a system for measuring the torque, caused by effusion, enclosed within a vertical vacuum chamber. The upper section of the envelope, a brass tube with a sliding glass tube inside, allowed easy access for replacing the torsional wire. Wires 40 cm. in length and 0.002 or 0.003 inch in diameter were used. The angle of rotation of the cell was measured with a gear-train assembly and a revolution counter used in conjunction with a small reflecting mirror and a light source with a null detector. The gear-train assembly was motor-driven to allow smooth angle adjustment. Reproducible measurements to within 0.01° were obtained with this system. The schematic is shown in Figure 2.

Effusion cells were identical to those used in the Knudsen assembly, except that they were mounted in a horizontal holder (Figure 3). The cells were heated by a fluidized sand bath heater, and the temperature was measured in a manner similar to that used for the Knudsen assembly. Torsional constants were measured by the method used by Scheer (*11*) and were reproducible to within 1%

Under molecular flow conditions, the vapor pressure of

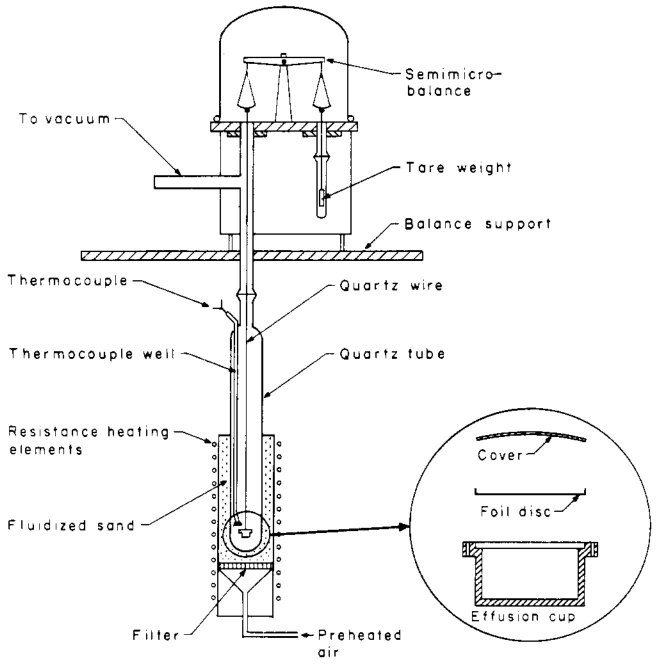

Figure 1. Knudsen effusion apparatus

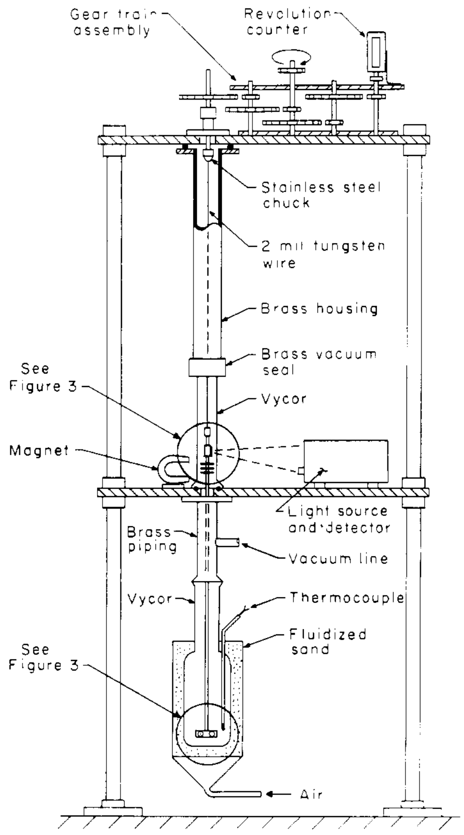

Figure 2. Torsional effusion apparatus

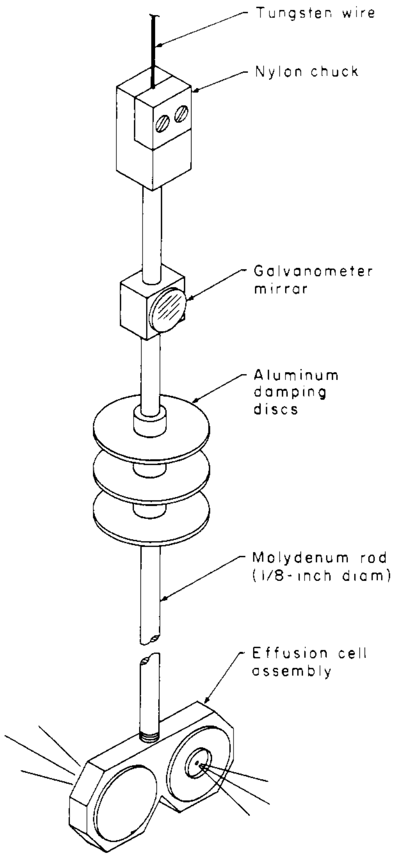

Figure 3. Schematic of effusion system

the sample can be calculated from the angular displacement by the equation:

$$P_T = \frac{2D\theta}{a_1q_1f_1 + a_2q_2f_2} \tag{2}$$

The reliability of the torsion apparatus was established by determining the vapor pressure of potassium chloride. Fifty-four datum points, using three different orifice sizes, yielded an average third-law heat of sublimation of 52.92 ± 0.47 kcal. per mole, in good agreement with the value of 53.39 ± 0.11 reported previously from Knudsen-effusion measurements (*5*).

RESULTS AND DISCUSSION

Results of 151 Knudsen measurements and 106 torsion measurements on cobalt dihalides are presented in Table II and Figure 4. The vapor pressure of each compound was determined using at least two different orifice sizes. Orifice sizes and torsional constants for each series are also shown in Table II. A least-squares fit of each set of data yielded the following equations:

CoF_2
(Knudsen) $\log P_{atm} = 7.880 \pm 0.003 - 14{,}490 \pm 80/T$
(Torsion) $\log P_{atm} = 9.122 \pm 0.031 - 15{,}820 \pm 192/T$
$CoCl_2$
(Knudsen) $\log P_{atm} = 8.797 \pm 0.007 - 10{,}880 \pm 95/T$
(Torsion) $\log P_{atm} = 9.585 \pm 0.083 - 11{,}520 \pm 218/T$
$CoBr_2$
(Knudsen) $\log P_{atm} = 8.292 \pm 0.062 - 10{,}070 \pm 41/T$
(Torsion) $\log P_{atm} = 10.280 \pm 0.087 - 11{,}580 \pm 147/T$
CoI_2
(Knudsen) $\log P_{atm} = 6.832 \pm 0.026 - 7{,}780 \pm 27/T$
(Torsion) $\log P_{atm} = 4.618 \pm 0.032 - 6{,}440 \pm 256/T$

Table II. Cobalt Dihalide

Temp., °K.	Log P_{atm}	$\Delta H^\circ_{298.15}$, Cal./Mole	Temp., °K.	Log P_{atm}	$\Delta H^\circ_{298.15}$, Cal./Mole
CoF_2 (Knudsen)					
Cell A 0.1043-cm. orifice diameter			Cell B 0.1420-cm. orifice diameter		
987.1	−6.6479	76,742	1075.2	−5.5429	77,801
995.9	−6.4496	76,513	1064.4	−5.7208	77,928
992.8	−6.6580	77,211	1056.4	−5.8296	77,900
981.7	−6.8154	77,095	1046.0	−5.9651	77,834
973.0	−6.9775	77,162	1036.2	−6.1226	77,914
1054.8	−5.8112	77,725	1025.0	−6.2704	77,785
1073.0	−5.6972	78,400	1014.4	−6.4364	77,782
1082.7	−5.4599	77,890	1003.4	−6.5720	77,611
1095.7	−5.3017	78,009	995.3	−6.7767	77,947
1100.1	−5.1798	77,665	985.7	−6.8850	77,703
1115.7	−5.2020	78,824	989.3	−6.8298	77,727
1069.9	−5.6523	77,985	998.3	−6.7277	77,947
1025.0	−6.3013	77,930	1009.4	−6.5426	78,242
1033.2	−6.1826	77,972	1018.5	−6.3933	78,221
992.3	−6.7995	77,617	1029.6	−6.2510	78,362
			1039.7	−6.0761	78,268
			1049.5	−5.9585	78,410
			1060.3	−5.8165	78,496
			1069.7	−5.6817	78,500
CoF_2 (Torsion)					
Cell A 2.57 torsion constant *A*. 0.2039-cm. diam., 1.29-cm. moment *B*. 0.2075-cm. diam., 1.29-cm. moment			Cell B 2.68 torsion constant *A*. 0.1550-cm. diam., 1.25-cm. moment *B*. 0.1540-cm. diam., 1.26-cm. moment		
1083.6	−5.4799	78,389	1098.1	−5.1444	77,357
1091.4	−5.3745	78,034	1094.0	−5.1864	77,290
1100.5	−5.2636	78,116	1082.1	−5.3041	77,118
1111.5	−5.1033	78,048	1073.8	−5.4348	77,180
1120.8	−4.9909	78,057	1068.7	−5.4659	76,997
1116.7	−5.0670	78,194	1060.4	−5.6785	77,462
			1053.0	−5.7142	77,104
			1046.9	−5.8604	77,389
$CoCl_2$ (Knudsen)					
Cell A 0.1498-cm. orifice diameter			Cell B 0.1028-cm. orifice diameter		
800.2	−4.8169	54,356	779.2	−5.1616	54,252
791.0	−4.9882	54,390	791.3	−4.9616	54,315
781.4	−5.1469	54,337	761.5	−5.5078	54,286
770.7	−5.3540	54,369	739.1	−5.9232	54,176
760.5	−5.5419	54,334	729.2	−6.1469	54,225
$CoCl_2$ (Knudsen) (*Continued*)					
Cell A 0.1498-cm. orifice diameter			Cell B 0.1028-cm. orifice diameter		
753.3	−5.6862	54,347	717.9	−6.3651	54,138
742.1	−5.8998	54,308	708.7	−6.5708	54,153
733.3	−6.0845	54,306	697.1	−6.7981	54,013
718.5	−6.4062	54,325	677.7	−7.1906	53,801
705.1	−6.6673	54,190	801.4	−4.7859	54,332
689.3	−6.9860	54,042	790.4	−4.9837	54,341
698.1	−6.8434	54,228	780.2	−5.1688	54,339
679.7	−7.2090	54,010	752.5	−5.7104	54,365
			772.3	−5.3359	54,411
Cell C 0.0518-cm. orifice diameter			789.3	−5.0008	54,343
			814.0	−4.5868	54,363
809.5	−4.5755	54,061			
800.3	−4.7700	54,191			
786.4	−4.9885	54,107			
776.1	−5.1970	54,169			
726.8	−6.1514	54,077			
767.6	−5.3652	54,205			
771.1	−5.2892	54,161			
714.9	−6.4002	54,026			
749.2	−5.7268	54,190			
732.9	−5.9843	53,941			
$CoCl_2$ (Torsion)					
Cell A 2.72 torsion constant A. 0.1020-cm. diam., 1.32-cm. moment B. 0.1018-cm. diam., 1.31-cm. moment			Cell B 2.68 torsion constant A. 0.1645-cm. diam., 1.30-cm. moment B. 0.1621-cm. diam., 1.30-cm. moment		
784.4	−5.1178	54,449	802.9	−4.7498	54,301
795.6	−4.8996	54,368	824.4	−4.3742	54,215
804.7	−4.6675	54,095	821.3	−4.4315	54,243
824.4	−4.3674	54,164	783.7	−5.0933	54,312
834.1	−4.2125	54,185	783.0	−5.1150	54,334
773.2	−5.3111	54,378	776.1	−5.2412	54,326
759.3	−5.6530	54,634	761.8	−5.5280	54,371
762.3	−5.5330	54,416	767.2	−5.4321	54,412
796.5	−4.9107	54,478	774.6	−5.2741	54,338
805.3	−4.8857	54,948	806.3	−4.7065	54,355
			795.1	−4.9030	54,347
			789.1	−4.9935	54,303
			800.2	−4.8037	54,315
			752.5	−5.7111	54,225
			745.3	−5.8446	54,332

Mass spectrometric studies of the vaporization of the cobalt halides indicated that the major species is the monomer; however, some dimerization has been reported (*2*, *12*). Figure 5 shows the extent of dimerization observed in a study using a Bendix time-of-flight mass spectrometer with a molybdenum effusion cell (*4*). Through use of these mass spectrometric data, the measured vapor pressures were corrected to represent true equilibrium pressures of $CoCl_2$ and $CoBr_2$. Free-energy functions calculated from estimated parameters presented by Brewer *et al.* (*1*) were used to calculate corrected third-law heats of sublimation (Table III). Second-law heats were also calculated by the method of Cubicciotti (*3*). Both second-law and third-law heats of sublimation are shown in Table IV.

Agreement between the heats of sublimation determined by Knudsen and torsion methods is excellent. Agreement between the third-law and second-law values is good for measurements made on $CoCl_2$ and $CoBr_2$ where the dimerization correction is applicable. Second- and third-law values do not agree at the higher temperatures at which CoI_2 was investigated, apparently because of decomposition and dimerization. The iodine background detected by mass spectrometry was so high that it was impossible to obtain dimerization data for CoI_2. One would expect, however, the extent of dimerization to be greater than that observed for $CoCl_2$ or $CoBr_2$. These phenomena are the apparent cause of the break in the CoI_2 vapor pressure curve at the higher temperature range. Lacking mass spectrometer data, the necessary corrections to the cobalt iodide sublimation energies could not be made.

Because no dimerization was observed for CoF_2, the dimer correction to the sublimation energies was not applicable. Lack of agreement between heats of sublimation calculated by the second-law and third-law methods is probably due to inaccuracies in estimating vibrational frequencies for CoF_2 (g) which were estimated from known values for

Vapor Pressure Data

Temp., °K.	Log P_{atm}	$\Delta H^\circ_{298.15}$, Cal./Mole	Temp., °K.	Log P_{atm}	$\Delta H^\circ_{298.15}$, Cal./Mole
$CoBr_2$ (Knudsen)					
Cell C 0.0507-cm. orifice diameter			Cell B 0.0730-cm. orifice diameter		
768.5	−4.7265	51,731	761.4	−4.9232	51,880
758.2	−4.9400	51,824	750.6	−5.1195	51,877
746.2	−5.1655	51,826	755.8	−5.0271	51,888
737.6	−5.3617	51,935	746.5	−5.2168	51,967
726.2	−5.5691	51,872	739.8	−5.3327	51,948
717.0	−5.7518	51,850	737.0	−5.3860	51,872
705.6	−5.9628	51,756	733.5	−5.4676	51,997
696.9	−6.1791	51,835	727.2	−5.5825	51,979
686.2	−6.3764	51,693	723.1	−5.6610	51,964
675.1	−6.5954	51,567	719.4	−5.7288	51,967
			710.1	−5.9020	51,905
			705.4	−6.0148	51,960
			701.0	−6.0963	51,931
			696.3	−6.1958	51,927
			694.5	−6.2607	52,011
			688.8	−6.3860	52,010
			680.9	−6.5311	51,915
			643.2	−7.1041	51,568
Cell A 0.1093-cm. orifice diameter			Cell A 0.1093-cm. orifice diameter		
712.7	−5.8114	51,722	659.9	−6.9698	51,583
733.4	−5.4278	51,882	670.7	−6.7281	51,652
745.4	−5.2094	51,920	681.4	−6.4980	51,731
755.2	−5.0203	51,918	691.4	−6.3077	51,847
765.4	−4.8271	51,898	694.6	−6.2536	51,908
672.6	−6.6924	51,675	712.8	−5.8575	51,898
662.3	−6.9125	51,597	719.0	−5.7275	51,900
653.5	−7.0926	51,469	722.9	−5.6475	51,903
639.0	−7.3452	51,104	706.5	−5.9713	51,850
645.0	−7.3161	51,485	700.7	−6.1204	51,923
$CoBr_2$ (Torsion)					
Cell A 2.68 torsion constant *A*. 0.1234-cm. diam., 1.285-cm. moment *B*. 0.1232-cm. diam., 1.340-cm. moment			Cell B 2.72 torsion constant *A*. 0.1385-cm. diam., 1.36-cm. moment *B*. 0.1375-cm. diam., 1.34-cm. moment		
777.2	−4.5885	51,795	731.1	−5.4812	51,922
790.8	−4.4219	52,011	746.7	−5.2159	52,026
759.9	−4.9968	52,130	757.8	−5.0231	52,113
738.4	−5.4642	52,337	749.9	−5.1928	52,164
729.0	−5.7024	52,495	740.3	−5.3569	52,110
735.3	−5.5286	52,349	727.6	−5.6351	52,197

Temp., °K.	Log P_{atm}	$\Delta H^\circ_{298.15}$, Cal./Mole	Temp., °K.	Log P_{atm}	$\Delta H^\circ_{298.15}$, Cal./Mole
$CoBr_2$ (Torsion) (*Continued*)					
Cell A 2.68 torsion constant			Cell B 2.72 torsion constant		
738.4	−5.4779	52,398	778.2	−4.6285	52,004
751.1	−5.1829	52,211	773.2	−4.7210	52,016
752.5	−5.0921	51,988	782.5	−4.5788	52,082
766.0	−4.8526	52,027	783.4	−4.5634	52,070
770.6	−4.7671	52,008	764.1	−4.9251	52,153
781.5	−4.6150	52,145	792.0	−4.4027	52,041
786.2	−4.5197	52,108			
Cell C 2.68 torsion constant *A*. 0.0503-cm. diam., 1.28-cm. moment *B*. 0.0503-cm. diam., 1.30-cm. moment			Cell D 2.72 torsion constant *A*. 0.1810-cm. diam., 1.36-cm. moment *B*. 0.1812-cm. diam., 1.34-cm. moment		
769.7	−4.7071	51,736	751.1	−5.1578	52,117
784.8	−4.4399	51,729	740.1	−5.3944	52,214
804.1	−4.0636	51,520	732.7	−5.5046	52,091
818.1	−3.8263	51,463	708.7	−5.9537	51,940
829.6	−3.6426	51,440	735.8	−5.4766	52,209
841.1	−3.4435	51,302	732.2	−5.5144	52,081
825.1	−3.7170	51,449	751.1	−5.1711	52,163
805.1	−4.0636	51,584	764.1	−4.9935	52,391
803.4	−4.1072	51,643			
789.7	−4.3849	51,821			
800.3	−4.1631	51,656			
781.5	−4.5398	51,884			
CoI_2 (Knudsen)					
Cell A 0.1368-cm. orifice diameter			Cell B 0.1178-cm. orifice diameter		
586.1	−6.4238	44,942	652.4	−5.1200	45,958
579.8	−6.5964	44,940	605.5	−6.0612	45,389
557.1	−7.1331	44,587	596.6	−6.2240	45,202
588.6	−6.3982	45,065	555.1	−7.1878	44,572
550.4	−7.3008	44,490	588.9	−6.4255	45,179
537.1	−7.6581	44,320	549.3	−7.3450	44,523
568.4	−6.8938	44,858	619.0	−5.7677	45,551
634.8	−5.4302	45,689	609.6	−5.9346	45,331
643.6	−5.2612	45,780	565.1	−6.9568	44,761
651.9	−5.1086	45,895	627.8	−5.5937	45,674
604.3	−6.0487	45,264	635.5	−5.4504	45,779
616.1	−5.8096	45,449	571.7	−6.7963	44,846
624.5	−5.6253	45,518	580.3	−6.6005	44,990
653.1	−5.0886	45,920			
596.2	−6.2132	45,106			

(*Continued on page 88*)

Table II. Cobalt Dihalide Vapor Pressure Data (*Continued*)

Temp., °K.	Log P_{atm}	$\Delta H^\circ_{298.15}$, Cal./Mole	Temp., °K.	Log P_{atm}	$\Delta H^\circ_{298.15}$, Cal./Mole
CoI_2 (Knudsen) (*Continued*)					
Cell C 0.1072-cm. orifice diameter					
663.7	−4.8525	45,922			
605.1	−5.9963	45,179			
590.6	−6.3438	45,071			
557.3	−7.1176	44,569			
587.4	−6.3848	44,949			
568.7	−6.8411	44,745			
624.7	−5.5795	45,401			
650.7	−5.1342	45,887			
640.7	−5.3254	45,774			
633.8	−5.4488	45,658			
613.3	−5.8568	45,381			
593.3	−6.2756	45,086			
CoI_2 (Torsion)					
Cell A 2.68 torsion constant *A*. 0.1130-cm. diam., 1.33-cm. moment *B*. 0.1095-cm. diam., 1.29-cm. moment			Cell B 2.65 torsion constant *A*. 0.1881-cm. diam., 1.33-cm. moment *B*. 0.1856-cm. diam., 1.36-cm. moment		
640.6	−5.2761	45,623	678.3	−4.9234	47,105
630.1	−5.4928	45,531	655.5	−5.1890	46,377
616.1	−5.7232	45,212	646.3	−5,3000	46,093
649.6	−5.2918	46,421	632.7	−5.6178	46,075
666.0	−5.0700	46,744	623.4	−5.7205	45,715
688.7	−4.7787	47,323	628.2	−5.6925	45,974
708.7	−4.3653	47,286	640.6	−5.4816	46,219
703.7	−4.4444	47,228	649.4	−5.2945	46,272
676.0	−5.0420	47,312	661.3	−5.1184	46,567
657.4	−5.3430	46,968			
658.0	−5.2918	46,850			
719.4	−4.3448	47,939			
730.2	−4.1434	47,899			

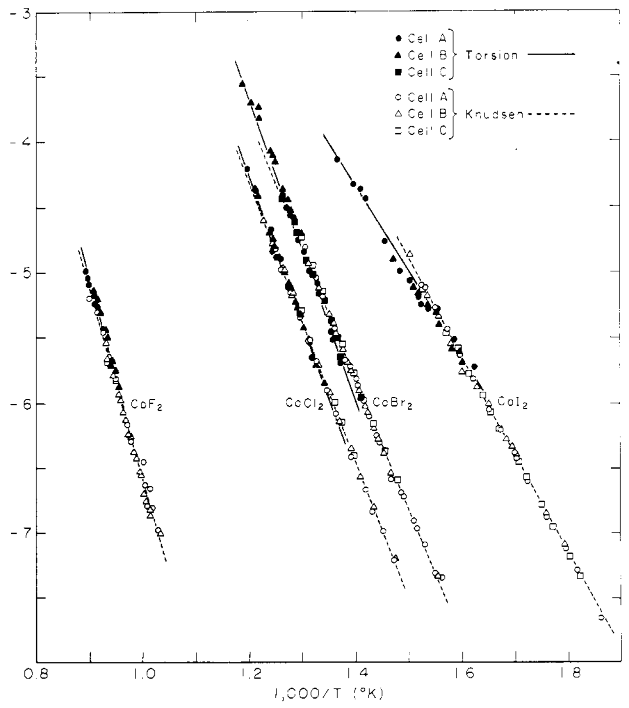

Figure 4. Vapor pressure of cobalt dihalides

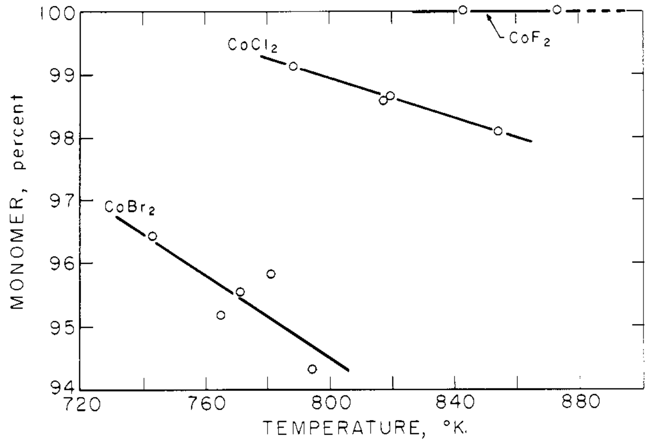

Figure 5. Extent of dimerization

Table III. Free Energy Functions for Cobalt Dihalides

Temp., °K.	$-\Delta \frac{(F^\circ_T - H^\circ_{298})^a}{T}$, cal. deg.$^{-1}$ mole^{-1} CoF_2	$CoCl_2$	$CoBr_2$	CoI_2
500	48.42	47.20	46.90	47.60
600	48.30	46.85	46.55	47.25
700	48.05	46.33	46.11	46.82
800	47.84	45.91	45.52	46.21
900	47.56	45.22	44.85	45.55
1000	47.31	44.51	44.12	44.82
1100	46.92	43.65	43.25	43.91
1200	46.53	42.80	42.30	42.95

[a] For reaction $CoX_{2\,(s)} = CoX_{2\,(g)}$.

Table IV. Cobalt Dihalide Heats of Sublimation

Compound	$\Delta H^\circ_{298.15}$, Cal./Mole 3rd law	2nd law
CoF_2		
(Knudsen)	77,860 ± 490	69,760 ± 490
(Torsion)	77,620 ± 480	68,210 ± 430
$CoCl_2$[a]		
(Knudsen)	54,230 ± 150	52,190 ± 200
(Torsion)	54,370 ± 160	55,410 ± 510
$CoBr_2$[a]		
(Knudsen)	51,890 ± 160	51,820 ± 190
(Torsion)	52,060 ± 260	55,170 ± 490
CoI_2		
(Knudsen)	45,230 ± 470	37,020 ± 650
(Torsion)	46,580 ± 750	31,600 ± 750

[a] Corrected for dimerization.

$CoCl_2$ (g) and $CoBr_2$ (g). Thus, free-energy functions used in the third-law calculation may be in error.

Both the vapor pressure equation and the heat of sublimation derived for CoF_2 are in good agreement with those found by Kana'an, Bensenbruch, and Margrave (*6*) (78.8 ± 0.3 kcal. per mole). Derived heats of sublimation for $CoCl_2$ agree well with the value calculated by Brewer from the data of Maier (*8*), Schaefer (*10*), and Schoonmaker (*12*) (54 kcal. per mole). Vapor pressure equations for $CoCl_2$ also tie in well with those determined at higher pressures by Schaefer. The heat of sublimation determined for $CoBr_2$ also agrees well with that estimated by Brewer (53 kcal. per mole).

CONCLUSIONS

Assuming a maximum error of ±10% in pressure readings caused by uncertainties in measuring orifice areas, lid thickness, moment arms, torsion constants, and deflection angles, the total error would not exceed ±0.4% in values calculated for ΔH°_{298} by the third-law method. The maximum probable error in temperature measurement is ±2°, which corresponds to a ±0.2% error in ΔH°_{298} values. The total uncertainty in ΔH°_{298} calculation resulting from experimental errors is then ±0.6%.

The uncertainties in values for the free-energy functions arise from errors of ±10% in vibrational frequencies and ±0.05 A. in bond distances. Thus the free-energy function may be in error by ±1.2%. Considering the small contribution made by dimerization corrections, the third-law heats of sublimation should be correct within ±2%. Considering all estimated errors, the selected sublimation energies for the cobalt dihalides are: CoF_2 78 ± 1.5, $CoCl_2$ 54 ± 1, $CoBr_2$ 52 ± 1, and CoI_2 46 ± 2 kcal. per mole.

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NOMENCLATURE

A = area of orifice, sq. cm.
a_1,a_2 = area of effusion orifices, sq. cm.
D = torsion constant, dyne-cm./deg.
f_1,f_2 = force correction factor
K = Clausing factor for orifice
M = molecular weight
P_K = vapor pressure, mm. of Hg
P_T = vapor pressure of sample, dynes/sq. cm.
q_1,q_2 = momentum arm lengths, cm.
t = time, seconds
T = temperature, ° K.
ΔW = weight loss, grams
θ = angular displacement, deg.

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Thermal Behavior of Some Resin Acid Esters

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The isomerization of the methyl esters of three of the four conjugated dienoic resin acids of pine gum in the presence and absence of base, as well as in the presence of added carboxylic acid, was examined.

THE THERMAL isomerization of levopimaric, palustric, and neoabietic acids and esters was investigated some time ago by Lawrence and coworkers (*3*). The isomerization of levopimaric, palustric, neoabietic, and abietic acids at 200° C. has recently been found to result in the formation of an equilibrium mixture of 81% abietic, 14% palustric, and 5% neoabietic acids (*3*). The isomerization of methyl abietate at 200° C. proceeded at the same rate as the acid and gave the same final distribution of abietate, palustrate, and neoabietate (*2*). Disproportionation was extensive in the case of the ester as compared to the acid (*2*). The addition of base very strikingly inhibited both isomerization and disproportionation. The temperature of 200° C. was selected for study, in that it is about 25° C. higher than the melting point of the highest melting of the four conjugated dienoic acids. Thus measurements are not complicated by lengthy "heat up" or melting periods at the beginning of each run. For comparison, the esters were then also run at 200° C.

It thus became of interest to investigate the thermal isomerization, in the presence and absence of added base, of the methyl esters of the other three conjugated dienoic resin acids found in pine gum. This was of special importance in view of the demonstrated inhibitory effect of small traces of base, accumulated during the preparation of the ester, upon the isomerization of methyl abietate (*2*).

The results are summarized in terms of half lives in Table I.

Table I. Half Lives of Conjugated Dienoic Resin Acids, Esters, and Esters in Presence of Base at 200° C.

	Half Lives, Min.		
	Acid (*3*)	Ester	Ester + 5 mole % KOH
Levopimaric	15	15	2.5 hr.
Palustric	40	84	50 days
Abietic	75	70 (*2*)	200 days (*2*)
Neoabietic	120	134 hr.	200 days

The rate of isomerization of the esters is in about the same order as the corresponding acids. Surprisingly, methyl levopimarate and methyl abietate isomerize at about the same rate as the free acids, whereas methyl palustrate isomerizes somewhat more slowly and methyl neoabietate very much more slowly than the corresponding acids. In the presence of base, again the same order of reactivities is approximately maintained.

Methyl palustrate and methyl neoabietate were isomerized in the presence of an equimolar amount of dehydroabietic acid. In both cases, the rate of isomerization was essentially the same as that of the corresponding free palustric and neoabietic acids. This would support the notion of an acid-catalyzed mechanism in the isomerization reaction.