Appendix A1: The British Patent No. 2064, of Dr. Charles Williams Siemens, 1857: "Refrigeration Apparatus"

B.-Z. Maytal and J.M. Pfotenhauer, *Miniature Joule-Thomson Cryocooling: Principles and Practice*,
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A.D. 1857 . . . . N° 2064.

Refrigerating Apparatus.

(*This Invention received Provisional Protection, but notice to proceed with the application for Letters Patent was not given within the time prescribed by the Act.*)

PROVISIONAL SPECIFICATION left by Charles William Siemens, at the Office of the Commissioners of Patents, with his Petition, on the 29th July 1857.

I, CHARLES WILLIAM SIEMENS, of John Street, Adelphi, in the County of Middlesex, do hereby declare the nature of the said Invention for "IMPROVEMENTS IN REFRIGERATING AND PRODUCING ICE, AND IN APPARATUS OR MACHINERY FOR THAT PURPOSE," to be as follows:—

The Invention relates to freezing and refrigerating by the expansion of air or elastic fluids. The air is first compressed by a cylinder or pump of any suitable construction, by which its temperature is raised, and it is cooled while in the compressed state, and it is then allowed to expand in a cylinder or engine of any suitable construction by which its temperature is lowered. The air thus cooled is brought in contact with the articles to be cooled or frozen, and is then conducted through an interchanger or apparatus by which it is made to cool the compressed air, which enters the interchanger in the opposite direction. The pump for compressing the air is worked by a steam engine or other power, and the engine in which the air expands is made to assist in working the pump. I prefer to connect the steam engine and the air engine and the pump to the same rod or moving part, so as to transmit the power directly from one to the other. If the atmosphere be at 70° Fahrenheit, and the air be heated 50° by the compression, and be then cooled to 70°, and allowed to expand, its temperature will be lowered to about 20°, more or less. This cold air will then enter the interchanger and cool the

Siemens' Improved Apparatus for Refrigerating and Producing Ice.

next portion of compressed air, say to 30°, and will itself be heated say to about 110°, and will pass away into the atmosphere. The compressed air at 30° being allowed to expand, will be cooled to about 20° below zero, and in passing through the interchanger will cool the next portion of compressed air, say to 10° below zero. This on expanding will be reduced to about 60° below zero, and so on. These temperatures are mentioned not as the absolute temperatures, but to shew that the principle of the Invention is adapted to produce an accumulated effect or an indefinite reduction of temperature.

I construct machinery or apparatus for carrying out the Invention by immersing the engine in brine or a solution of chloride of calcium or other suitable fluid which will not congeal at the temperature which it is required to produce. I cause the air, after expanding in the engine, to pass into a series of tubes immersed in the brine or other fluid. These tubes are perforated on their under sides, so that the air passes through the brine in a multitude of streams or bubbles and thus cools the brine; or the air is admitted into a casing surrounding the brine vessel, and allowed to pass through perforations in the sides. The vessel which contains the brine is covered, and the cold air is conveyed from it through the interchanger, which consists of a series of tubes inclosed in a case. The cold air is conveyed through the tubes, while the compressed air passes in the contrary direction through the case or vice versa. The compressed air thus enters warm and passes out cold, while the expanded air enters cold and passes out warm. The water or other liquids or articles to be cooled or frozen, are immersed in the aforesaid brine or other fluid; thus the heat which is continually abstracted from the articles to be cooled or frozen, is carried off by the heated air. This current of heated air may be allowed to escape into the atmosphere, or it may be employed for any purpose for which such a current of heated air may be required. The construction of the interchanger may be varied, or two or more regenerators or respirators filled with wire gauze or metallic plates, or other suitable materials may be employed alternately for the compressed and expanded air. The water or other liquid to be cooled or frozen may also be conducted through tubes in the interchanger, or exposed to the contact of the cold air, so as to cool it down before it enters the vessels in which it is to be frozen. When it is required to supply cold air to a cellar or chamber of any sort, the cold expanded air is conducted into such chamber, and on leaving the chamber it passes through the interchanger as before.

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Appendix A2: Equations of State

A2.1. Van der Waals Equation of State

The Van der Waals equation of state is mainly applicable for obtaining closed form solutions, and for describing the basic behavior, trends and phenomena, if one is willing to tolerate less accurate quantitative results.

$$P = \frac{R \cdot T}{v - b} - \frac{a}{v^2} \tag{A2.1}$$

$$Z = 1 + \frac{b \cdot \rho}{1 - b \cdot \rho} - \frac{a \cdot \rho}{R \cdot T} \tag{A2.2}$$

$$\Pi = \frac{8\Theta}{3\Phi - 1} - \frac{3}{\Phi^2} \tag{A2.3}$$

$$a = \frac{27}{64}\frac{R^2\, T_C^2}{P_C} = \frac{9}{8}\, R\; T_C\; v_C = 3\, P_C\, v_C^2 \tag{A2.4}$$

$$b = \frac{1}{8} \cdot \frac{R \cdot T_C}{P_C} = \frac{v_C}{3} \tag{A2.5}$$

$$P_C = \frac{a}{27b^2} \tag{A2.6}$$

$$T_C = \frac{8a}{27bR} \tag{A2.7}$$

$$Z_C = \frac{3}{8} \tag{A2.8}$$

$$Z^3 - \left(\frac{\Pi}{8\Theta} + 1\right)Z^2 + \frac{27\Pi}{64\Theta^2}Z - \frac{27\Pi^2}{64\Theta^3} = 0 \tag{A2.9}$$

A2.2. Peng-Robinson Equation of State

The Peng-Robinson equation of state provides a cubic EOS which may be considered as an advanced enhancement of the Van der Waals EOS. It also enables closed form expressions with much higher quantitative accuracy.

$$P = \frac{R \cdot T}{v - b} - \frac{a(T)}{v \cdot (v + b) + b \cdot (v - b)} \tag{A2.10}$$

$$a(T) = 0.45724\frac{R^2 \cdot T_C^2}{P_C} \cdot \alpha(T) \tag{A2.11}$$

$$b = 0.07780\; \frac{R\, T_C}{P_C} \tag{A2.12}$$

$$\alpha^{1/2} = 1 + m \cdot \left[1 - (T/T_C)^{1/2}\right] \tag{A2.13}$$

Formally, the acentricity factor of a gas is defined on the basis of the saturation curve as proposed by Pitzer,

$$\omega = -1 - \log_{10}\; \frac{P_S\,(T/T_C = 0.7)}{P_C} \tag{A2.14}$$

where P_S is the saturation pressure. On the logarithmic scale, it describes the extent that the saturation pressure deviates from that of the non-quantum noble gases argon, krypton and xenon, for which it vanishes, $\omega = 0$. The acentric factor is implemented into the equation through,

$$m = 0.37464 + 1.5422\; \omega - 0.26992\; \omega^2 \tag{A2.15}$$

$$A = \frac{a \cdot P}{R^2 \cdot T^2} \tag{A2.16}$$

$$B = \frac{b\, P}{R\, T} \tag{A2.17}$$

A proper rearrangement leads to the expressions,

$$T \cdot \frac{da(T)}{dT} = -m \cdot a(T) \cdot \left(\frac{T}{\alpha \cdot T_C}\right)^{1/2} \tag{A2.18}$$

$$Z^3 + C_2 \cdot Z^2 + C_1 \cdot Z + C_0 = 0 \tag{A2.19}$$

$$C_1 = A - 3B^2 - 2B \tag{A2.20}$$

$$C_2 = B - 1 \tag{A2.21}$$

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$$C_3 = B^3 + B^2 - A \cdot B \qquad (A2.22)$$

$$Z_C = 0.307 \qquad (A2.23)$$

A2.3. Virial Equation of State (Proposed by K. Onnes in 1912)

There are two versions of the Virial EOS, one expanded by pressure and the other expanded by density.

$$Z = \frac{P \cdot v}{R \cdot T} = 1 + B \cdot \rho + C \cdot \rho^2 + D \cdot \rho^3 + \ldots \quad \equiv$$
$$\equiv 1 + B' \cdot P + C' \cdot P^2 + D' \cdot P^3 \ldots \qquad (A2.24)$$

The coefficients of these two, $B(T)$, $C(T)$, $D(T)$ etc. are solely temperature dependent, as are $B'(T)$, $C'(T)$, $D'(T)$ etc., which are related to each other by the equations,

$$B' = \frac{B}{R \cdot T} \qquad (A2.25)$$

$$C' = \frac{(C - B^2)}{(R \cdot T)^2} \qquad (A2.26)$$

$$D' = \frac{D + 2B^3 - 3B \cdot C}{(R \cdot T)^3} \qquad (A2.27)$$

$$\frac{dB'}{dT} = \frac{1}{R \cdot T}\left(\frac{dB}{dT} - \frac{B}{T}\right) \qquad (A2.28)$$

$$\frac{dC'}{dT} = \frac{1}{(R \cdot T)^2}\left(\frac{B^2 - C}{T} + \frac{dC}{dT} - 2B\frac{dB}{dT}\right) \qquad (A2.29)$$

The van der Waals equation of state expended by density is,

$$B = b - \frac{a}{RT} \qquad (A2.30)$$

$$C = b^2 \qquad (A2.31)$$

$$D = b^3 \qquad (A2.32)$$

A2.4. Truncated Virial Equation of State

$$Z = \frac{P\ v}{R\ T} = 1 + B'\ P = 1 + \frac{B\ P}{R\ T} \qquad (A2.33)$$

A2.5. Interrelating the Third Parameter of the Principle of Corresponding States

$$Z_C = 0.29056 - 0.08775 \cdot \omega \qquad (A2.34)$$

The quantity Z_C ranges for most of the substances from 0.22 to 0.30. A more complex molecule with a larger positive value of ω has a smaller value of Z_C.

Riedel proposed another acentricity factor based on the saturation line, but at the critical state

$$\alpha_C = \frac{d(\log P_S)}{d(\log T_S)} \quad @\ (T_C,\ P_C) \qquad (A2.35)$$

where P_S is the saturation pressure corresponding to the saturation temperature, T_S.

Riedel's acentricity factor is related to Pitzer's acentricity factor by,

$$\alpha_C = 5.811 + 4.919\omega \qquad (A2.36)$$

Appendix A3: Parameters of Gases

		M [g/mol]	T_C [K]	P_C [MPa]	T_{BOIL} [K]	T_M [K]	ω	Z_C
Helium-3	^3He	3.017	3.3	0.1188	3.2		−0.473	0.302
Helium-4	^4He	4.003	5.2	0.227	4.2		−0.365	0.302
Hydrogen	H_2	2.016	33.0	1.30	20.4	13.8	−0.214	0.306
Deuterium	D_2	4.032	38.3	1.66	23.6	18.6	−0.176	0.312
Neon	Ne	20.18	44.4	2.68	27.1	24.6	−0.029	0.311
Nitrogen	N_2	28.01	126.2	3.34	77.3	63.3	0.037	0.290
Carbon monoxide	CO	28.01	132.8	3.45	81.7	68.1	0.051	0.295
Fluorine	F_2	37.997	144.4	5.22	85.0	53.5	0.054	0.288
Argon	Ar	39.948	150.8	4.87	87.3	83.8	0.001	0.291
Oxygen	O_2	32.00	154.6	5.08	90.2	54.4	0.025	0.288
Methane	CH_4	16.04	190.6	4.60	111.7	90.7	0.011	0.286
Krypton	Kr	83.30	209.4	5.51	119.9	115.9	−0.002	0.288
R-14	CF_4	88.005	227.7	3.74	145.2	89.3	0.178	0.276
Xenon	Xe	131.30	289.7	5.82	165.1	161.3	0.004	0.287
Ethylene	C_2H_4	28.05	282.7	5.11	169.4	104.0	0.087	0.280
Ethane	C_2H_6	30.07	305.5	4.89	184.5	89.9	0.099	0.288
Nitrous oxide	N_2O	44.013	309.7	7.22	184.2	182.3	0.165	0.274
Acetylene	C_2H_2	26.04	308.0	6.20	189.6	192.34	0.184	0.270
R-13	$CClF_3$	104.46	302.1	3.82	192.0	91.6	0.170	0.278
Carbon dioxide	CO_2	44.02	304.2	7.37		215.7	0.281	0.274
R-13B1	CF_3Br	148.91	340.2	3.96	215.4	105.2	0.171	0.275
Propylene	C_3H_6	42.079	364.9	4.62	225.5	87.9	0.141	
Propane	C_3H_8	44.09	369.8	4.25	231.1	85.5	0.152	0.281
Isobutane	iC_4H_{10}	58.124	408.2	3.64	261.4	113.6	0.185	0.278
1-butene	$1\text{-}C_4H_8$	56.11	419.6	4.02	266.9	87.8	0.191	
n-butane	nC_4H_{10}	58.124	425.2	3.80	272.7	134.8	0.201	

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