

The fundamental triple point of substances on the phase diagram: the secret becomes clear

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Abstract. This article analyzes the positions of the triple points of various elementary substances and simple compounds on the phase diagram. Pressures at triple points vary greatly — by 10–12 orders of magnitude for most substances, and in some cases, by 40 orders of magnitude! This enormous spread of values is attributed to the very strong, nearly exponential, dependence of the saturated vapor pressure on the reciprocal temperature near the sublimation and boiling lines. A good correlation has been established between the pressure at the triple point of a substance and the ratio of the temperature at the critical point to the temperature at the triple point. The relationship between the phase diagrams of substances and the position of the triple and critical points on them is examined, along with the effective interparticle interaction potential. The evaporation of solid objects in space conditions is discussed.

Keywords: phase diagrams, triple point, critical point

1. Introduction

The concept of the triple point of substances is commonly introduced at the very start of physics education. On the P , T -phase diagram, this is the point where three distinct phases of a substance are in thermodynamic equilibrium. For a one-component system, according to the Gibbs phase rule, three phases can coexist in equilibrium only at a specific pressure and temperature. It is a trivial consequence of two equations (the equality of the Gibbs free energies for different phases) in

two variables (temperature and pressure) having, in the general case, a single solution. For all the substances, with the exception of helium isotopes, there exists a triple point of crystal, liquid, and gas equilibrium on the phase diagrams (Fig. 1a). For many substances, the phase diagrams between different crystalline modifications are possible. In this case, the phase diagram will also exhibit triple points crystal 1–crystal 2–liquid or crystal 1–crystal 2–gas (Fig. 1c). There also exist a few examples of first-order phase transitions between different liquid phases. Then the phase diagrams also exhibit the triple points liquid 1–liquid 2–crystal (see Fig. 1d). In order to distinguish the triple point of equilibrium of the three states of matter (solid, liquid and gaseous) from triple points of other types, it is often referred to as the primary or fundamental triple point. Our paper will focus specifically on this point. The pressure at the triple point of most substances is lower than atmospheric pressure, and the phase diagrams are frequently depicted with no triple point whatsoever, starting instead from normal pressure. Meanwhile, the sublimation curve is absent, and the melting and boiling curves are spaced by temperature (Fig. 1e). That said, many may recall examples of substances for which the triple point is located at pressures above atmospheric pressure. One notable example is the famous ‘dry ice,’ a solid modification of carbon dioxide CO_2 . For this substance, upon heating at normal pressure, one observes sublimation instead of melting and boiling.

At first glance, the fundamental triple point of substances holds no interest for modern physics, retaining merely historical value. Notably, the triple point of water was used as the primary reference point for the Kelvin and Celsius temperature scales. For a number of substances, the triple point also serves as a fixed calibration point for thermometers. At present, the triple point lies outside the scope of interest in physics research. In this respect, it has not been as ‘fortunate’ as the critical point, which to this day remains an object of numerous studies. Research on the critical point, at which the boiling line terminates, has indeed led to the emergence of a large number of new concepts in the physics

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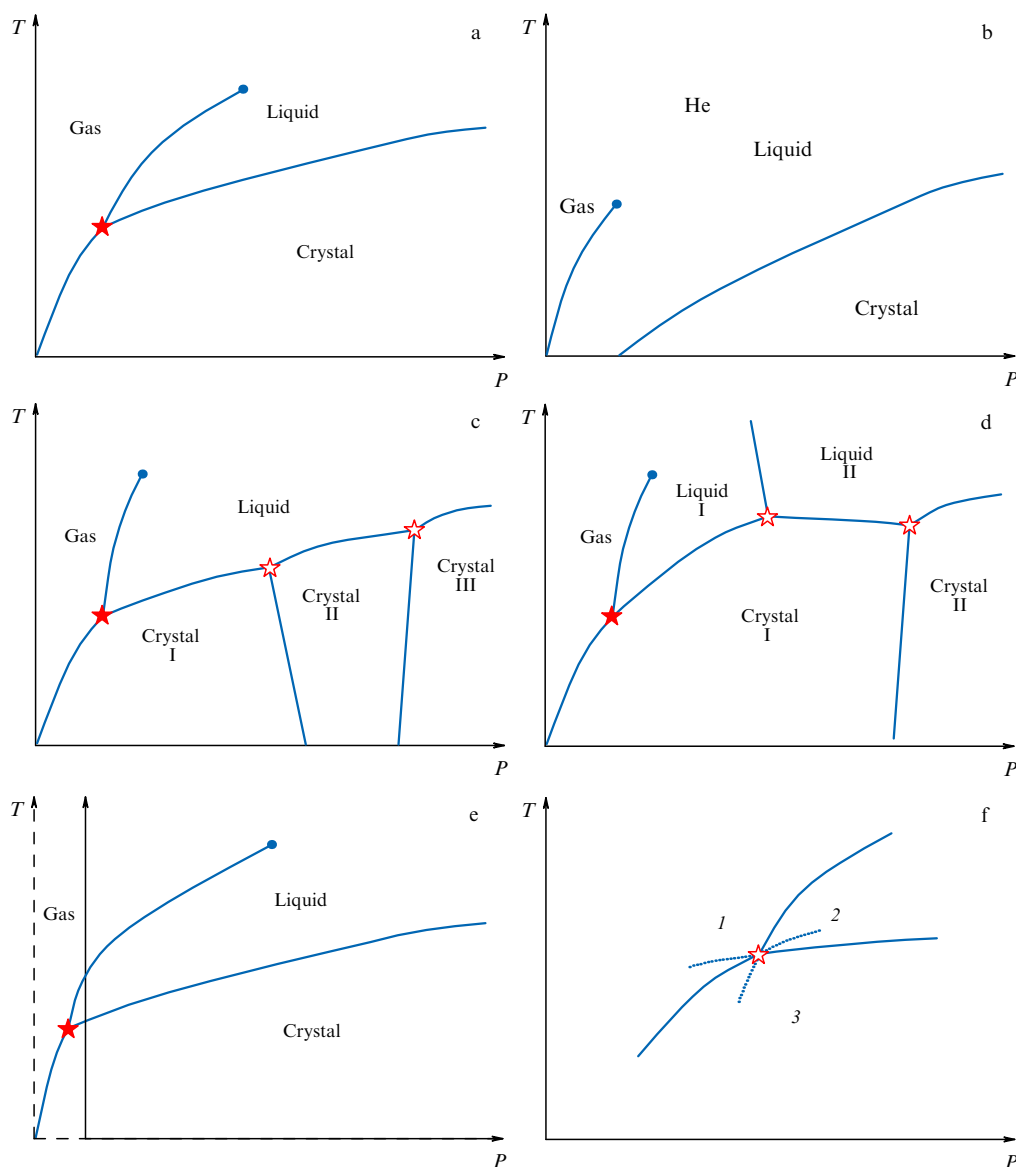


Figure 1. Generalized P , T —phase diagrams of substances. Standard phase diagram (a); phase diagram of helium (b); phase diagram of a substance with first-order phase transitions in a solid state (c); phase diagram of a substance with first-order phase transitions in solid and liquid states (d); phase diagram of a substance, where atmospheric pressure is taken as the initial pressure (e); an illustration of the junction rule on a phase diagram near the triple point with the possibility of extending the equilibrium lines beyond the triple point into the metastable region (f). The triple points are shown by asterisks: fundamental triple points by solid ones, and the rest by open ones. The critical points on the liquid–gas curve are shown by a solid circle.

of phase transitions, such as critical phenomena, critical anomalies, critical exponents, etc. As for the triple point, only one paper on the junction rules for triple points has been published in *Physics–Uspekhi* recently [1]. The rule states that the formal continuation of the equilibrium line between any two phases beyond the triple point must extend into the stability region of the third phase (Fig. 1f). The junction rule can readily be proven from the fact that, in first-order phase transitions, the metastable existence of a phase beyond the equilibrium line within the stability region of another modification is always possible.

The slope of the melting lines of substances on the phase diagram is $0.001\text{--}0.1\text{ K bar}^{-1}$ ($1\text{ bar} = 10^5\text{ Pa} = 0.987\text{ phys. atm.}$); consequently, the temperature at the triple point of most substances is close to their melting temperature at normal pressure. The melting temperatures of various substances differ by 2–3 orders of magnitude, similarly to the temperatures of the critical points. These temperatures

correlate reasonably well with the effective interparticle interaction energy or cohesive energy (energy of cohesion) of different classes of substances [2]. At the same time, the pressure at the triple points of different substances varies by many orders of magnitude. What are the factors that determine the pressure at the fundamental triple point of substance? It is to this question that this paper is devoted.

2. Triple-point pressure: nonstop surprises

Figure 2 illustrates the position of the triple points of several elementary substances and simple compounds. It should be noted that, for certain substances, the data on the pressure at the triple point may differ by a factor of several, according to various sources. The first point that stands out is the vast spread of the positions of the triple points with respect to pressure—by no less than 12 orders of magnitude, from 10^{-5} Pa to 10^7 Pa (as will be shown below, the pressure

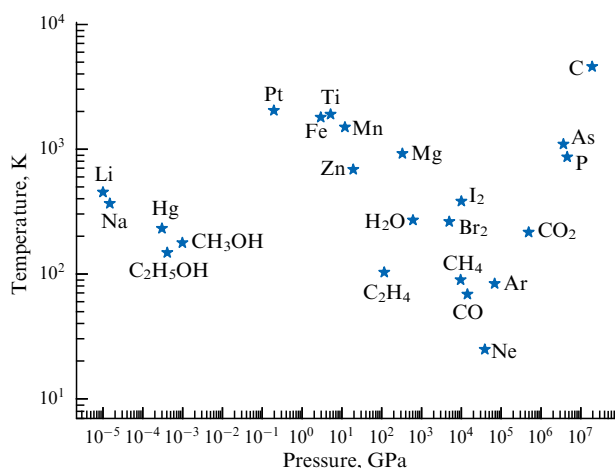


Figure 2. Coordinates of the triple points of different substances on a phase diagram. Temperature and pressure are shown on logarithmic scales. The data were collected from a number of reference books [3].

difference is far greater)! The second surprising observation is the absence of any noticeable correlation with the cohesive energy and the type of interparticle interaction. For example, the triple points of carbon, arsenic and red phosphorus are located at pressures tens and hundreds of times higher than atmospheric pressure, whereas the triple points of sodium and lithium are 10 orders of magnitude below atmospheric pressure. The triple point of methane corresponds to a pressure of 0.1 atm, and that of methanol, to 10^{-8} atm. Bromine and mercury are the only elementary substances that are in the liquid state under normal conditions; yet, the pressure at the triple points of these substances differs by more than 7 orders of magnitude. The pressure at the triple point of CO_2 is 7 orders of magnitude higher than that of platinum. Noble gases with extremely weak van der Waals chemical interaction exhibit triple points at pressures close to atmospheric, and iron and titanium, at pressures 5 orders of magnitude lower. Adding data on other elementary substances and compounds will merely broaden and densely fill this 12-order-of-magnitude interval of values. Yet this offers no elucidation of the overall picture. For example, the triple point of indium chloride is located at a pressure exceeding atmospheric pressure by a factor of 10, and the triple point of zinc chloride, at a pressure 5 orders of magnitude below atmospheric. Most metal oxides have triple points corresponding to pressures several orders of magnitude lower than atmospheric pressure, whereas rhenium oxide has a triple point at a pressure exceeding atmospheric by a factor of 25. At first glance, it is difficult to discern any system in the positions of the triple points of different substances; except, perhaps, one can detect that most metals have low values of pressure at the triple points—though there are some exceptions. Curiously, this issue has not been discussed in the literature previously (to the best of author's knowledge). As we show further below, the picture only appears to be tangled. We shall attempt to unravel this 'enigmatic' behavior of triple points.

3. Pressure near the sublimation and boiling curves

As stated earlier, at the triple point the equality of the Gibbs chemical potentials G must hold for all three states of matter

[4]. Let us recall that

$$G = E - TS + PV,$$

where E —energy (for condensed phases, it takes a negative value), T , S , P , V —temperature, entropy, pressure and volume, respectively. When considering the thermodynamic equilibrium between crystal and liquid near the triple point, we can neglect the contribution PV due to its small magnitude. The slight difference in binding energies of crystal and liquid upon melting is compensated by a small entropy jump. Thus, the consideration of the crystal-liquid equilibrium provides little information for determining the pressure at the triple point; it is far more informative to consider the equilibrium of the crystal and the liquid with the gas. We can also neglect the terms E and PV for the gas, since both terms are of the order of $k_B T$ per particle of the substance (k_B is the Boltzmann constant), which is substantially smaller in magnitude than the binding energy in condensed phases. As a result, on the equilibrium lines of crystal–gas (sublimation) and liquid–gas (boiling) an approximate equality of the binding energies of the crystal and the liquid with the $-TS$ term for the gas must hold. Entropy of the gas is expressed as $S = S_0 + a \ln T + b \ln V$ [4]. In the vicinity of the triple point, one can neglect the first two terms compared to the third one. Given that for gas $V \sim 1/P$, we immediately obtain the formula, familiar from school, for the pressure near the sublimation and boiling lines

$$P = P_0 \exp \left(-\frac{E}{k_B T} \right), \quad (1)$$

where E is the cohesive energy of the crystal or liquid, taken in absolute value, which is also the heat of sublimation or vaporization. This formula, as a purely empirical one, was first proposed for the vapor pressure of water by the German physicist Ernst Ferdinand August—the inventor of the psychrometer—exactly 200 years ago. August's formula for the pressure of saturated vapors is well known, and, in modern physics textbooks, it is derived from the Clausius–Clapeyron equation [4] $dT/dP = \Delta V/\Delta S$. For the equilibrium of a condensed phase with the gas $\Delta V \approx V_{\text{gas}} = k_B T/P$, $\Delta S = E/T$. After integrating the Clausius–Clapeyron equation, we immediately obtain expression (1). This comes as no surprise, since the Clausius–Clapeyron equation itself is derived by differentiating the equality of the Gibbs chemical potentials. Basically, we could very well start this chapter with this well-known formula without taking a needlessly round-about approach, but our aim was to elucidate the physics of thermodynamic equilibrium of condensed phases with the gas. The main contribution to the chemical potential of the gas is determined by its entropy, which depends logarithmically on the volume and, consequently, on the inverse proportion of pressure: $S = -\ln P + f(T)$, where $f(T)$ is a certain function of temperature, specific to each substance [4].

It should be noted that expression (1) is approximate, since P_0 and E terms can be temperature-dependent, and there are many versions of the modified August's equation. The first variants were proposed by the French engineer Charles Antoine as early as 1888, so the simplest version of this equation (expression (1)) is frequently referred to as the Antoine equation. Although expression (1) is well known, it is pertinent to present the temperature-pressure dependence in the T , P —plane (Fig. 3). The pressure remains exponentially

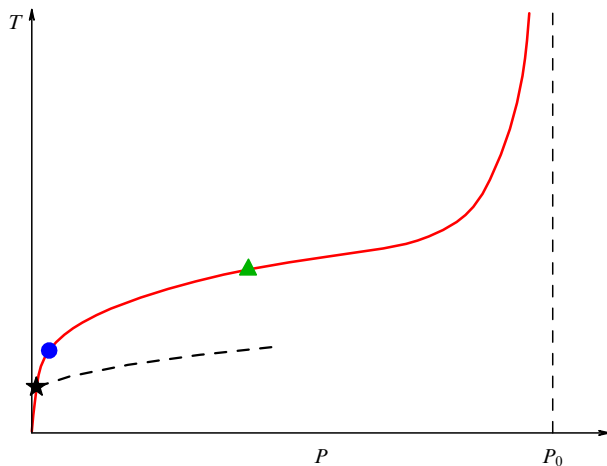


Figure 3. The dependence of temperature on the saturated vapor pressure in accordance with the August formula $P = P_0 \exp(-E/k_B T)$. The triple point, the critical point and the inflection point on the curve are shown by an asterisk, a circle, and a triangle, respectively. The melting line is shown schematically by a dashed line.

small at moderate temperatures. At unphysically high temperatures at $k_B T = E/2$ there is an inflection point on the curve. Finally, in the infinite-temperature limit, the pressure asymptotically tends to the value of P_0 . Naturally, the real sublimation and boiling curves terminate at considerably lower temperatures and pressures. The sublimation curve ends at the triple point, and the boiling one — at the critical point. The critical-point temperature of substances is lower than E/k_B by a factor of 4–7, i.e., the boiling curve does not reach the inflection point for any substance in Fig. 3. Correspondingly, the pressure at the critical point is 2–3 orders of magnitude lower than the pressure P_0 .

What is the physical significance of P_0 ? For the most part, this question remains open. This value is usually considered an empirical fitting parameter. However, for a monoatomic ideal gas, we can write down a precise expression for the Gibbs energy [4]

$$G = k_B T \ln \left[\frac{P}{(k_B T)^{5/2}} \left(\frac{2\pi\hbar^2}{M} \right)^{3/2} \right],$$

where M is an atomic mass, $\hbar$ is Planck's constant. Let us rewrite this expression as $G = -k_B T \ln(P_0/P)$, where

$$P_0 = k_B T \left(\frac{k_B T M}{2\pi\hbar^2} \right)^{3/2}. \quad (2)$$

This formula can be rewritten in the form of $P_0 = k_B T/V_0$, where $V_0 = (2\pi\hbar^2/k_B T M)^{3/2} = \lambda^3$, where λ is the thermal de Broglie wavelength. Hence, the value P_0 in the expression for the entropy of the gas is of a purely quantum nature. This is, effectively, the kinetic energy density of a gas atom (in reality, the atomic nucleus), which is considered a quantum object with a certain wavelength. For characteristic temperatures of 10^2 – 10^3 K and mass numbers of atoms or molecules ranging from 10 to 100, for the pressure P_0 we get the values of 10 GPa–10 TPa. These values are rather close in terms of order of magnitude to the characteristic values of the bulk moduli of condensed phases, i.e., to the density of the interparticle interaction energy. However, the proximity of these values is probably coincidental. Indeed, the characteristic values of $k_B T$ in gases are 2–3 orders of magnitude lower

than the interparticle interaction energy in condensed phases. Meanwhile, the de Broglie wavelength for gas particles at these temperatures is an order of magnitude smaller than the interparticle distances in condensed phases. This is attributed to the atomic or molecular mass being 4–5 orders of magnitude larger than the mass of the electron. As a result, the uncertainty in the momentum of gas particles is an order of magnitude higher than that for an electron in a condensed phase, while the uncertainty in the coordinate is an order of magnitude lower. Therefore, the proximity of the quantum density of the thermal energy of gas particles to the binding energy density in condensed phases is for the most part coincidental. The only thing that connects these values is that the genesis of both energy densities is linked to the Heisenberg uncertainty relation: for atoms in the first case, and for electrons in the second.

In this way, in quantitative terms the gas entropy is of quantum nature and is determined by the ‘granularity’ of space: the number of cells for gas particles is equal to the ratio of the volume per one gas particle to the volume of a cell whose linear size equals the de Broglie wavelength of the gas particle. Note that, at these temperatures, the de Broglie wavelength is smaller than both the interparticle distance and the sizes of the atoms and molecules themselves. There is nothing unusual about this: the wavelength is determined primarily by the mass of the atomic nucleus; therefore, the de Broglie wavelength pertains rather to the nucleus, whose size is many orders of magnitude smaller than the atomic size.

As follows from expression (2), the value P_0 depends quite strongly on the temperature, which is another indication of the approximate character of equation (1). At pressures close to P_0 , the gas entropy tends to zero, and at higher pressures it becomes negative — a clearly unphysical result. The same paradox occurs upon lowering the temperature. In both cases, this is due to the de Broglie wavelength becoming comparable to the interparticle distance, which renders particles indistinguishable and violates classical Boltzmann statistics.

In addition, the contribution of PV for the crystal or liquid at high pressures can no longer be neglected when comparing the Gibbs energies of different phases. Finally, at high temperatures, the term TS also cannot be disregarded for condensed phases. In any case, since, in practice, expression (1) is used only up to pressures of 0.001–0.01 P_0 , it should be considered rather empirical.

It is possible to estimate the value P_0 experimentally for both the sublimation curve and the boiling line. Figure 4a depicts experimental data for the saturated vapor pressure of different substances over a wide temperature range on both the sublimation and boiling curves. Extrapolation into the region of infinite temperatures formally gives the value P_0 . As the extrapolation data show, the value P_0 obtained in this way ranges from 7 GPa to 7 TPa for various substances, which, at first glance, is consistent with the estimates from expression (2). However, it should be noted that the estimates were made for the temperature range of 10^2 – 10^3 K, whereas the values of the pre-exponential factor in Figure 4 were obtained from the extrapolation to infinite temperatures.

Let us remind that expression (1) is approximate, since, in reality, the sublimation and vaporization energies depend on the temperature. This dependence is weak at low temperatures, but as the critical point is approached, it can become very significant; at the critical point itself, both the entropy jump and the volume jump vanish. And the further linear

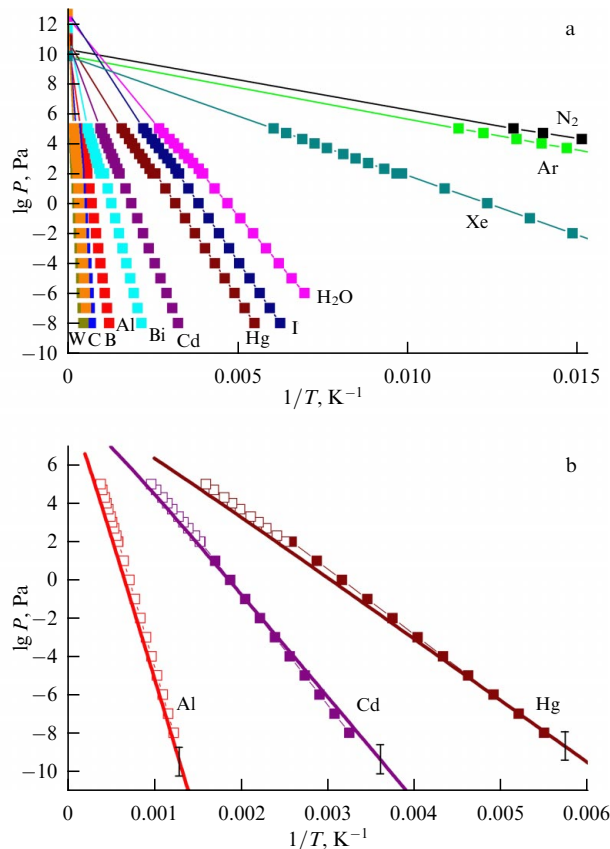


Figure 4. Experimental data for several substances on the saturated vapor pressure at different temperatures [5] (a). The saturated vapor pressure of elementary substances as a function of temperature, calculated within the framework of the ideal gas model and the Debye model, according to equation (3) (bold lines) in comparison to reference data [5] (symbols and thin lines) (b). Data on the heat of sublimation (the sum of the melting heat and the heat of vaporization), the Debye temperature and the heat capacity are taken from reference books. The possible error of the calculated curve due to the uncertainties of these data is shown. Values of E ; θ ; C_P/k_B are taken as follows: Hg—63 kJ mol⁻¹; 100 K; 3.2; Al—294 kJ mol⁻¹; 400 K; 3.3; Cd—106 kJ mol⁻¹; 200 K; 3.5.

extrapolation in Fig. 4 into the region of ultrahigh temperatures is entirely unjustified. Alternative estimates of pre-exponential factor can be obtained from the values of the heat of vaporization and the boiling temperatures of substances at normal pressure, for which reliable experimental data are available. In this case, the pressure of saturated vapor is 1 atm (10⁵ Pa), and from equation (1) one can directly estimate the value P_0 . These estimates for different substances are 1–2 orders of magnitude smaller than those obtained by extrapolation to ultrahigh temperatures in Fig. 4. Thus, the estimated value of P_0 for mercury is 10 GPa, for sodium — 3 GPa, for iron — 50 GPa, for water — 50 GPa.

As stated above, the value P_0 depends strongly on temperature, whereas the experimental dependences for the saturated vapor pressure are nearly linear in Fig. 4. The reason for this becomes clear, if one writes the condition of equality of the Gibbs energies more accurately without neglecting the term $-TS$ for condensed phases (one can still neglect the term PV , at least up to atmospheric pressure):

$$-k_B T \ln \left(\frac{P_0}{P} \right) = E - TS.$$

From this we obtain:

$$P = P_0 \exp \left(-\frac{E + TS}{k_B T} \right) = P_0 \exp \left(-\frac{E}{k_B T} \right) \exp \left(-\frac{S}{k_B} \right).$$

One can estimate the entropy of condensed phases from the temperature dependences of the heat capacity C_P :

$$S = \int \left(\frac{C_P}{T} \right) dT.$$

For the heat capacity in the Debye approximation, it is convenient to split this integral into two: from zero to the Debye temperature θ , and from the Debye temperature up to the required temperature T . The first integral, when integrating the heat capacity C_V , is identical for all substances and equals to 2.85. Since the heat capacity C_P is slightly greater than C_V , the first integral is close to 3.5. Above the Debye temperature, over a wide temperature range, the heat capacity remains almost constant (C_V is close to 3, C_P —from 3 to 4). Then the second integral is $\int (C_P/T) dT = C_P \ln(T/\theta)$. As a result, for the saturated vapor pressure we have

$$P = k_B^{5/2} \exp(-3.5) T^{(5/2 - C_P/k_B)} \theta^{C_P/k_B} \left(\frac{M}{2\pi\hbar^2} \right)^{3/2} \exp \left(-\frac{E}{k_B T} \right). \quad (3)$$

It is evident that the contribution of the entropy of the condensed phase $\exp(-S/k_B)$ largely compensated the strong temperature dependence of P_0 . The entropy jump ΔS does not enter expression (3) upon melting, since the heat of vaporization simultaneously decreases by the value ΔST , and the value $E - TS$ at the melting point does not change. Figure 4b presents the curves calculated from the formula (3) for mercury, cadmium, and aluminium, compared with the experimental reference data; we observe a good agreement. Note that the heat capacity of the melts (referred to the Boltzmann constant) at elevated pressures (where the interval between the melting temperature and the boiling temperature is rather large) drops upon heating, and the heat capacity can be close to 2.5 over a wide temperature range. At the same time, the pre-exponential factor in expression (3) ceases to depend on temperature entirely, and the August formula (1) becomes exact. In this case, the constant P_0 depends only on the atomic mass and the Debye temperature. For characteristic values of these parameters, for elementary substances with $M \approx 60$; $\theta \approx 300$ K (such values are exhibited, for instance, by copper) the pre-exponential factor $P_0 \exp(-S/k_B)$ equals to 100 GPa. In other words, in this case the pre-exponential factor is just the density of kinetic energy for gas particles, considered as the de Broglie quantum wave at the Debye temperature with a correction coefficient on the order of 0.03.

4. How to determine pressure at the triple point?

The strong exponential dependence of the pressure on the reciprocal temperature for the sublimation and boiling curves, discussed in the previous paragraph, clearly accounts for the wide range of pressures at the triple point for different substances. Moving upward (the increase of temperature) along the sublimation curve, the pressure at the triple point

will be lower the sooner this curve ‘meets’ the melting curve. Moving downward in temperature from the critical point along the boiling curve, the pressure at the triple point will be lower the ‘later’ the boiling curve ‘runs into’ the melting curve. From expression (1) for the pressure along the sublimation curve, we obtain the following for the pressure at the triple point

$$P_{\text{tr}} \approx P_0 \exp\left(-\frac{E}{k_B T_m}\right), \quad (4)$$

where P_{tr} is the pressure at the triple point, T_m is the melting temperature (which, in the pressure range under consideration, can be regarded as constant and equal to the temperature at the triple point). For most substances, one can use the melting temperature at normal pressure; for substances with a pressure at the triple point higher than atmospheric, one should use the triple-point temperature. For P_0 , we take the value of the order of 100 GPa.

As mentioned above, the critical-point temperature is lower than the E/k_B ratio by a factor of 4–7, and the pressure is 2–3 orders of magnitude lower than the pressure value P_0 . For a rough estimate, one can take the mean value from this interval ($E/k_B T \approx 5.5$; the pressure at the critical point is lower than P_0 by a factor of about 300). Then, for the pressure at the triple point, one easily obtains the following expression

$$P_{\text{tr}} \approx P_0 300^{-T_{\text{cr}}/T_m}, \quad (5)$$

where T_{cr} is the critical-point temperature. Both expressions (4) and (5) provide a good estimate of the pressure at the triple point with an error margin within 1–2 orders of magnitude. In particular, for the triple point of mercury, expression (4) gives the pressure of 10^{-4} Pa, whereas expression (5)— 10^{-5} Pa (the reference value is 3×10^{-4} Pa). For argon, expression (4) gives 10^3 Pa, expression (5)— 10^4 Pa (reference value is 6×10^4 Pa). For water, the corresponding values are 100 Pa, 10^4 Pa, and 600 Pa; for iron, 10 Pa, 0.1 Pa, and 3 Pa, etc. Therefore, the principal factors that determine the pressure at the triple point are the ratio of the heat of vaporization to the value $k_B T_m$, or the ratio of the critical-point temperature to the melting temperature. It turns out that, for different substances, these ratios vary by nearly an order of magnitude. It is the substantial variation of these ratios for different substances that leads to a very wide range of the pressure values at the triple point. At the same time, a difference of 1–3 orders of magnitude in the pre-exponential factor P_0 turns out to be less significant. Figure 5 presents the pressure values at the triple point as functions of the ratios $E/k_B T_m$ and T_{cr}/T_m ; both graphs show a good correlation. The T_{cr}/T_m ratio changes from 1.4–1.5 for As, P, CO_2 and C to 7–8 for Li, Na, and Hg; whereas the $E/k_B T_m$ ratio ranges from 4–6 to 30–40. It becomes clear that the high temperature values at the triple point for noble gases are explained by the low value of the ratio $T_{\text{cr}}/T_m = 1.8$ (it is precisely this ratio that occurs for a system of particles with the Lennard–Jones potential). Thus, the 12-order-of-magnitude scatter in pressure is explained by a variation of ‘only’ a factor of 5–6 in the ratio of the critical-point temperature to the melting temperature (and by the exponential dependence of the pressure on the reciprocal temperature). It turns out that the melting temperature of substances is not as directly

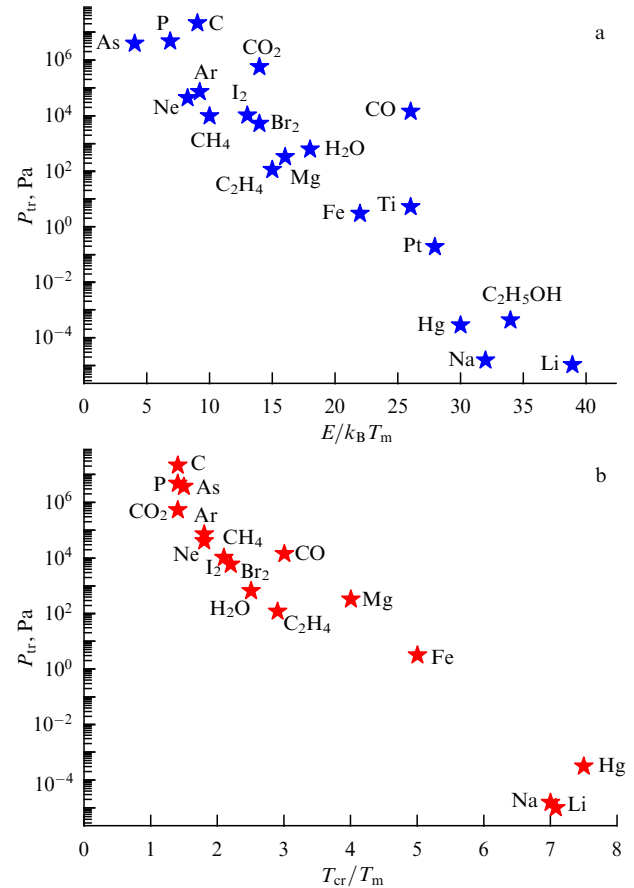


Figure 5. (a) The pressure at the triple point of several substances as a function of the ratio of the heat of vaporization E to the melting temperature ($k_B T_m$) of a given substance; (b) the pressure at the triple point P_{tr} of several substances as a function of the ratio of the critical-point temperature T_{cr} to the melting temperature T_m of a given substance.

linked to the cohesive energy, as the boiling and critical-point temperatures. We shall return to this question below. The good correlation between the pressure value at the triple point and the T_{cr}/T_m ratio, in principle, allows one to make a ‘reverse’ estimate: for those refractory substances whose triple-point parameters have been reliably measured, one can evaluate the critical-point temperature—something that is extremely difficult to achieve experimentally.*

5. A ‘curious case’ of gallium and the vaporization of spacecraft

Since it has become clear how to estimate the pressure at the triple point, one can make such estimates for the substances for which no experimental data on the parameters of the triple point are available. Among elementary substances, gallium exhibits the widest interval between the melting and boiling lines. For gallium, the melting temperature is 302 K, the boiling temperature (at normal pressure) is 2480 K, and the critical-point temperature is 4950 K. The heat of vaporization of gallium is rather high, around 270 kJ mol^{-1} . As a result, gallium exhibits record-high ratios of $T_{\text{cr}}/T_m \approx 16$; $E/k_B T_m \approx 105$! From expressions (4) and (5), the triple-point pressure values for gallium are 10^{-36} Pa and 10^{-30} Pa,

*The author is grateful to the reviewer for this valuable comment.

respectively. At first glance, these values are unrealistically low; however, for gallium, there are precision measurements of vapor pressure in the temperature range from 1230 K to 1518 K [6]. The authors of this paper proposed an equation (expression (8) in [6]) describing the dependence of the vapor pressure on temperature.

At the melting temperature, this expression gives a pressure value of 10^{-32} Pa, so the value interval of 10^{-30} – 10^{-36} Pa, which we obtained, appears to be absolutely correct. Thus, the scatter of the pressure values at the triple point for different substances amounts to at least 40 orders of magnitude, not 12, which represents one of the most extensive intervals for physical quantities. For example, a difference of 40 orders of magnitude is observed between the linear dimensions of the proton and the size of the entire Universe. The pressure at the triple point of gallium corresponds to roughly one atom per cubic kilometer. In other words, from an experimental standpoint, the sublimation curve for gallium does not exist, and the melting line starts essentially from zero pressure. Are there any substances for which the pressure at the triple point is even lower than that of gallium? In principle, this is not ruled out. Such a substance would need to have high cohesive energy and very low melting temperature at normal pressure. This may be observed for crystalline lattices, which have soft phonon modes along certain directions. For example, sodium and lithium exhibit melting temperatures close to room temperature in the megabar pressure range due to the enormous softening of the shear mode in the fcc lattice (see [7] and the references in this work). Perhaps something similar may be observed for certain compounds even at normal pressure. From a thermodynamic standpoint, a low melting temperature implies a small difference between the energies E for solid and liquid phases, and/or a significant entropy jump upon melting.

Once, at a conference, —Kourovka 2014— the author of this paper was asked a question: “If the generalized phase diagram of substances (Fig. 1a) is correct, then why do spacecraft not vaporize (sublimate) in space?” The answer was: “They do, but very slowly.” It satisfied the questioner; and the answer is obviously correct. However, in the context of this paper, it is interesting to estimate: just how slowly? Let us first evaluate how water ice sublimates in space. From expression (1) it follows that the pressure of the saturated water vapor at 100 K is 10^{-12} Pa, at 20 K — 10^{-110} Pa! The latter value corresponds to the concentration of a single water molecule per entire Universe (it is irrelevant whether one adopts 15 billion light-years, or 40 billion light-years, as the size of the Universe). Of course, this estimate is made merely for dramatic effect, since this ‘solitary’ molecule will never traverse the entire Universe, and no thermodynamic equilibrium will be established. At the same time, such estimates provide insight that the sublimation curves start from virtually zero pressures at sufficiently high temperatures. As a result, ice comets in space begin to vaporize noticeably only at temperatures higher than 150 K, passing by the Sun and other stars at relatively small distances. One can make the same estimates for spacecraft materials. For steels and for aluminium and titanium alloys, the “one atom per entire Universe” concentration will correspond to temperatures of 150–200 K, and experimentally noticeable vaporization can only occur at temperatures higher than 700–900 K. Thus, we need not worry about spacecraft — provided we do not send them directly into the Sun.

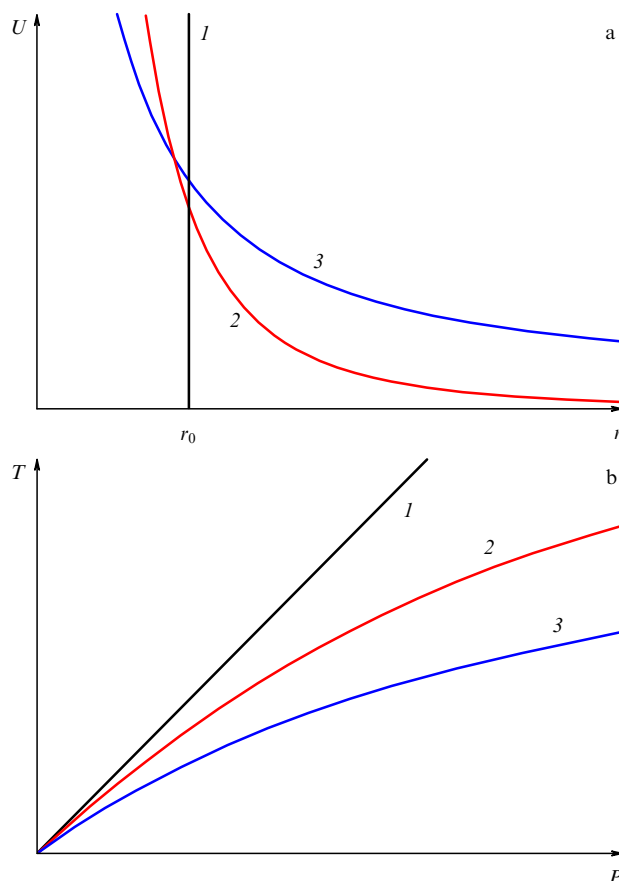


Figure 6. Hard-sphere and soft-sphere potentials (a) and the corresponding melting lines (b). The numeral 1 refers to hard spheres, while 2 and 3 refer to soft spheres, with 3 corresponding to the ‘softer’ one.

6. Interparticle interaction — a key to controlling the position of the triple point and the critical points

As mentioned above, most metals exhibit very low values of pressure at the triple point and, consequently, high values of the T_{cr}/T_m ratio. This allows one to suggest that the mutual positions and the spread in temperature between the melting and boiling lines can be determined by the type of the effective interparticle interaction. Let us discuss this point in more detail. One observes melting for the simplest interaction potentials, including systems of hard spheres and soft spheres (potential $U(r) = A/r^n$, where r is the interparticle distance, and n is the exponent $n > 3$). What is essential for melting is the availability of free volume for the movement of particles and the degree of ‘softness’ of the potential (in the case of a ‘soft’ potential, the spheres can ‘squeeze’ past one another more easily). The melting line for hard spheres system is a straight line, and the melting lines of ‘soft’ spheres are described by the equation $T_m \sim P^{n/(n+3)}$ [8] (Fig. 6). The ‘softer’ the potential, i.e., the smaller the value of the parameter n , the lower the melting line lies. The boiling lines are absent for systems with a purely repulsive potential. For the boiling line to appear on the phase diagram, an attractive branch of the potential is required. Meanwhile, for boiling, in contrast to melting, it is critically important that there exist an inflection point on the dependence of the interparticle potential on distance and a corresponding inflection point on the dependence of the interaction energy of particles on

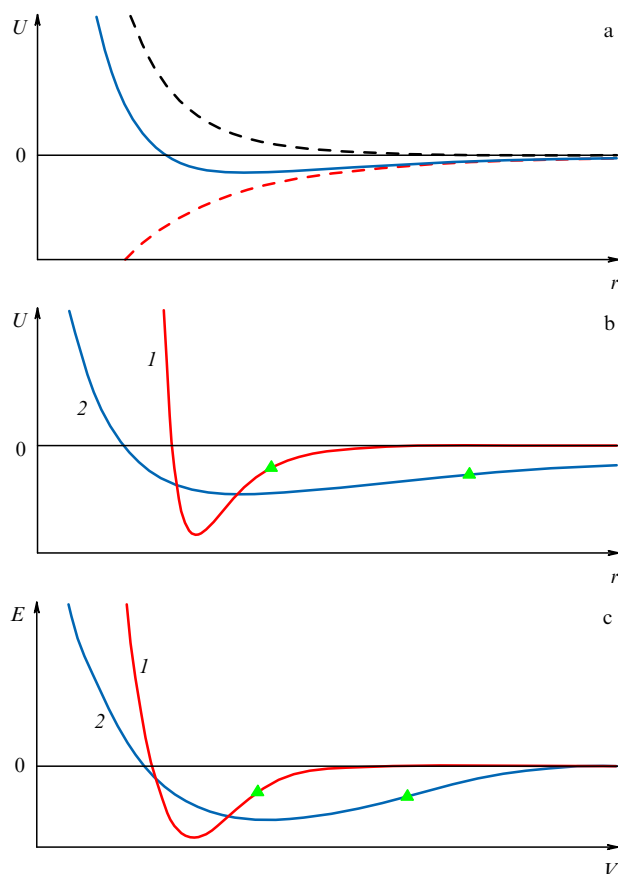


Figure 7. Schematic representation of interparticle interaction potentials with repulsive and attractive branches (a); effective pairwise interaction potentials with different degrees of ‘softness’ of the repulsive and attractive branches. 1—‘stiffer’ interaction potential; 2—‘softer’ interaction potential (b); dependences of the interparticle interaction energy on the volume, corresponding to these potentials (c). The positions of the inflection points are indicated by triangles on the corresponding curves.

volume [9] (Fig. 7b, c). The inflection point on the dependence of energy on volume (Fig. 7c) signifies the vanishing of the bulk modulus and the loss of thermodynamic stability of the expanded substance. This loss of stability (taking into account the contribution of temperature to the bulk modulus) corresponds to the spinodal line for the liquid–gas curve, which terminates at the critical point (Fig. 8a). It is apparent that the ‘softer’ the repulsive and attractive branches of the potential are, the greater the degree of stretching of the relative volume at zero temperature at which the instability will be reached, and the higher the temperatures and pressures at which the critical point will be located. At the same time, as mentioned above, a ‘softer’ potential leads to a lower melting temperature. As a result, ‘softer’ potentials of interparticle interaction result in a larger ‘gap’ between the melting and boiling lines (Fig. 8b). An increase in the degree of ‘hardness’ of both branches of the potential leads to a rise in the melting temperature, an increase in the pressure at the triple point, and a decrease in the temperature and pressure at the critical point. As a result, the boiling curve shortens and effectively rotates downward relative to the melting curve (Fig. 8b). In the limiting case of a very narrow well for interaction potentials (sometimes referred to as the ‘sticky’ sphere potential), the boiling curve falls below the melting curve (Fig. 8c). In this case, instability in the system sets in at a degree of expansion insufficient for melting, and a segment of the former boiling

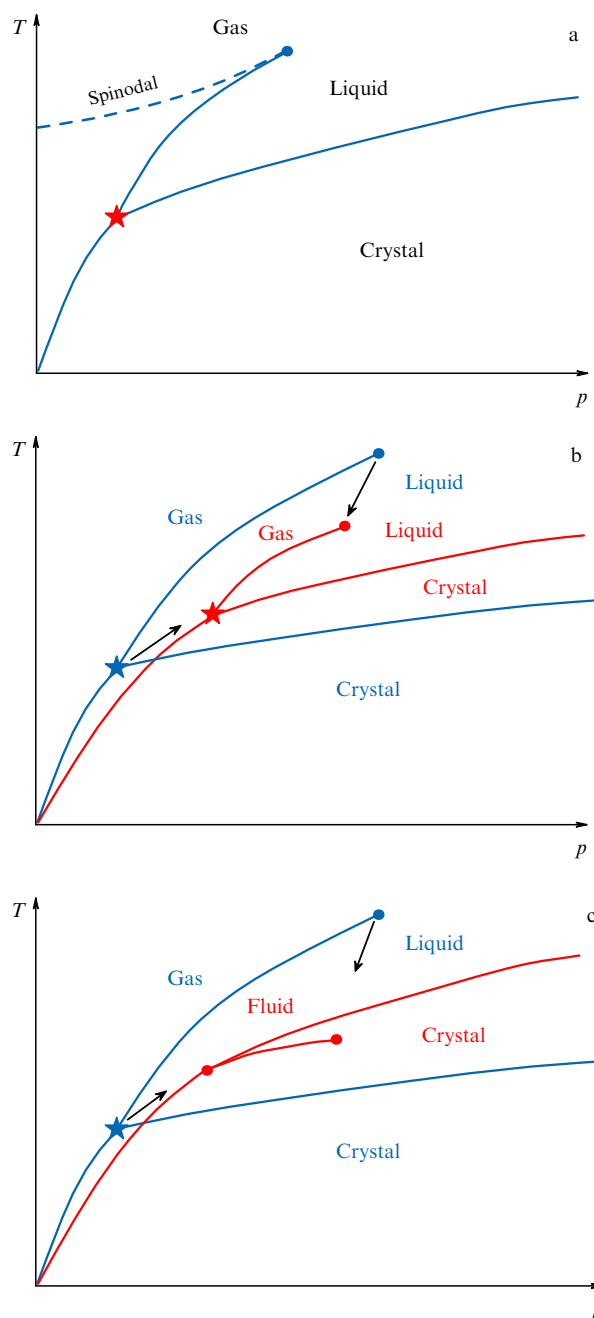


Figure 8. The spinodal curve for the liquid–gas transition on a phase diagram of a substance (dashed line) (a); the change in the phase diagram as a function of the effective width of the potential well; trends in the change of the positions of the triple and critical points with increasing ‘stiffness’ of the potential branches are indicated by arrows (b); the phase diagram of a substance with extremely narrow interaction potential (the ‘sticky’ sphere potential); the boiling line ‘slides’ under the melting line (c).

curve corresponds to a transition between two crystalline phases: from a ‘sticky’-sphere crystal to a hard-sphere one (a narrow ‘glue interlayer’ of the attractive part of the potential ‘ruptures’ earlier than melting occurs). For n, m -potential ($U(r) = A/r^n - B/r^m$), the ‘slide’ of the boiling line under the melting line occurs at values n and m that are unrealistically high for ordinary inorganic substances: $n > 20$; $m > 10$. However, such an effective interaction potential can only take place for macromolecular systems such as fullerites and colloidal crystals.

Based on the analysis presented above, one can immediately predict that, for most simple metals with relatively ‘soft’ effective interaction potential, the ‘gap’ between the boiling and melting curves will be wide, and the pressure at the triple point will be low. And, conversely, for noble gases with a relatively hard potential of the Lennard-Jones type ($n = 12$; $m = 6$), the T_{cr}/T_m ratio will be small, and the pressure at the triple point will be relatively high. In most real substances, the interparticle interaction potential, of course, is not pair or isotropic. Low values of the melting temperature may be caused, in particular, by the complex many-body character of the interaction, leading to the softening of certain phonon branches and/or shear rigidity in certain directions. Nevertheless, it is evidently the character of the interaction that determines the difference between the melting and boiling temperatures over the entire pressure range from the triple point to the critical point, and governs the pressure value at the triple point.

7. Conclusion

In summary, we have demonstrated that the enormous, 40-order-of-magnitude interval of pressures for the triple points of different substances is associated with two causes. First, with the extremely (close to exponential) high dependence of saturated vapor pressure on reciprocal temperature in the vicinity of the sublimation and boiling curves. Second cause is the significant difference for different substances (of an order of magnitude) of the ratio of the vaporization energy to the value of $k_B T_m$, and the ratio of the critical-point temperature to the melting temperature. The first factor is due to the logarithmic dependence of the gas entropy on the volume per particle. The second factor stems from the character of the effective interparticle interaction, in particular, the degree of ‘softness’ of interparticle potential.

One might consider these conclusions rather trivial. Nevertheless, there are questions that remain open. Although the formula for the saturated vapor pressure has already been known for 200 years, to this day the physical meaning of the pre-exponential factor P_0 in equation (1) remains not entirely clear. It has become evident that it is the density of kinetic energy of the gas particle, considered as a quantum wave, with a correction term related to the entropy of the condensed phase. It is well known that the ideal gas is a model system, which, when considered, frequently leads to unphysical results. In particular, at the pressure P_0 , the entropy of the ideal gas vanishes. Apparently, further analysis requires a rigorous examination of the entropy of real gases (fluids) over a wide pressure range. Another question that remains open is the existence of physical upper and lower limits on the pressure at the triple point. An upper limit does appear to exist: $P_{tr} < 0.01 P_0$ and numerically less than 100 MPa. As for a lower limit, no physical reasons have been identified yet.

The issues addressed in this paper may have been discussed previously by others; however, the author is not aware of this. In conclusion, it should be noted that searching for puzzles and surprises in simple and seemingly long-studied areas of physics, and contemplating these puzzles, frequently proves to be quite useful and brings researchers joy and pleasure.

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