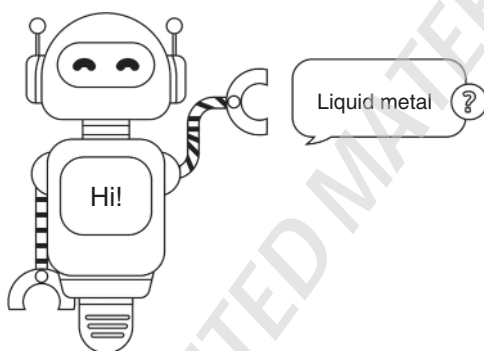


1

Introduction



The seeds of science are grown for the harvest of the people.
Source: Dmitri Mendeleev (1834–1907). Public Domain.

1.1 The Discovery and Development History of Liquid Metal

In the world of metals, the general “members” are solid. Generally, only when the metals are heated to a relatively high temperature, the metals will exhibit a red-dish liquid state. In fact, even if there are no severe high-temperature conditions, we can observe the flowing liquid metal. The most common liquid metal is mercury, which is found in the thermometers we use every day. In ancient China, mercury was also endowed with mysterious colors. Emperor Qin Shi Huang, the first emperor of China, built a model of a river infused with mercury in his tomb, representing his ruling power over the land and his expectation of immortality [1]. In Europe, it is well-known that the philosophy of alchemy laid the foundation for the principles and rules of modern chemistry, and mercury is the core of alchemy research. European alchemists believed that mercury is the main component of all metals and can be combined with other metals to become gold [2]. Although not as expected by ancient alchemists, mercury can indeed dissolve almost all metals to form a soft alloy, that is, amalgam, which is regarded as a metal solvent and has a

wide range of applications. Unlike mercury, which always appears in a liquid state in a general environment, the melting point of gallium is just around room temperature. We can easily switch the state of gallium between solid and liquid. For example, if we put gallium on the palm, we can observe its transition from solid to liquid (different from mercury). This may be the reason why people are fascinated by gallium.

As early as the nineteenth century, the special property of gallium became the subject of a classic prank among chemists. One popular trick is “a disappearing spoon.” Since gallium looks like aluminum and molds easily, is to fashion gallium spoons and serve the unsuspecting guests with tea. Upon stirring the tea, the gallium spoon melts rapidly. And watch your guests’ surprised looks when their tea “eats” their spoons [3]. More in practical, its low-melting point and high boiling point mean that gallium could exhibit metallic properties in the liquid phase across a range of useful, desirable, and accessible temperature.

Recently, scientists have played a new trick with gallium. They have written the smallest book in the world with the help of focused gallium ion beam. Teeny Ted from Turnip Town (2007), published by Robert Chaplin, is certified by Guinness World Records as the world’s smallest reproduction of a printed book. The book, costing an enormous \$15 000 (around £10 000), yet made is a 30 micro-tablet book carved on a pure crystalline silicon page by using a focused ion beam, is measured to be just 0.07 mm by 0.10 mm, according to Simon Fraser University. As we know, gallium is typically used as a liquid metal ion source for a focused ion beam. It is gallium as the liquid metal ion source used in the focused ion beam that created the smallest book in the world. The book even has its own ISBN reference, ISBN-978-1-894897-17-4, though the readers will require a scanning electron microscope to read the story of a turnip contest [4].

Liquid metals can bring us much more than that. In fact, they have become a part of our daily lives. Liquid metal may exist as a dental implant in our teeth, as fusible metal in automatic fire-fighting devices, or it could exist as a central processing unit (CPU) coolant in our computers. In the future, liquid metal could also be found in our foldable smartphones. Now, it’s time to enter the world of liquid metals and learn more about this fascinating substance.

1.1.1 A Vindication for Mendeleev’s Prediction

Gallium has only a short history. It was first discovered only a little over a 100 years ago. Particularly, gallium was the first chemical element in the history of chemistry that was predicted theoretically and then verified in nature in 1875.

The periodic table is undoubtedly the most commonly used tool in chemistry. In fact, it greatly facilitates scientific research and the memory and analysis of elements. Before Dmitri Mendeleev arranged the elements as the periodic tables that we are familiar with now in 1869, there were various periodic tables. However, in contrast to the previous scientists, Mendeleev’s method of dividing the elements is more concise and beautiful, which is widely recognized and has been used ever since. He reasoned that there should be an as-yet-undiscovered element. Based on the position of

the element in the table, he predicted some of their characteristics and properties. The main reason that Mendeleev's periodic table is so convincing may come from the fact that he initially left gaps in it to predict the existence of elements and then to be confirmed later.

As early as 1875, the French chemist Lecoq de Boisbaudran discovered gallium and successfully extracted and purified this new metal. The measured properties of this new element were surprisingly in agreement with Mendeleev's prediction and confirmed his placement of the eka-elements in the periodic table. At present, the industry of gallium production and purification technology has been highly mature, and the purity of gallium can reach 99.9999% [3, 5].

1.1.2 Gallium's Applications in the Semiconductor Industry

With the discovery of gallium arsenide (GaAs) compounds as semiconductor materials, in the early 1960s, gallium alloy began to attract the attention of various researchers. Perhaps alloying with various metals easily is the most crucial characteristic of gallium. And the low-melting point property of gallium can be conferred to the final gallium alloy, making the resulting material more easily workable, stable, and cost-effective. In the semiconductor industry, its alloying with other elements and phase transition properties are highly valuable. Thus, a lot of gallium applications are concentrated in the semiconductor industry. GaAs, as gallium's most common alloy and a new type of high-quality semiconductor, has launched a research boom, which is widely used in preamplifiers and high-speed logic chips in mobile phones, while AlGaAs and InGaAs are often applied as the light-emitting materials. Blue light-emitting diodes (LEDs) were successfully developed in the early 1990s, and the development of white LEDs also followed. Since then, a "lighting revolution" have begun. With gallium consumption soaring, coupled by commercial speculation, the price of gallium rose substantially. After nearly 20 years of development, white LED lighting technology has made great achievements. Compared with the traditional lighting technology, LED lighting technology has the advantages of high-efficiency, energy-saving, long life, green environmental protection, and high light efficiency, which has been supported by governments all over the world. At present, the research and production of GaAs have been mostly turned to the LED industry [3].

1.1.3 Tackling Fundamental Problems in Fuel in Energy Science

In addition to its contribution to the semiconductor field, gallium chemistry has also addressed many fundamental questions in energy science. Early studies have shown that the zeolite doped with gallium can effectively catalyze methylcyclohexane [6]. The ring is opened and broken to form short alkanes, which is used to recover gasoline pyrolysis products. Moreover, gallium zeolites can also catalyze the aromatization of *n*-decane [7]. Emerging studies have shown that GaN nanowires can even catalyze the formation of benzene from methane [8]. Breaking the C—H bond of methane is not easy, which will contribute to these processes mentioned above.

The relative inactive methane exhalations and undesired by-products of gasoline production can be converted into useful petrochemicals. These reactions are crucial for the conversion, which are of great significance for fine chemical production and fuel storage.

1.2 Liquid Metal Family

It is common knowledge that the existing form (solid, liquid, and gas) of all elements and chemical compounds rely on conditions of temperature and pressure. But when it comes to metal, the first thing we think about is bulky objects and high melting point. It is hard to believe that some metals exist in liquid form at room temperature. One of the most intriguing properties of gallium is its liquid state at room temperature. When you cut off a piece of solid gallium with a knife and put it in your hand for a closer look, an interesting thing happens: It melts and turns into a silvery drop that rolls around in your hand like a drop of water on a lotus leaf. The reason for this curious phenomenon is that the melting point of gallium is only 29.8 °C, below the human body temperature, so it will melt in the hand. In addition, although gallium's melting point is low, the boiling point can be as high as 2200 °C. In other words, from about 30 °C to about 2000 °C, gallium would remain in liquid state, while mercury would boil at 360 °C. Therefore, gallium can be used to make high-temperature thermometers that can measure temperatures below 1500 °C [3].

Herein, we define metals and alloys with melting point between room temperature and 300 °C as liquid metals. Single-component liquid metals are predominantly composed of post-transition metals (Ga, In, Tl, Sn, Pb, Al, and Bi), zinc-group metals (Zn, Cd, and Hg), and alkali metals (Li and Na). We note that alloys possess much lower melting point than the pure metal. For example, the melting point of eutectic gallium and indium alloy (EGaIn) is only 16 °C [9]. So there are much more liquid metal alloys. Tables 1.1 and 1.2 list the melting point of several liquid metals and alloys. To enrich the content of this book, we will also introduce some molten metals (such as copper, gold, etc.), which have similar properties compared to liquid metals [10] (Figure 1.1).

In recent decades, low-melting point liquid metals have been used in many different fields. Gallium base liquid metal at room temperature has unique surface properties and physicochemical properties. It can achieve a variety of morphological changes such as deformation, movement, separation, and fusion through a variety of energy fields such as electric, magnetic, and concentration gradient fields or surface modification. Liquid metals show a promising application in microfluidics, biomedicine, and robotics, and other fields.

At present, numerous studies devoted to liquid metals are dispersed and need to be unified. All the emerging applications in the fields of catalysis, synthesis, microfluidics, soft electronics, sensor, and therapy exploit the same phenomena that occur in liquids and at metal interfaces. Integrating these seemingly unrelated research directions into a single field of liquid metal is quite challenging. But it will facilitate the development of innovative applications that take full advantage of the unique properties of liquid metals and its alloys [10].

Table 1.1 Atomic number and melting point of liquid metals.

| Elements | Atomic number | Name (abb.) | Melting point (°C) |
|-------------|---------------|-------------|--------------------|
| Lithium | 3 | Li | 180.5 |
| Sodium | 11 | Na | 97.8 |
| Aluminum | 13 | Al | 660.3 |
| Cadmium | 48 | Cd | 321.1 |
| Mercury | 80 | Hg | -38.8 |
| Zinc | 30 | Zn | 419.5 |
| Gallium | 31 | Ga | 29.8 |
| Indium | 49 | In | 156.6 |
| Thallium | 81 | Tl | 304.0 |
| Tin (white) | 50 | Sn | 231.9 |
| Lead | 82 | Pb | 327.5 |
| Bismuth | 83 | Bi | 271.4 |

Table 1.2 The composition and melting point of several eutectic binary alloys, ternary alloys, quaternary alloys, and quinary alloys.

| Alloyed elements | Element A (at%) | Element B (at%) | Element C (at%) | Element D (at%) | Element E (at%) | Melting point (°C) |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|
| Ga/In(EGaIn) | 85.8 | 14.2 | 0 | 0 | 0 | 15.4 |
| Ga/Sn | 91.7 | 8.3 | 0 | 0 | 0 | 21.0 |
| Ga/Bi | 38.3 | 61.7 | 0 | 0 | 0 | 222.0 |
| In/Sn | 52.7 | 47.3 | 0 | 0 | 0 | 116.9 |
| In/Bi | 79.2 | 20.8 | 0 | 0 | 0 | 72.5 |
| Pb/Au | 84.6 | 15.4 | 0 | 0 | 0 | 215.0 |
| Sn/Tl | 56.6 | 43.4 | 0 | 0 | 0 | 170.2 |
| Ga/In/Sn (Galinstan) | 78.3 | 14.9 | 6.8 | 0 | 0 | 13.2 |
| In/Sn/Bi (Field's alloy) | 60.1 | 18.8 | 21.1 | 0 | 0 | 62.0 |
| Bi/Pb/Sn (Rose's alloy) | 43.1 | 23.5 | 33.4 | 0 | 0 | 95.0 |
| Bi/Pb/Sn/Cd (Wood's alloy) | 41.5 | 20.9 | 18.3 | 19.3 | 0 | 70.0 |
| Bi/Pb/Sn/Cd/In (French's alloy) | 31.5 | 17.1 | 14.4 | 11.7 | 25.3 | 46.9 |

