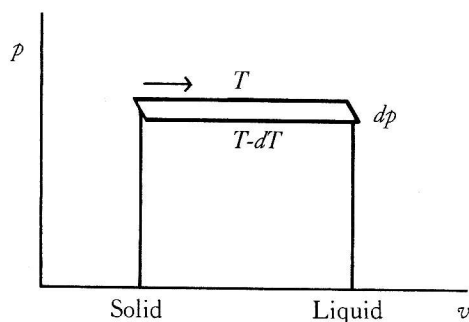


## Appendix 8

### The Influence of Pressure on the Melting Point of Ice

One of the earliest applications of thermodynamics, which goes back to Clapeyron and James Thomson, concerns the influence of pressure on the melting point of ice.

One can argue, going back to the original ideas of Carnot, as follows: Make a Carnot engine in which 1 gram of a solid at the melting point melts at temperature  $T$  and under pressure  $p$ . To melt the solid, we must supply the melting heat  $r$ ; the solid on melting changes volume, and the volume decreases from  $v_s$  to  $v_l$ , where  $v_s$  and  $v_l$  are the specific volumes of solid and liquid. The melting occurs isothermally. We now decrease the pressure adiabatically to  $p - dp$ , and correspondingly the temperature varies from  $T$  to  $T - dT$ . We then freeze the liquid again isothermally at this temperature, and close the cycle by returning adiabatically to the original conditions.



The heat supplied in the first melting, multiplied by the efficiency of the cycle (which according to Carnot is  $dT/T$ ) gives the work obtained. This work, according to the figure, is  $dp(v_s - v_l)$ . We thus have

$$\frac{dp}{dT} = \frac{1}{T} \frac{r}{v_l - v_s}.$$

This formula is called the Clapeyron formula. Note that the sign of  $dp/dT$  is the same as that of  $v_l - v_s$  for water, since ice floats on water,  $v_l - v_s$  is negative.

In the case of the melting of water,  $r = 79.71$  cal/g, which can be transformed to joules at the rate 4.184 joules = 1 cal. The specific volume of water is 1.00016; that of ice is 1.0905 in  $\text{cm}^3/\text{g}$ ; the melting temperature at atmospheric pressure is 273.16 K. Inserting these numbers in the equation, one obtains  $dp/dT = -1.351 \times 10^8$  dynes/cm, or  $-133.36$  atmospheres/degree. The melting point decreases at high pressure. In a glacier, the ice at the bottom melts under the pressure of the incumbent mass, and the glacier "flows."

As an example, we will derive Clapeyron's formula also by the standard procedure of expressing that  $dS$  is a perfect differential. First, what is a perfect differential? If we have an expression of the type

$$dz = A(x, y) dx + B(x, y) dy,$$

we say that it is a perfect differential if there is a function  $z(x, y)$  such that  $dz$  is the differential of such function. A necessary and sufficient condition for this to happen is that

$$\frac{\partial A(x, y)}{\partial y} = \frac{\partial B(x, y)}{\partial x}$$

When this condition is satisfied, it is also possible to integrate  $dz$  in the plane  $x, y$ , and the integral on a closed path is zero, from which it follows that the integral from a point  $P$  to a point  $Q$  does not depend on the integration path. The converse of the last property is also true.

All this may be immediately applied to thermodynamics. We may restate the second principle by asserting that there is a function  $S$  of the state such that  $dS = dQ/T$  is a perfect differential. Note that  $dQ$  is NOT a perfect differential.

In our specific case, we choose  $T$  and  $V$  as variables and write the first and second principles combined as

$$dS = \frac{dU + pdV}{T} = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] dV. \quad (1)$$

By the property of the total differentials

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial}{\partial V} \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial V} \right)_T + p \right] \quad (2)$$

and, executing the derivatives and simplifying, we obtain the general equation

$$\frac{1}{T} \left( \frac{\partial U}{\partial V} \right)_T - \left( \frac{\partial p}{\partial T} \right)_V + \frac{p}{T} = 0. \quad (3)$$

When a unit mass of ice melts at constant temperature, the heat supplied is

$$r = u_w - u_i + p(v_w - v_i).$$

The greatest part goes to the change of internal energy  $u_w - u_i$ ; the remainder goes to external work  $p(v_w - v_i)$ , where  $v_w - v_i$  is the change of volume accompanying the melting.

We thus have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{u_w - u_i}{v_w - v_i} = \frac{r - p(v_w - v_i)}{v_w - v_i}$$

which, introduced in the general equation (3), gives Clapeyron's result

$$\frac{r}{v_w - v_i} = T \frac{dp}{dT}.$$

## Appendix 9

### The Absolute Scale of Temperature and the Gas Thermometer

The first principle of thermodynamics says that for a gas

$$dQ = dU + pdV. \quad (1)$$

Gay-Lussac's experiment (expansion of a gas in a vacuum) contemplates a situation in which the external work vanishes because there is no pressure opposing the expansion when the gas expands in a vacuum. The experiment occurs in an isolated system to which no heat is supplied, and hence  $dQ = 0$ . The experiment shows that the temperature is not changed by the expansion.

Using  $V$  and  $T$  as variables, equation (1) gives

$$dQ = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + pdV = 0, \quad (2)$$

and since  $dT$  is by experiment zero (as are  $dQ$  and  $pdV$ ) we must have

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \quad (3)$$

This relation and the equation of state  $pV = RT$  define a perfect gas.

Using the general equation (3) of Appendix 8, which embodies the second principle of thermodynamics, we have that, at constant volume,

$$dp/p = dT/T. \quad (4)$$

On the other hand, in a conventional gas thermometer, the temperature  $\theta$  is defined by the equation of state, with  $\alpha$  constant:

$$pV = p_0 V_0 (1 + \alpha \theta) \quad (5)$$

$$\left(\frac{\partial U}{\partial V}\right)_\theta = 0. \quad (6)$$

At constant volume we have, from equation (5),

$$\frac{dp}{p} = \frac{d\theta}{1/\alpha + \theta}, \quad (7)$$

which, compared with the previous expression of  $dp/p$  from equation (4) yields

$$T = 1/\alpha + \theta$$

Thus, the gas thermometer gives absolute temperatures.

## Appendix 10

### Maxwell's Distribution of Velocities of Molecules in His Own Words

Maxwell read a paper at the meeting of the British Association of Aberdeen in September 1859. It was published in the *Philosophical Magazine* in 1860, and it contains the following heuristic argument on the velocity distribution.

"If a great many equal spherical particles were in motion in a perfectly elastic vessel, collisions would take place among the particles, and their velocities would be altered at every collision; so that after a certain time the *vis viva* will be divided among the particles according to some regular law, the average number of particles whose velocity lies between certain limits being ascertainable though the velocity of each particle changes at every collision.

Prop. IV. To find the average number of particles whose velocities lie between given limits, after a great number of collisions among a great number of equal particles.

Let  $N$  be the whole number of particles. Let  $x, y, z$  be the components of the velocity of each particle in three rectangular directions, and let the number of particles for which  $x$  lies between  $x$  and  $x + dx$ , be  $Nf(x)dx$ , where  $f(x)$  is a function of  $x$  to be determined.

The number of particles for which  $y$  lies between  $y$  and  $y + dy$  will be  $Nf(y)dy$ ; and the number for which  $z$  lies between  $z$  and  $z + dz$  will be  $Nf(z)dz$  where  $f$  always stands for the same function.

Now the existence of the velocity  $x$  does not in any way affect that of the velocities  $y$  or  $z$ , since these are all at right angles to each other and independent, so that the number of particles whose velocity lies between  $x$  and  $x + dx$ , and also between  $y$  and  $y + dy$ , and also between  $z$  and  $z + dz$ , is

$$Nf(x)f(y)f(z)dx dy dz.$$

If we suppose the  $N$  particles to start from the origin at the same instant, then this will be the number in the element of volume  $(dx dy dz)$  after unit of time, and the number referred to unit of volume will be

$$Nf(x)f(y)f(z).$$

But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$f(x)f(y)f(z) = \phi(x^2 + y^2 + z^2).$$

Solving this functional equation, we find

$$f(x) = Ce^{Ax^2}, \quad \phi(r^2) = C^3e^{Ar^2}.$$

If we make  $A$  positive, the number of particles will increase with the velocity, and we should find the whole number of particles infinite. We therefore make  $A$  negative and equal to  $-\frac{1}{\alpha^2}$ , so that the number between  $x$  and  $x + dx$  is

$$NCe^{-x^2/\alpha^2}dx.$$

Integrating from  $x = -\infty$  to  $x = +\infty$ , we find the whole number of particles,

$$NC\sqrt{\pi}\alpha = N, \therefore C = \frac{1}{\alpha\sqrt{\pi}},$$

$f(x)$  is therefore

$$\frac{1}{\alpha\sqrt{\pi}} e^{-x^2/\alpha^2}$$

Whence we may draw the following conclusions:—

1st. The number of particles whose velocity, resolved in a certain direction, lies between  $x$  and  $x + dx$  is

$$N \frac{1}{\alpha\sqrt{\pi}} e^{-x^2/\alpha^2} dx \quad (1)$$

2nd. The number whose actual velocity lies between  $v$  and  $v + dv$  is

$$N \frac{4}{\alpha^3\sqrt{\pi}} v^2 e^{-v^2/\alpha^2} dv \quad (2)$$

3rd. To find the mean value of  $v$ , add the velocities of all the particles together and divide by the number of particles; the result is

$$\text{mean velocity} = \frac{2\alpha}{\sqrt{\pi}} \quad (3)$$

4th. To find the mean value of  $v^2$ , add all the values together and divide by  $N$ ,

$$\text{mean value of } v^2 = \frac{3}{2}\alpha^2. \quad (4)$$

This is greater than the square of the mean velocity, as it ought to be."

## Appendix 11

### Boltzmann's Epitaph

Forgetting all the reservations and difficulties besetting the definition of  $W$ , the probability of a state, we can show an interesting feature of the relation between probability and entropy, assuming that there is a functional relation,

$$S = f(W). \quad (1)$$

Consider two separate independent systems having entropies  $S_1$  and  $S_2$  and probabilities  $W_1$  and  $W_2$ .

Combining the two systems, the entropies add. The composite system has the entropy

$$S = S_1 + S_2. \quad (2)$$

On the other hand, the probability is the product of the probabilities  $W_1, W_2$ .

The function  $S$  of equation (1) thus has the property that

$$f(W_1) + f(W_2) = f(W_1 W_2), \quad (3)$$

which is satisfied by

$$f(W) = k \log W$$

with  $k$  constant.

We thus have Boltzmann's epitaph,

$$S = k \log W.$$

## The Essentials of Boltzmann's H-theorem

Let  $f(\mathbf{r}, \mathbf{v}, t)d\mathbf{r}d\mathbf{v}$  be the probability that at time  $t$  a monatomic molecule is contained in a space volume-element and a velocity volume-element around  $\mathbf{r}$  and  $\mathbf{v}$  in a six-dimensional representative space. The distribution function changes in time for two reasons. First, the motion of the particles, apart from collisions, produces a flow in six-dimensional space  $\left(\frac{\partial f}{\partial t}\right)_{\text{flow}}$ . From analytical mechanics, using Liouville's theorem, one obtains for this, in the absence of forces,  $-\mathbf{v} \cdot \text{grad}_{\mathbf{r}}f$ , to which one adds a term due to possible potential fields  $-\mathbf{a} \cdot \text{grad}_{\mathbf{v}}f$ . The other cause of change is collisions, and one has the term  $\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}$ . Collisions can throw out of the volume element certain molecules as well as bringing in others, taking them from all the six-dimensional space.

In the first case  $f(\mathbf{v}, \mathbf{r}, t)$  decreases because a molecule of velocity  $\mathbf{v}$  collides with one of velocity  $\mathbf{v}_1$ , and after the collision the two molecules have velocities  $\mathbf{v}'$  and  $\mathbf{v}'_1$ . In the second case, in which  $f(\mathbf{v}, \mathbf{r}, t)$  increases, the molecules colliding have before the collision velocities  $\mathbf{v}'$  and  $\mathbf{v}'_1$ , and after the collision velocities  $\mathbf{v}$  and  $\mathbf{v}_1$ . The frequency of collisions of the first kind is proportional to  $ff_1$ , and the frequency of collisions of the second kind is proportional to  $f'_1f'$ . Here and in the integral of equation (1),  $f'_1$  stands for  $f(\mathbf{v}'_1, \mathbf{r}, t)$ , etc.

The collisional term was calculated by Boltzmann and is the integral in equation (1), which is the famous Boltzmann transport equation

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \text{grad}_{\mathbf{r}}f + \mathbf{a} \cdot \text{grad}_{\mathbf{v}}f = \int d\mathbf{v}_1 \int d\Omega g I(g, \theta) [f'_1f' - ff_1]. \quad (1)$$

Here  $\mathbf{a}$  is the acceleration due to an outside potential  $U(\mathbf{r})$  that may be present. Clearly, for a molecule of mass  $m$ ,  $\mathbf{a} = -\text{grad}_{\mathbf{r}}U/m$ . The indexes on grad denote on which variables one has to take the derivatives.

In the integral,  $g$  is the magnitude of the relative velocity of the colliding molecules, before the collision;  $I(g, \theta)$  is the appropriate differential collision cross section for collisions producing a deflection  $\theta$  and for which the final velocity is contained in the solid angle element  $d\Omega$ .

Boltzmann proved that, for a general  $U(\mathbf{r})$ , any initial distribution  $f(\mathbf{r}, \mathbf{v}, 0)$  will in time change to the stationary Maxwell-Boltzmann distribution, which is time-independent

$$f(\mathbf{r}, \mathbf{v}) = Ae^{-\beta[mv^2/2 + U(\mathbf{r})]}, \quad (2)$$

where  $A$  is determined by the total number of molecules that normalize the function and  $\beta = 1/kT$ . The last equation determining  $\beta$  is obtained by considering the total energy.

Boltzmann's proof proceeds by showing that there is a positive quantity  $H$ , which under the influence of the collisions decreases or is stationary

$$\frac{dH}{dt} \leq 0. \quad (3)$$

This famous quantity  $H$ , for which the theorem is named, is

$$H(t) = \int d\mathbf{r} \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \log f(\mathbf{r}, \mathbf{v}, t). \quad (4)$$

Ultimately,  $H$  will be identified with the entropy, with its sign changed, except for an arbitrary constant; thus, the decrease of  $H$  is the increase of entropy brought about by the collisions.

Boltzmann proved that  $H$  is constant only if for all collisions

$$ff_1 = f'_1f'. \quad (5)$$

The stationary state by virtue of equation (1) also satisfies the equation

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \text{grad}_{\mathbf{r}}f + \mathbf{a} \cdot \text{grad}_{\mathbf{v}}f = 0$$

Equations (1) and (3) determine the Maxwell-Boltzmann distribution for normal cases.

Boltzmann's equation (1) has been studied incessantly since it was formulated in 1872, and it even has practical applications, for instance, to isotope separation. On its centennial, a conference in Vienna was devoted to a review of its status and its consequences. The proceedings of this conference are an eloquent testimonial to the vitality of Boltzmann's equation.

## Dilemmas Posed by the Equipartition of Energy

Here is a sample of the paradoxes connected with the equipartition of energy. Consider a perfect gas, either monatomic or polyatomic. Thermodynamics give for the molar heat at constant volume  $C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$  and for the molar heat at constant pressure  $C_p = \left(\frac{dQ}{dT}\right)_p = \left(\frac{dU}{dT}\right)_V + p \left(\frac{dV}{dT}\right)_p$ . The last term, because of the equation of state, is  $R$ . Hence

$$C_p - C_V = R. \quad (1)$$

If molecules have  $n$  degrees of freedom, the equipartition theorem requires

$$C_V = nR/2$$

and because of equation (1)

$$C_p/C_V = (n + 2)/n$$

The ratio  $C_p/C_V$  can be accurately measured, for instance, from the velocity of sound.

For a monatomic gas, assume 3 degrees of freedom per atom, corresponding to the motion of a material point; one has  $C_p/C_V = \frac{5}{2} = 1.667$ . Experiments on noble gases support this result. The question may be raised, however, about the degrees of freedom corresponding to the electronic motions in the atom. This difficulty could not be answered by classical physics. Furthermore we may assume that a diatomic molecule is similar to a rigid body shaped like a dumbbell. It then has 6 degrees of freedom, and  $C_p/C_V$  should have the value  $\frac{8}{5} = 1.3333$ . Experiment shows that  $C_p/C_V = \frac{7}{5} = 1.40$ . For a dumbbell model, we can not deny the 3 degrees of freedom corresponding to the coordinates of the center of mass, nor the 2 coordinates that orient the dumbbell in space. More questionable may appear the sixth degree of freedom, corresponding to the rotation along the line connecting the two atoms forming the dumbbell molecule. Classically, it should certainly be counted, but in fact it is hidden, frozen, as the internal degrees of freedom in the atoms. The reason is to be found in quantum theory.

## The Marvelous Equation of van der Waals and Clausius' Virial Theorem

The equation of van der Waals for  $N$  molecules of a real substance is

$$\left(p + \frac{aN^2}{v^2}\right)(v - bN) = NkT \quad (1)$$

and may be inferred qualitatively starting from the perfect gas equation

$$pv = NkT \quad (2)$$

by remarking that the volume accessible to the molecules is not  $v$ , but is diminished by the volume occupied by the molecules themselves when they are in contact,  $Nb$ . Furthermore, to the pressure exerted by the walls of the gas container we must add a pressure due to attractive forces that may exist between the molecules. This additional pressure is proportional to  $N^2/v^2$  because we may think of it as due to the force acting on a thin surface layer of the gas exerted by the molecules of the bulk of the gas and not counterbalanced on the side of the wall. The number of molecules in the surface layer is proportional to  $N/v$ , and the number of attracting molecules is also proportional to  $N/v$ ; hence the additional pressure is  $aN^2/v^2$ .

We may improve this crude qualitative argument using a theorem of Clausius (1870), called the virial theorem.

Given  $N$  material points of mass  $m$ , we call the virial of the system the quantity

$$V = -\frac{1}{2} \sum m_i \mathbf{r}_i \cdot \mathbf{F}_i, \quad (3)$$

where  $\mathbf{F}_i$  is the force acting on the point  $i$  of coordinates  $\mathbf{r}_i$ . Using the equation  $\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i$  and the identity

$$\ddot{\mathbf{r}} \cdot \mathbf{r} = \frac{d}{dt} \dot{\mathbf{r}} \cdot \mathbf{r} - \dot{\mathbf{r}}^2,$$



we obtain

$$V = -\frac{1}{2} \frac{d}{dt} \sum m_i \dot{\mathbf{r}}_i \cdot \mathbf{r}_i + \frac{1}{2} \sum m_i \dot{\mathbf{r}}_i^2.$$

By taking the time average of the virial over a sufficiently long time  $\tau$  we have

$$\langle V \rangle = -\frac{1}{2\tau} \sum m_i \dot{\mathbf{r}}_i \cdot \mathbf{r}_i \Big|_0^\tau + \frac{1}{2} \left\langle \sum m_i \dot{\mathbf{r}}_i^2 \right\rangle$$

The first right hand term vanishes because the difference between the initial and final values of  $\sum m_i \dot{\mathbf{r}}_i \cdot \mathbf{r}_i$  stays finite, while  $\tau$  increases indefinitely. We obtain thus the "virial theorem":

$$\langle V \rangle = \langle E_{\text{kin}} \rangle = \frac{3}{2} NkT \quad (4)$$

the last equality is due to the equipartition theorem.

We apply the virial theorem to a gas confined to a cube of side  $L$  contained in the first octant of a coordinate system, with sides on the axes and a corner in the origin of the coordinates. In the computation of the virial, it is convenient to distinguish the part due to exterior forces  $V_e$  and the part due to intermolecular forces  $V_i$ . The virial is the sum of the two. We calculate first  $V_e$ . The exterior forces give the pressure on the wall. For the walls perpendicular to the  $x$  axis, we have, at abscissa  $L$ ,  $\sum F_i L = -pL^3$ , while the wall containing the origin does not contribute to the virial because  $x = 0$ . Extending this argument to all walls and summing the results, we have

$$\langle V_e \rangle = \frac{3}{2} pL^3 = \frac{3}{2} pV \quad (5)$$

where  $V$  is the gas volume.

From equations (4) and (5) we thus have

$$\frac{3}{2} NkT = \frac{3}{2} pV + \langle V_i \rangle. \quad (6)$$

If there are no intermolecular forces,  $\langle V_i \rangle = 0$ , and we obtain the perfect gas equation.

We give now the outline of an evaluation of  $\langle V_i \rangle$  based on a plausible model, leading to van der Waals's equation. We assume that the force between molecules contains a short-range strongly repulsive zone due to a hard core and a long-range attractive zone where the force varies as  $r^{-n}$  with  $n$ , in practice, near 6.

Consequently, it is expedient to divide  $V_i$  into  $V_{ic}$  due to the hard core and  $V_{ia}$  due to the attractive force.

To evaluate the part of the virial due to the hard core, we consider the change of momentum due to the collisions. The corresponding short-range and short-dura-

tion forces contribute to the virial when the centers of the molecules are at a distance  $2r_0$  and are applied with the frequency at which the collisions occur. A calculation gives as final result

$$\langle V_{ic} \rangle = -4\left(\frac{4}{3}\pi r_0^3 N\right)p = -\frac{2}{3}pbN \quad (7)$$

where  $b$ , sometimes called the covolume, is 4 times the volume occupied by the molecules (this is the van der Waals constant  $b$ ).

The contribution to the virial made by the long-range attractive forces  $f(r)$  is for each pair of molecules with their centers at distance  $> 2r_0$ ,  $-f(r) \cdot r$ . Multiplying this quantity by the number of such pairs  $4\pi r^2 dr \cdot (N/v) \cdot \frac{1}{2}N$  and integrating,

$$V_{ia} = 2\pi \frac{N^2}{v} \int_{2r_0}^{\infty} f(r)r^3 dr \quad (8)$$

Using now equations (6), (7), and (8), we have

$$NkT = pV - pbN + \frac{N^2}{v} \frac{2\pi}{3} \int_{2r_0}^{\infty} f(r)r^3 dr \quad (9)$$

Calling

$$a = \frac{2\pi}{3} \int_{2r_0}^{\infty} f(r)r^3 dr$$

and neglecting small terms containing  $ab$ , equation (9) can be rewritten in the van der Waals form:

$$NkT = (v - bN) \left( p + \frac{aN^2}{v^2} \right)$$

For instance, for  $\text{CO}_2$ , using as units atmospheres, liters, and degrees Kelvin and referring to one mole  $N = 6.022 \cdot 10^{23}$ ;  $Nk = R = 0.08206$ ;  $N^2 a = 3.592$ ;  $Nb = 0.04267$ .

For the zone in the  $pV$  plane in which liquid and gas coexist, van der Waals isotherms are replaced by horizontal straight lines corresponding to the pressure of the saturated vapor. These lines intercept the van der Waals isotherms at three points and form two loops with the same. Where are these horizontal lines to be located? Maxwell gave the criterion that the two loops must have the same area. His thermodynamical argument considers a cycle formed by the horizontal line and the van der Waals isothermal. If we follow this cycle, we go around the two loops, leaving one to the right and one to the left. The loops thus have opposite signs. Consider now the cycle mentioned above. It is completely isothermal; thus, it has efficiency zero, and no mechanical work can be performed. The mechanical work is given by the area of the cycle, which thus must be zero. Hence the two loops must have equal areas.