A condensation diagram. By Mr P. I. DEE, Pembroke College.

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Introduction.

When a mass of air, saturated with water vapour at room temperature θ_1, is expanded adiabatically, the temperature falls to a lower temperature θ_2. In general the resulting density of water vapour is greater than the equilibrium value at the temperature θ_2 and condensation commences. This condensation causes heating of the gas and the temperature rises until finally at some temperature θ_3 the density of uncondensed vapour is equal to the equilibrium vapour density at θ_3. ($\theta_1 > \theta_3 > \theta_2$.) Condensation then ceases and the air rises slowly to room temperature by heat conduction through the walls of the apparatus.

In many experiments using a rapid expansion under conditions where a dense cloud is formed, the amount of vapour which may be thus condensed can be correctly calculated from the above considerations, the rate of heat conduction from the walls to the colder gas being negligibly small compared with the rate of heating of the gas due to condensation. Powell* has shown that in some cases, such as obtained in a small apparatus at high temperatures, the above considerations are invalidated by the diffusion of vapour from the walls to the gas. We shall consider the idealised case above, assuming that there is neither heat conduction nor inflow of vapour from the walls of the apparatus. C. T. R. Wilson† and J. J. Thomson‡ have used the above assumptions to calculate by successive approximation the amount of water vapour available to form a cloud, the former in his estimation of the number of drops in dense clouds and the latter in the determination of the electronic charge.

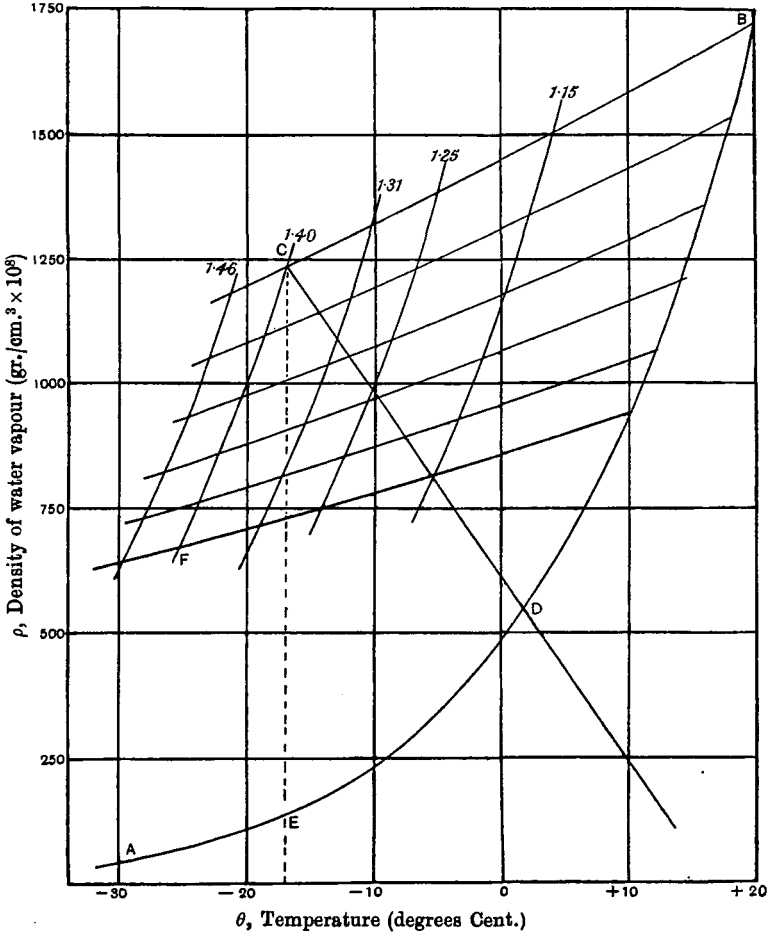
In the course of a number of investigations which have recently been made on the condensation process it has frequently been necessary to determine theoretically this amount of available water vapour, when air initially at room temperatures is subjected to adiabatic expansions of different magnitudes. It is possible to construct a diagram from which this quantity may readily be obtained, together with other useful data as to the state of the gas. Since the construction of the diagram is a somewhat laborious task, it is hoped that a reproduction of it may be of use to other workers in this field. The values for the amount of "available" water vapour, supersaturation, etc. are given by the diagram correct to

* *Proc. Roy. Soc.* 119, p. 553 (1928).
† *Phil. Trans.* 189 A, p. 265 (1897).
‡ *Phil. Mag.* (5), 46, p. 528 (1898).

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5% for the idealised case defined above. Using expansions greater than 1·36, produced in 0·02 sec., in an apparatus of a litre capacity at temperatures less than 20° C., these values have been verified experimentally within the limits of error of the calculation. Under such conditions a sufficiently dense cloud is always formed, even in the absence of ionisation, to justify the above assumptions.

Description of diagram and method of use.



The abscissae represent temperature in °C., and the ordinates density of water vapour in gr. per c.c. × 10^{-8}.

The curve AB shows the density of water vapour in equilibrium with a flat surface at temperatures between − 30° C. and + 20° C.

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Curves such as BC represent the corresponding instantaneous values of temperature and vapour density during the actual expansion of the gas initially represented by the point B; the straight line CD gives the same quantities as the temperature rises as a result of condensation. (The gradient of CD depends upon the air pressure and temperature; it has been drawn for the case when the temperature before expansion is 20° C., and the final AIR pressure (P) after the expanded gas has returned to 20° C. is 76 cm.) The lines CF have been drawn connecting points on the BC curves which correspond to the same expansion ratio.

As an example of the use of the diagram, we will consider the case when a volume v_1 of saturated air at 20° C. is expanded to a volume v_2. ($v_2/v_1 = 1{\cdot}40$.) Let the final air pressure P be 76 cm. The point $B(+20, 1724)$ represents the state of the gas before expansion, from which we calculate that the density of water vapour at the instant of completion of the expansion is $\frac{1724}{1{\cdot}40} = 1231$. The abscissa for an ordinate (1231) on the curve BC is (-17), so that the point $C(-17, 1231)$ represents the state of the gas at the instant of completion of the expansion. The gas is now heated by condensation, the temperature and vapour density at any instant being given by the straight line CD. At D, the point of intersection of this line with the curve AB, the existing vapour density is the saturation value at the existing temperature $(+1{\cdot}7)$, so that $D(+1{\cdot}7, 545)$ gives the state of the gas when condensation ceases. The radius of the fully grown water drops at the temperature θ_3 is in general greater than 10^{-5} cm., so that an error of less than 1% is made by treating them as a flat surface in calculating the equilibrium vapour pressure at θ_3. Thus the amount of condensed vapour per c.c. of the expanded gas is given by $(1231 - 545 = 686) \times 10^{-8}$ gr. and the equilibrium temperature after formation of the cloud is $+1{\cdot}7$° C.

The ratio of the ordinate of C to the ordinate of the curve AB for the same temperature (-17) gives the supersaturation corresponding to the 1·40 expansion of the gas, initially at 20° C., viz. $\frac{1231}{139} = 8{\cdot}9$.

Construction of the diagram.

AB. The saturation water vapour density ρ at any temperature θ was obtained from the equation

$$\rho = \frac{18}{22400} \times \frac{p}{760} \times \frac{273}{\theta}.$$

(Molecular weight of water = 18, molecular volume at N.T.P. = 22400 c.c., p mm. = water vapour pressure at θ° K.)

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The values thus obtained agree closely with those obtained from Callendar's equation for steam, the difference being $<1\%$ at 20° C. and less at lower temperatures. The water vapour pressure at temperatures below 0° C. were taken from the tables of Scheel and Heuse*. See Table I.

TABLE I.

Temp. °C.	−30	−25	−20	−15	−10	−5	+1
Saturation density (gr./c.c. × 10^8)	46·3	71·6	109	162	237	342	518
Temp. °C.	+5	+10	+12	+14	+16	+18	+20
Saturation density (gr./c.c. × 10^8)	679	939	1065	1205	1360	1534	1724

BC. The temperatures θ_2 corresponding to expansion ratios v_2/v_1 were obtained from the adiabatic equation $\frac{\theta_2}{\theta_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$, where θ_1, v_1 and θ_2, v_2 are the initial and final values of the absolute temperature and volume respectively, and $\gamma = 1{\cdot}402$ is the ratio of specific heats of air†. The vapour densities corresponding to these temperatures are then given by $\rho_1 v_1/v_2$, where ρ_1 is the initial saturation density at θ_1. See Table II.

TABLE II.

Init. Temp. $= \theta_1$° C.	+10°	+12°	+14°	+16°	+18°	+20°
$\frac{v_2}{v_1} = 1{\cdot}15$	−5·5° 816	−3·5° 926	−1·7° 1048	+0·2° 1183	+2·1° 1334	+4·0° 1500
1·25	−14·3° 751	−12·5° 852	−10·7° 964	−8·8° 1088	−6·9° 1228	−5·1° 1379
1·31	−19·1° 717	−17·3° 813	−15·6° 920	−13·8° 1039	−12·0° 1170	−10·2° 1316
1·40	−25·7° 671	−24·0° 761	−22·3° 861	−20·6° 972	−18·8° 1096	−17·0° 1231
1·46	−29·9° 643	−28·3° 729	−26·5° 825	−24·8° 932	−23·0° 1051	−21·3° 1180

The upper figure in each case $= \theta_2$ in ° C., the lower = vapour density in expanded gas in gr./c.c. × 10^{-5}.

* *Ann. der Physik*, 29, p. 723 (1909).

† Powell (*loc. cit.*) has investigated the dependence of γ on the partial pressures of air and water vapour. For an air pressure of 20 cm. and a temperature of 20° C., the resulting value of γ is 1·39. The maximum error thus introduced into the determination of the quantities required is 2%; for pressures greater than 20 cm. and temperature less than 20° C. it is smaller.

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CD. Consider 1 c.c. of the expanded gas at the point *C*.

Let ρ_2 be the density of vapour at the instant of completion of the expansion when the temperature is θ_2. Let ρ, θ be subsequent instantaneous values during the condensation, and let the condensation of a mass of vapour $-d\rho$ raise the temperature of the whole mass of air, condensed water and vapour by $d\theta$. Then we have

$$-L\,d\rho = \{m_a c_a + (\rho_2 - \rho) + \rho c_s\}\,d\theta,$$

where L = latent heat of steam; m_a = mass of air per c.c.; c_a, c_s are specific heats of air and water vapour at constant volume respectively.

The solution of this equation gives

$$\frac{L}{1-c_s}\log_e\left\{1+\frac{(\rho_2-\rho)(1-c_s)}{m_a c_a+\rho_2 c_s}\right\} = \theta - \theta_2.$$

Now $m_a c_a$ is large compared with $(\rho_2 - \rho)(1 - c_s)$ under the conditions for which this diagram was constructed and to a degree of approximation indicated later we may write

$$L(\rho_2 - \rho) = (m_a c_a + \rho_2 c_s)(\theta - \theta_2).$$

CD is therefore a straight line of slope

$$S = \left\{\frac{m_a c_a + \rho_2 c_s}{L}\right\} \text{ gm. cm.}^{-3} \text{ deg.}^{-1}.$$

Let P be the final air pressure when the temperature is θ_1.

Then at any temperature

$$m_a = \frac{0{\cdot}00129 \times P \times 273}{76 \times \theta_1}.$$

L, the latent heat of steam *at constant volume* in the temperature range θ_2 to θ_3, the temperature at which condensation ceases, is 575 cal./gr. (error in treating L constant $< 1\%$), $c_a = 0{\cdot}172$, $c_s = 0{\cdot}33$.

Hence

$$S = \frac{1}{575}\left\{\frac{0{\cdot}00129 \times 273 \times 0{\cdot}172}{76} \times \frac{P}{\theta_1} + 0{\cdot}33\rho_2\right\} \text{ gm. cm.}^{-3} \text{ deg.}^{-1}$$

$$= 1{\cdot}74\left\{80\,\frac{P}{\theta_1} + \frac{\rho_2}{3000}\right\} \text{ gm. cm.}^{-3} \text{ deg.}^{-1} \times 10^{-8},$$

where ρ_2 is expressed in gr./c.c. $\times 10^{-8}$.

For the case given $P = 76$, $\theta_1 = 293$, $\rho_2 = 1231$, $S = 36{\cdot}8$.

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It is found that this gradient does not vary appreciably with the temperature or expansion ratio, and that, if the particular gradient for $P = 76$, $\theta_1 = 283$, $v_2/v_1 = 1{\cdot}40$ is plotted ($S = 37{\cdot}7$), an error of less than 3% in the gradient is made for all temperatures between $\theta_1 = 10°$ C. and 20° C., and all expansion ratios from 1·25 to 1·50, by taking a gradient of $37{\cdot}7 \times P/76$ for pressures between $P = 20$ and $P = 76$ cm.

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