On the Tendency of Solutions to Tend Toward Ideal Solutions at High Temperatures

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The rule of Lupis and Elliott (LE rule) proposed for the first time in 1966 is reformulated in this article as, "Real solid, liquid and gaseous solutions (and pure gases) gradually approach the state of an ideal solution (perfect gas) as temperature increases at any fixed pressure and composition." This rule is rationalized through the heat expansion of phases and loss of any interaction with increased separation between the atoms. It is shown that the rule is valid only if the standard state is selected properly, *i.e.*, if mixing does not involve any hidden phase changes, such as melting. It is shown that the necessary and sufficient practical conditions to obey the LE rule is the equality of signs of the heat of mixing and excess entropy of mixing and the nonequality of signs of heat of mixing and excess heat capacity of mixing of the same solution. It is shown that these two conditions are fulfilled for most of the experimentally measured high-temperature solutions. The LE rule is compared with the existing laws of thermodynamics. It is shown that the LE rule can be considered as a potential fourth law of materials thermodynamics.

I. INTRODUCTION

LUPIS and Elliot started their 1-page note[1] with the phrase: "Quite generally an increase in the temperature tends to bring a system closer to ideality." In this article, this statement will be called for brevity as the Lupis-Elliott rule (LE rule). This statement was confirmed by showing that the heat of mixing and excess entropy of mixing of the same solution should have the same signs.[1,2] The latter statement has been discussed and confirmed both theoretically and experimentally in the number of papers.[3–12]

The current author derived his exponential equation for the temperature dependence of excess Gibbs energy of solution[13] from this principle. This equation was an answer to the problem raised in 2001 by Chen *et al.*[14] on the appearance of artificial inverted miscibility gaps in many calculated phase diagrams. This equation has been applied successfully to the thermodynamic optimization of the Zn-Zr,[15] Ru-Zr,[16] Ru-Ti,[17] Cr-Ge,[18] Mg-Si,[19] Al-Er,[20] Gd-Tl,[21] Mg-Zn, Mg-Nd, Mg-Zn-Nd,[22] Co-Gd,[23] and Zr-Si-N[24] systems. Neither high-temperature nor low-temperature artifacts appeared in these 12 fully optimized systems, despite the conclusion based on a simplified analysis[25] (for further discussion, see References 26–28). The successful application of the exponential equation for all the 12 systems studied so far is additional proof to the validity of the LE rule.

The goal of this article is to discuss the conditions of the validity of the statement by Lupis and Elliott[1] and to check their validity against up-to-date experimental data.

II. THE FORMULATION OF THE LE RULE

The LE rule is formulated in this article as: "Real solid, liquid and gaseous solutions (and pure gases) gradually approach the state of an ideal solution (perfect gas) as temperature increases at any fixed pressure and composition."

The LE rule is equally valid for gaseous, liquid, and solid solutions. However, that does not mean that solid, liquid, or gaseous solutions can exist at any high temperature. This only means that all solutions will follow the tendency described by the LE rule, and thus, the equations describing the temperature dependence of the excess properties of all solutions (solid, liquid or gas) should obey the LE rule. After a phase change (melting, boiling, *etc.*), the tendency predicted by the LE rule within a given solid or liquid solution phase will be interrupted, but the same tendency will start again in a newly formed phase.

Mathematically, the LE rule can be expressed through different excess thermodynamic quantities (for their definitions, see the Appendix[29–31]).

(a) From combining the LE rule with the definition of the ideal solutions, the activities of all components (a_i) in all real solutions approach the mole fraction of the same component (x_i) as temperature approaches infinity at any fixed pressure and composition

$$\lim_{T \to \infty} a_i = x_i \qquad [1]$$

(b) As follows from Eqs. [1] and [A5], the activity coefficients of all components in all solutions approach unity as temperature approaches infinity at any fixed pressure and composition

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$$\lim_{T \to \infty} \gamma_i = 1 \qquad [2]$$

(c) As follows from Eqs. [2], [A6], and [A13], the partial excess molar Gibbs energies of all components and thus also the integral excess molar Gibbs energy of the solution approach zero as temperature approaches infinity at any fixed pressure and composition

$$\lim_{T \to \infty} \Delta G_i^E = \lim_{T \to \infty} \Delta G^E = 0 \qquad [3]$$

(d) As follows from Eqs. [3] and [A7] through [A13], all derivatives of the partial and integral excess molar Gibbs energies approach zero as temperature approaches infinity at any fixed pressure and composition:

$$\lim_{T \to \infty} \Delta S_i^E = \lim_{T \to \infty} \Delta S^E = 0 \qquad [4]$$

$$\lim_{T \to \infty} \Delta H_i = \lim_{T \to \infty} \Delta H = 0 \qquad [5]$$

$$\lim_{T \to \infty} \Delta C_{p,i}^E = \lim_{T \to \infty} \Delta C_p^E = 0 \qquad [6]$$

$$\lim_{T \to \infty} \Delta V_i^E = \lim_{T \to \infty} \Delta V^E = 0 \qquad [7]$$

$$\lim_{T \to \infty} \Delta \beta_i^E = \lim_{T \to \infty} \Delta \beta^E = 0 \qquad [8]$$

$$\lim_{T \to \infty} \Delta \kappa_i^E = \lim_{T \to \infty} \Delta \kappa^E = 0 \qquad [9]$$

(e) As follows from the proposed postulate and the comparison of Eqs. [A14] and [A15], the compression factor will approach unity as temperature approaches infinity at any fixed pressure and gas composition

$$\lim_{T \to \infty} Z = 1 \qquad [10]$$

In the mathematical formulation of the LE rule, the mathematical limit of $T \to \infty$ is used. It obviously does not mean that solid or liquid solutions exist at that high temperature. It only means that all real solutions within their stable T-range tend to obey the LE rule.

III. THE RATIONALIZATION OF THE LE RULE

The LE rule can be rationalized in the following way. Any deviation from ideal behavior is caused by the special interactions among atoms, molecules, ions, *etc.* in the solutions. The special interaction means that

attraction and/or repulsion between the atoms, molecules, *etc.* is caused by a variety of known and unknown physical and chemical phenomena. As temperature increases at any fixed pressure and composition, the molar volumes (and thus the average distances between atoms and molecules) of all phases gradually increase*.

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*There are very few cases when molar volume of any solution (at fixed pressure and composition) does not gradually increase with temperature. In those rare cases, it takes place in a limited temperature range. In a wider temperature range, molar volume of all solutions increases with temperature.

Any type of physical or chemical interaction between atoms and molecules diminishes as the distance between the atoms and molecules increases. Thus, any kind of deviation from the ideal behavior will diminish as temperature increases at any fixed pressure.

This reasoning is most obvious for pure gases and gaseous mixtures, as the validity of Eq. [10] and that of the proposed postulate for gases follows from the equations of state ([A16] and [A17]).

IV. ON THE CHOICE OF THE STANDARD STATE

The validity of the LE rule is restricted in terms of selecting the standard state. The LE rule is valid only if the reference states of all the components are selected as pure components in the same state as that of the solution. This is because only in this case, "mixing" actually means mixing, without additional hidden phase changes, such as melting, *etc.* Thus, the LE rule is valid only for the process when 2 pure components of the same state dissolve each other to create a solution of the same state: $A(\Phi) + B(\Phi) = A\text{-}B(\Phi)$. This process is accompanied by the ideal and the excess Gibbs energies of mixing and for the latter the LE rule is valid.

However, the LE rule is not valid when mixing includes the hidden phase change, such as in the process: $A(\alpha) + B(\Phi) = A\text{-}B(\Phi)$. This process involves the hidden phase change $A(\alpha) = A(\Phi)$ in addition to the previously defined process of mixing $A(\Phi) + B(\Phi) = A\text{-}B(\Phi)$. As a result, the measured total excess Gibbs energy of mixing involves the Gibbs energy change of the process $A(\alpha) = A(\Phi)$ in a hidden way. As the Gibbs energy change of the phase change $A(\alpha) = A(\Phi)$ does not approach zero as T increases at any fixed pressure, the LE rule is not valid for the complex process $A(\alpha) + B(\Phi) = A\text{-}B(\Phi)$.

It should be recognized, at this point, that since the introduction of the concepts of an ideal solution, activity, and fugacity by Lewis[32] approximately 100 years ago, the LE rule remained hidden for many systems because reference states were selected in different ways as given previously. It was mostly done for convenience. For example, the convenient reference state of NaCl at room temperature in water solution is a solid crystal, *i.e.*, the excess properties of liquid H_2O-NaCl solutions are usually described in accordance to the

process: H_2O(liquid) + NaCl(solid) → H_2O-NaCl(liquid). Although it was "convenient," it was not scientific, as this process includes two subprocesses, melting and mixing. The LE rule is valid only for mixing; it is not valid for melting. Thus, the LE rule is not valid for the complex (melting + mixing) process, either.

Fortunately, in high-temperature systems, it has been a trend within the CALPHAD community for the last decades to select the previously mentioned proper reference states. It was understood that this is the only scientific system, although it is not always the most convenient one to use. However, only this system allows deep scientific analysis of the excess properties of solutions, and only this system allowed the formulation of the LE rule.

V. EXPERIMENTALLY MEASURABLE CONDITIONS OF THE VALIDITY OF THE LE RULE

Strictly speaking, the validity of the LE rule should be checked by checking experimentally the validity of Eqs. [1] through [9]. Unfortunately, none of those equations can be checked at infinite temperature, as such is not experimentally achievable and as none of the solid or liquid solutions can exist at such temperature. Thus, we have to define practical means to check the approximate validity of the LE rule using experimental data collected in the experimentally achievable, medium temperature range.

Lupis and Elliot[1,2] confirmed the validity of their rule by showing that in most binary metallic systems known in the 1960s,[33] the heat of mixing and excess entropy of mixing of a given solution have the same sign. This condition is written as follows:

$$\tau \equiv \frac{\Delta H}{\Delta S^E} > 0 \qquad [11]$$

Equation [11] ensures the validity of the LE rule only in a limited T-range. Within a limited temperature range, both mixing enthalpy and excess entropy of mixing are usually considered to be T-independent quantities. This statement is identical to the statement that the excess heat capacity of the solution is zero. Under these simplified conditions, the excess Gibbs energy will inevitably cross zero and change its sign at $T = \tau$. Thus, the system will not obey the LE rule at higher temperatures, as shown in Figure 1(a). Thus, the fulfillment of the condition in Eq. [11] is a necessary but not sufficient condition to obey the LE rule.

The measurement of the excess heat capacity of solutions is possible if the heat of mixing is measured with high precision as a function of temperature in a wide T-range. If such data are known, then the second condition of the validity of the LE rule is written as follows:

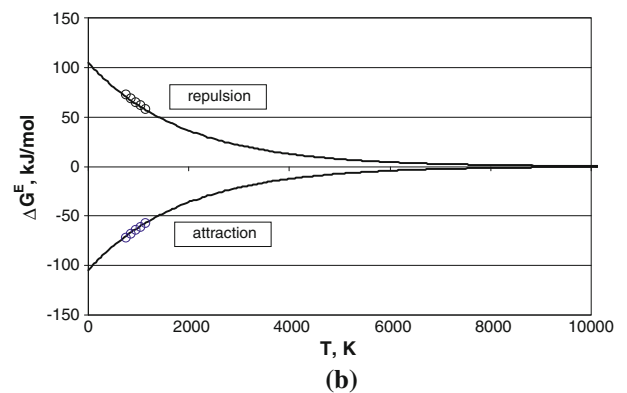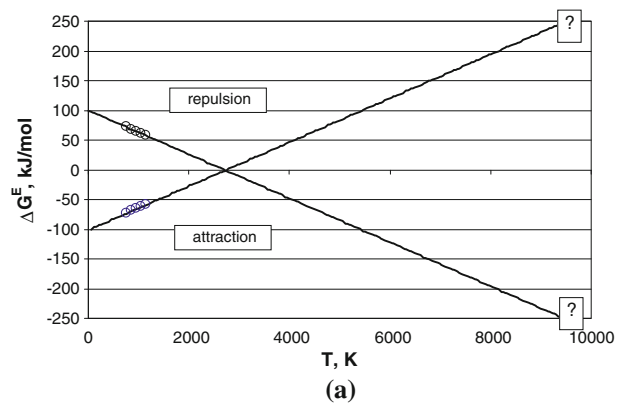$$\tau_C \equiv \frac{\Delta H}{\Delta C_p^E} < 0 \qquad [12]$$

Fig. 1—Temperature dependence of the integral excess Gibbs energy of two binary solutions as function of temperature with components attracting and repulsing each other (see text on lines). Data points: simulated experimental values in the limited T-range. (a) The linear extrapolation of data points, supposing the validity of Eq. [11] and zero excess heat capacity, showing that the excess Gibbs energy tends to infinity contradicting the LE rule at higher temperatures. (b) Extrapolation of data in accordance with the LE rule in accordance with Eqs. [11] and [12], showing that the excess Gibbs energy tends to zero in accordance with the LE rule.

In other words, it means that the signs of heat of mixing and excess heat capacity of the same solution should be different. In this case, the heat of mixing will diminish in absolute value with increasing T. Combining Eqs. [11] and [12], it follows that the excess entropy of mixing will also diminish in absolute value with T. Thus, the excess Gibbs energy will also diminish in absolute value with T, as shown in Figure 1(b). Therefore, Eq. [11] is the necessary, whereas Eq. [12] is the sufficient practical condition for the LE rule to be obeyed.

As infinite temperatures are not achievable, the only practical way to make sure that solutions obey the LE rule is to check the validity of Eqs. [11] and [12] against available experimental data. This comparison is performed in the next chapter.

VI. EXPERIMENTAL VALIDATION OF CONDITIONS (EQS. [11] AND [12])

Water-based and organic liquid-based solutions with large thermodynamic databases are stable in such a low and limited T-interval that checking the validity of

Eqs. [11] and [12] is practically impossible. Moreover, low-temperature databanks often use inappropriate standard states, with their recalculation being a cumbersome task.

Thus, high-temperature systems, such as solid and/or liquid metallic alloys will be used here to check the validity of the LE rule. From almost 10,000 binary metallic alloys, thousands are stable in the entire concentration range and in a wide T-interval (several hundred degrees). Moreover, through the efforts of many scientific groups during the last century, a reasonably correct database has been developed for more than 200 such metallic systems, at least at one given temperature.

In this article, the data collected in the recent handbook of Predel on thermodynamics of metallic systems[34] will be used. This handbook covers 2887 binary alloys. Of them, 209 metallic solutions (176 liquid and 33 solid) have full experimental excess thermodynamic description. The latter means that integral enthalpy of mixing is measured by calorimetry in the entire concentration range at least at one T, whereas the activity of at least one component is measured at a similar T by electromotive force (EMF), vapor pressure, or other techniques also in the entire concentration range. The latter allows the calculation of the activity of the second component using the Gibbs-Duhem equation. From here, the integral excess Gibbs energy of mixing can be calculated. From the comparison of the integral heat of mixing and the integral excess Gibbs energy of mixing, the integral excess entropy of mixing can be calculated. Although this algorithm seems to be difficult, it is still the most reliable method to determine the correct sign and magnitude of the excess entropy of mixing. Other methods, such as the determination of the heat of mixing and excess entropy of mixing from the T-dependence of the activity alone, are excluded in this article, as they are less reliable. The data obtained by CALPHAD optimization alone are also excluded from this article, as in the absence of experimental data, the CALPHAD method does not provide a reliable sign and values for the excess entropy of mixing of a single phase.

As the tendency to obey the LE rule will be judged by the sign of excess properties, we should define reliability limits. We will call the data having "reliable sign" if both of the following conditions are fulfilled:

(a) If the integral excess entropy of mixing at equimolar**

**As the excess Gibbs energy is zero by definition for pure components, the most reliable concentration to check the validity of the LE rule in binary solutions is at the equimolar composition. The author believes that the LE rule is valid at any composition, including the diluted solutions. However, experimental data are less certain in the diluted composition regions, and so these data are not considered in this article.

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composition is more negative than –1 J/mol K or more positive than +1 J/mol K.
(b) If the heat of mixing and the excess Gibbs energy of mixing at equimolar composition are more negative than –1 kJ/mol or more positive than +1 kJ/mol.

These limits are chosen based on the experience of the author on the reliability of measured excess thermodynamic functions, with special reference to the way excess entropy of mixing is calculated (not measured), being a difference of two, independently measured values. Of the 209 systems with full thermodynamic description, 94 have no reliable sign of at least one of the excess properties (see Tables I, II with remark "?"). Thus, only the remaining 115 systems with full thermodynamic description and reliable signs for all the three excess properties will be used to evaluate the tendency to obey the LE rule.

All the 209 data points (each representing one binary liquid or solid equimolar solution) are shown in Figure 2. The borders of the reliability limits of signs are shown as dotted lines in Figure 2.

The 209 systems with full thermodynamic description were divided into two categories. The systems are called "simple" if neither their integral heat of mixing nor their integral excess entropy of mixing change their sign in the composition interval between 10 and 90 at. pct of the components. The system is called "complex" if such a sign change is taking place. Of the 209 systems, 172 (82 pct) seem to be simple systems. Data for simple and complex systems are presented in Tables I and II, respectively. It is interesting to note that although 60 pct of simple systems have reliable sign, only 32 pct of complex systems have reliable sign. Thus, it seems that some complex systems only seem to be complex because the absolute values of the experimental data is approximately zero.

In simple systems, the signs of the integral heat of mixing and integral excess entropy of mixing were compared at the equimolar composition to decide whether the given system obeys Eq. [11]. Based on this criterion, in the group of the 103 simple systems with reliable sign, 102 (99 pct) obey the proposed postulate (see Table I with remark "OK"), whereas only 1 of them (the liquid Au-Si system) does not obey the LE rule (see Table I with remark "NO"). It is expected that measurements in the future might change this conclusion[†].

[†]There is one more problematic system (the liquid Al-Cu system) that should be judged as not obeying the LE rule according to Ref. 34. For the heat of mixing of the Al-Cu liquid solution, the handbook in Ref. 34 refers to the handbook in Ref. 33, where data of Yazawa and Itagaki are preferred (obtained from private communication with the authors in 1969[33]). However, it is mentioned[34] that other previous publications[35,36] indicate more negative heat of mixing values. Apparently, these previous works are closer to reality, as proved by recent measurements of the Sommer group[37,38] and supported also by a CALPHAD assessment.[39] If these previous[35,36] and recent[37,38] data are used for heat of mixing in combination with the activity data given in Ref. 34, the Al-Cu system also confirms the validity of the LE rule (see the second row for the Al-Cu system in Table I).

Out of the 12 complex systems with full thermodynamic description and reliable sign of data (see Table II), 8 (67 pct) obey the LE rule. Statistically, it is much lower than for the simple systems. However, in all the four systems that seem to disobey the LE rule, the excess

Table I. Summary Table of Integral Excess Thermodynamic Properties of Binary Alloys at 50 At. Pct of Composition for Simple Systems[34] (See Text)

#	System	State	T [K (°C)]	ΔH (kJ/mol)	ΔG^E (kJ/mol)	ΔS^E (J/mol K)	Remark[‡]
1	Ag-Au	S	800 (527)	−4.7	−3.6	−1.4	OK
2	Ag-Au	L	1350 (1077)	−4.2	−2.6	−1.2	OK
3	Ag-Cu	L	1423 (1150)	+4.2	+3.5	+0.52	?
4	Ag-La	L	1346 (1073)	−18	−11	−5.1	OK
5	Ag-Pb	L	1273 (1000)	+3.7	+1.4	+1.8	OK
6	Ag-Pd	S	1200 (927)	−5.1	−2.9	−1.8	OK
7	Ag-Te	L	1320 (1047)	−16	−1.5	−11	OK
8	Ag-Tl	L	1073 (800)	+3.1	+1.3	+1.7	OK
9	Ag-Zn	L	1023 (750)	−7.5	−4.6	−2.8	OK
10	Al-Au	L	1540 (1267)	−34	−24	−6.6	OK
11	Al-Ca	L	1373 (1100)	−22	−14	−5.8	OK
12	Al-Cd	L	1373 (1100)	+6.5	+5.9	+0.44	?
13	Al-Ce	L	1673 (1400)	−30	−8	−13	OK
14	Al-Cu	L	1373 (1100)	−9.0	−14	+3.6	NO
			1373 (1100)	−17*	−14	−2.3	OK
15	Al-Fe	L	1873 (1600)	−19	−12	−4.0	OK
16	Al-Ga	L	1023 (750)	+0.68	+0.41	+0.26	?
17	Al-Ge	L	1200 (927)	−3.3	−4.1	+0.67	?
18	Al-In	L	1173 (900)	+4.8	+5.1	−0.26	?
19	Al-La	L	1693 (1420)	−59	−23	−21	OK
20	Al-Mg	L	1073 (800)	−3.3	−2.4	−0.8	?
21	Al-Ni	L	1873 (1600)	−50	−32	−9.6	OK
22	Al-Si	L	1473 (1200)	−2.8	−3.5	+0.48	?
23	Al-Sn	L	973 (700)	4.0	2.8	1.2	OK
24	Al-Zn	L	1000 (727)	2.5	1.5	1.0	OK
25	Au-Cs	L	900 (627)	−42	−37	−5.2	OK
26	Au-Cu	S	800 (527)	−5.1	−5.2	+0.13	?
27	Au-Cu	L	1550 (1277)	−6.9	−6.2	−0.45	?
28	Au-Fe	L	1473 (1200)	+4.0	+1.1	+2.0	OK
29	Au-Fe	S	1123 (850)	5.5	−3.7	8.2	OKX
30	Au-Ga	L	1400 (1127)	−16	−15	−1.0[†]	OK
31	Au-In	L	823 (550)	−19	−17	−2.5	OK
32	Au-Ni	S	1150 (877)	7.7	4.5	2.8	OK
33	Au-Ni	L	1820 (1547)	3.7	0.6	1.7	?
34	Au-Si	L	1685 (1412)	−5.9	−10	+2.7	NO
35	Au-Tl	L	973 (700)	0.14	−1.9	2.1	?
36	Ba-Mg	L	1030 (757)	−6.3	−3.3	−2.9	OK
37	Bi-Cd	L	773 (500)	0.78	−0.38	1.5	?
38	Bi-Cu	L	1373 (1100)	6.0	2.1	2.8	OK
39	Bi-Hg	L	594 (321)	0.5	0.63	−0.22	?
40	Bi-In	L	900 (627)	−1.8	−2.1	0.33	?
41	Bi-Li	L	1000 (727)	−38	−31	−7.0	OK
42	Bi-Mg	L	1123 (850)	−22	−20	−1.8	OK
43	Bi-Na	L	773 (500)	−29	−24	−7.0	OK
44	Bi-Pb	L	700 (427)	−1.1	−1.2	0.18	?
45	Bi-Sb	L	1200 (927)	0.55	−2.3	2.4	?
46	Bi-Sn	L	600 (327)	0.02	0.2	−0.30	?
47	Bi-Tl	L	750 (477)	−4.2	−4.4	0.27	?
48	Bi-Zn	L	873 (600)	4.5	2.7	2.1	OK
49	K-KBr	L	1044 (771)	12	4.4	7.3	OK
50	Ca-Cu	L	1273 (1000)	−5.7	−5.8	0.08	?
51	Ca-Mg	L	1010 (737)	−6.0	−2.9	−3.1	OK
52	Ca-Ni	L	1120 (847)	−9.6	−5.0	−4.1	OK
53	Cd-Ga	L	700 (427)	2.8	2.7	0.14	?
54	Cd-In	L	800 (527)	1.4	1.0	0.55	?
55	Cd-Li	L	874 (601)	−16	−9.9	−7.0	OK
56	Cd-Mg	S	543 (270)	−5.5	−4.8	−1.3	OK
57	Cd-Mg	L	923 (650)	−5.6	−4.6	−1.1	OK
58	Cd-Na	L	673 (400)	−3.2	0.64	−3.8	?
59	Cd-Pb	L	773 (500)	2.7	2.0	0.93	?
60	Cd-Sn	L	773 (500)	1.8	0.95	1.1	?

Table I. Continued

#	System	State	T [K (°C)]	ΔH (kJ/mol)	ΔG^E (kJ/mol)	ΔS^E (J/mol K)	Remark[‡]
61	Cd-Tl	L	750 (477)	2.3	1.6	0.93	?
62	Cd-Zn	L	800 (527)	2.1	2.1	0.0	?
63	Ce-Mg	L	1130 (857)	−10	−8.6	−1.2	OK
64	Co-Cu	L	1473 (1200)	9.7	8.5	0.8	?
65	Co-Fe	S	1650 (1377)	−1.3	1.3	−1.6	OKX
66	Co-Fe	L	1873 (1600)	−2.6	1.3	−2.1	OKX
67	Co-Ge	L	1723 (1450)	−24	−14	−6.0	OK
68	Co-Mn	S	1023 (750)	0.5	−5.6	6.0	?
69	Co-Ni	S	1473 (1200)	0.22	0	0.15	?
70	Co-Ni	L	1780 (1507)	0.42	0	0.24	?
71	Co-Pt	S	1273 (1000)	−14	−12	−1.2	OK
72	Co-Si	L	1873 (1600)	−47	−29	−9.5	OK
73	Cr-Fe	S	1600 (1327)	5.9	1.7	2.6	OK
74	Cr-Fe	L	1873 (1600)	5.2	−0.98	3.3	?
75	Cr-Ge	L	1773 (1500)	−13	3.8	−9.5	?
76	Cr-Mn	S	1473 (1200)	−3.8	−1.0	−1.9	OK
77	Cr-Mo	S	1873 (1600)	5.9	3.8	1.1	OK
78	Cr-Pd	L	2023 (1750)	−5.3	−3.1	−1.1	OK
79	Cr-Si	L	1900 (1627)	−26	−26	−0.05	?
80	Cr-Ti	S	1653 (1380)	46	6	24	OK
81	Cr-V	S	1550 (1277)	−2.4	−3.8	0.65	?
82	Cs-CsH	L	1000 (727)	4.3	3.9	0.43	?
83	Cu-Fe	L	1823 (1550)	11	7.5	1.9	OK
84	Cu-Ge	L	1423 (1150)	−5.2	−2.2	−2.1	OK
85	Cu-La	L	1373 (1100)	−12	−11	−0.5	?
86	Cu-Mg	L	1120 (847)	−8.9	−7.8	−1.0	OK
87	Cu-Mn	S	1100 (827)	3.2	1.2	1.8	OK
88	Cu-Ni	L	1753 (1480)	3.0	3.0	0.0	?
89	Cu-Ni	S	1273 (1000)	2.3	3.2	−0.70	?
90	Cu-Pb	L	1473 (1200)	6.8	5.2	1.1	OK
91	Cu-Pd	S	1350 (1077)	−11	−6.0	−3.7	OK
92	Cu-Pd	L	1873 (1600)	−14	4.0	−9.6	OKX
93	Cu-Si	L	1700 (1427)	−9.0	4.1	−7.7	OKX
94	Cu-Ti	L	1496 (1223)	−3.3	−3.0	−0.20	?
95	Cu-Tl	L	1573 (1300)	8.4	5.4	1.9	OK
96	Cu-Y	L	1823 (1550)	−19	−8.8	−5.6	OK
97	Cu-Zn	L	1200 (927)	−10	−5.8	−3.5	OK
98	Fe-Ge	L	1873 (1600)	−14	−13	−0.3	?
99	Fe-Mn	L	1823 (1550)	−1.0	−0.5	−0.27	?
100	Fe-Mn	S	1174 (901)	−1.9	−1.7	−0.17	?
101	Fe-Ni	L	1873 (1600)	−4.0	−2.6	−0.75	?
102	Fe-Ni	S	1473 (1200)	−3.8	−2.7	−0.75	?
103	Fe-Pd	L	1850 (1577)	−27	−6.7	−11	OK
104	Fe-Pd	S	1565 (1292)	−20	−7.3	−8.1	OK
105	Fe-Si	L	1873 (1600)	−41	−20	−11	OK
106	Fe-Ti	L	1873 (1600)	−17	−13	−2.1	OK
107	Fe-V	L	2193 (1920)	−9.2	−3.2	−2.7	OK
108	Fe-V	S	1600 (1327)	−5.3	−6.4	0.7	?
109	Ga-Hg	L	600 (327)	1.7	0.5	2.0	?
110	Ga-In	L	1223 (950)	1.1	1.5	−0.32	?
111	Ga-Mg	L	923 (650)	−12	−8.5	−3.4	OK
112	Ga-Pb	L	1100 (827)	3.9	4.6	−0.6	?
113	Ga-Sn	L	743 (470)	0.87	0.60	0.30	?
114	Ga-Te	L	1120 (847)	−35	−17	−15	OK
115	Ga-Tl	L	1000 (727)	3.8	3.5	0.3	?
116	Ga-Zn	L	750 (477)	1.6	0.85	1.0	?
117	Gd-Sm	S	1173 (900)	7.5	−8.9	14	OKX
118	Ge-In	L	1250 (977)	0.39	1.2	−0.65	?
119	Ge-Mg	L	1388 (1115)	−25	−18	−4.7	OK
120	Ge-Ni	L	1870 (1597)	−29	−20	−5.0	OK
121	Ge-Pd	L	1820 (1547)	−55	−43	−6.5	OK
122	Ge-Sn	L	1773 (1500)	0.65	0.56	0.05	?

Table I. Continued

#	System	State	T [K (°C)]	ΔH (kJ/mol)	ΔG^E (kJ/mol)	ΔS^E (J/mol K)	Remark[‡]
123	Ge-Tl	L	1273 (1000)	3.4	3.4	0.0	?
124	Hg-In	L	298 (25)	–2.3	–2.0	–0.74	?
125	Hg-Na	L	673 (400)	–20	–14	–9.5	OK
126	Hg-Sn	L	450 (177)	0.88	1.2	–0.60	?
127	Hg-Zn	L	573 (300)	0.37	0.91	–0.94	?
128	In-K	L	753 (480)	–6.8	–2.1	–6.3	OK
129	In-Mg	L	923 (650)	–7.0	–1.4	–6.1	OK
130	In-Na	L	723 (450)	–9.0	–4.4	–6.4	OK
131	In-Ni	L	1750 (1477)	–11	–8.7	–1.3	OK
132	In-Pb	L	1000 (727)	0.96	0.94	0.02	?
133	In-Sb	L	973 (700)	–3.1	–3.8	0.7	?
134	In-Te	L	950 (677)	–38	–24	–15	OK
135	In-Tl	L	773 (500)	0.58	0.79	–0.29	?
136	In-Zn	L	700 (427)	3.1	2.3	1.1	OK
137	K-Pb	L	848 (575)	–19	–11	–9.2	OK
138	K-Tl	L	798 (525)	–11	–6.3	–5.9	OK
139	La-Mg	L	1133 (860)	–8.5	–4.9	–3.2	OK
140	La-Sn	L	1283 (1010)	–70	–46	–19	OK
141	Li-Mg	L	887 (614)	–3.3	–1.6	–1.9	OK
142	Li-Pb	L	900 (627)	–23	–19	–4.4	OK
143	Li-Tl	L	985 (712)	–19	–12	–7.3	OK
144	Li-Zn	L	820 (547)	–11.5	–7.1	–5.4	OK
145	Mg-Pb	L	973 (700)	–8.3	–7.7	–0.6	?
146	Mg-Si	L	1350 (1077)	–16	–8.6	–5.5	OK
147	Mg-Sn	L	1073 (800)	–13.4	–14.0	+ 0.56	?
148	Mg-Sr	L	1054 (781)	–5.1	–3.6	–1.4	OK
149	Mg-Zn	L	923 (650)	–5	–3.8	–1.3	OK
150	Mn-P	L	1600 (1327)	–44	–40	–2.5	OK
151	Mn-Si	L	1700 (1427)	–26	–26.7	0.41	?†
152	Na-Pb	L	700 (427)	–16.6	–12.4	–6.0	OK
153	Na-Tl	L	673 (400)	–11.4	–8.4	–4.4	OK
154	Ni-Pd	L	1873 (1600)	1.2	1.9	–0.35	?
155	Ni-Pt	S	1625 (1352)	–9.3	–8.7	–0.36	?
156	Ni-Rh	S	1100 (827)	1.9	–2.0	3.5	OKX
157	Pb-Sn	L	1050 (777)	–1.4	–0.35	–1.0	?
158	Pb-Te	L	1210 (937)	–27	–17	–8.6	OK
159	Pb-Tl	S	523 (250)	–1.9	–1.1	–1.5	OK
160	Pb-Tl	L	773 (500)	–1.0	–0.6	–0.5	?
161	Pd-Rh	S	1575 (1302)	5.6	5.0	0.4	OK
162	Pd-Si	L	1600 (1327)	–54	–32	–14	OK
163	Pd-Te	L	1173 (900)	–27	–26	–1	OK
164	Pr-Zn	L	1400 (1127)	–28	–18	–7.4	OK
165	Sb-Sn	L	905 (632)	–1.4	–1.7	0.3	?
166	Sb-Te	L	935 (662)	–8.6	–3.0	–6.0	OK
167	Se-Te	L	714 (441)	–2.3	1.1	–4.6	OKX
168	Sm-Y	S	1173 (900)	12	–11	20	OKX
169	Sn-Te	L	1100 (827)	–24	–15.2	–8.0	OK
170	Sn-Tl	L	723 (450)	0.7	5.2	–6.2	?
171	Sn-Zn	L	750 (477)	3.1	1.5	2.1	OK
172	Te-Tl	L	950 (677)	–24	–21	–3.2	OK

*Al-Cu: This value is taken from Ref. 35 through 38 rather than from Ref. 34—see text.

†Au-Ga: Figs. 3–5 of pp. 367–368 of subvolume 5a[34] contradict each other. The excess entropy value is taken from Figs. 3 and 4. Similarly, for the Mn-Si system, there is a contradiction among Figs. 2 through 4 of pp. 149–150 of subvolume h,[34] resolved in a similar way.

‡"OK" means the system obeys Eq. [11]. "NO" means the system does not seem to obey Eq. [11]. "?" means data do not afford to make definite conclusion (excess entropy of mixing is between –1 and + 1 J/mol K, or heat of mixing and/or excess Gibbs energy of mixing is between –1 and + 1 kJ/mol), and so these data were not used to judge on the validity of the LE rule. "OKX" means that although the system seems to obey Eq. [11], the excess Gibbs energy of mixing has a different sign.

entropy of mixing is between 1.5 and 1.7 J/mol K, i.e., in a proximity to the range of the experimental error.

It should also be mentioned that in 9 of the 102 simple systems and in 1 of the 8 complex systems (i.e., in 10 out of 110 systems) obeying the LE rule, the $-T \cdot \Delta S^E$ term overcompensates the ΔH term at the temperature of the measurement, i.e., the ΔG^E term seems to have a different sign compared with that of ΔH and ΔS^E

Table II. Summary Table of Integral Excess Thermodynamic Properties of Binary Alloys at 50 At. Pct of Composition for Complex Systems[34] (See Text)

#	System	State	T [K (°C)]	ΔH (kJ/mol)	ΔG^E (kJ/mol)	ΔS^E (J/mol K)	Remark*
1	Ag-Al	L	1273 (1000)	−4.0	−5.9	+1.5	NO
2	Ag-Bi	L	1273 (1000)	+2.0	+0.6	+1.1	?
3	Ag-Ga	L	1300 (1027)	−1.8	−2.8	+0.8	?
4	Ag-Ge	L	1250 (977)	+2.2	−0.2	+1.9	?
5	Ag-In	L	1100 (827)	−4.2	−4.8	+0.5	?
6	Ag-Sb	L	1250 (977)	0	−3.1	+2.5	?
7	Ag-Si	L	1673 (1400)	+2.8	+3.8	−0.59	?
8	Ag-Sn	L	1250 (977)	−0.9	−1.8	+0.7	?
9	Al-Mn	L	1600 (1327)	−17	−9.5	−4.7	OK
10	Au-Bi	L	973 (700)	+0.65	−0.8	+1.5	?
11	Au-Pb	L	1200 (927)	−0.7	−2.9	1.8	?
12	Au-Sb	L	1023 (750)	−15	−11	−4.3	OK
13	Au-Te	L	1281 (1008)	−2.5	−4.4	+1.5	NO
14	Bi-BiBr$_3$	L	800 (527)	0	−2.4	3	?
15	Bi-BiI$_3$	L	800 (527)	5.5	1.5	5.0	OK
16	Cd-Hg	L	600 (327)	−2.6	−2.3	−0.58	?
17	Cd-Sb	L	693 (420)	−2.3	−2.7	0.58	?
18	Co-Sn	L	1573 (1300)	−1.0	−1.5	0.3	?
19	Cr-Ni	S	1550 (1277)	6.2	0.78	3.5	?
20	Cu-Ga	L	1273 (1000)	−7.8	−8.0	0.2	?
21	Cu-In	L	923 (650)	−3.5	−2.4	−1.2	OK
22	Cu-Pt	S	1350 (1077)	−12	−11	−0.85	?
23	Cu-Sb	L	1190 (917)	−3.5	−5.5	1.7	NO
24	Cu-Sn	L	1400 (1127)	−1.8	−4.2	1.7	NO
25	Ga-Na	L	773 (500)	−5.7	−4.5	−1.5	OK
26	Hg-Pb	L	600 (327)	0.20	0.92	−1.2	?
27	In-Sn	L	700 (427)	−0.20	−0.77	0.81	?
28	K-Na	L	384 (111)	0.74	0.79	−0.12	?
29	Mg-Tl	L	923 (650)	−6.9	−7.5	0.7	?
30	Mn-Ni	S	1050 (777)	−14	−12	−2	OK
31	Mn-Ni	L	1743 (1470)	−11	−10.7	−0.2	?
32	Mn-Sn	L	1517 (1244)	−2.2	2.5	+0.2	?
33	Na-Sn	L	1073 (800)	−18	−8.6	−8.8	OK
34	Nb-U	S	1173 (900)	4.6	−5.2	8.4	OKX
35	Ni-Pd	S	1273 (1000)	−0.5	−2.7	1.7	?
36	Pb-Sb	L	892 (619)	0.03	0.56	−0.60	?
37	Sb-Zn	L	850 (577)	−2.3	−3.0	0.8	?

*"OK" means the system obeys Eq. [11]. "NO" means the system does not seem to obey Eq. [11]. "?" means data do not afford to make definite conclusion (excess entropy of mixing is between −1 and +1 J/mol K, or heat of mixing and/or excess Gibbs energy of mixing is between −1 and +1 kJ/mol), and so these data were not used to judge on the validity of the LE rule. "OKX" means that although the system seems to obey Eq. [11], the excess Gibbs energy of mixing has a different sign.

(see Tables I and II, remark "OKX"). This might mean that those 10 systems (9 pct) do not obey the LE rule. However, one should remember that there are different types of chemical and physical interactions between the atoms/molecules/ions, *etc.* in solutions. Although the proposed postulate is valid for each type of those interactions, they might have different signs and different action radii in the same solution (this is a widely known fact in colloid chemistry). That might mean that the *T*-dependence of the excess Gibbs energy of some equimolar solutions might cross zero and might have a maximum/minimum point. Nevertheless, according to the LE rule, the excess Gibbs energy eventually will tend to zero even in these binary systems (see Figure 3).

According to Sommer, the excess heat capacity of liquid solutions is one of the most neglected thermodynamic quantities.[40] The available experimental data are shown in Tables III and IV and in Figure 4 as function of heat of mixing, in accordance with compilations[11,34] (the same systems with similar data are compiled in References 41 and 42).

Of the 14 systems of Table III, only one system (Au-Sb) seems not to obey the LE rule. However, it was not measured by calorimetry; rather, it was evaluated from the *T*-dependence of the excess Gibbs energy, being a less reliable method. Moreover, in Table IV, the same system obeys the LE rule; hence, this data point of Table III is neglected in Figure 4. Of 41 systems in Table IV, only the Cd-Ga system does not obey the LE rule. Thus, in the 48 systems shown in Tables III and IV, 98 pct obey the LE rule, with a single exception. It is supposed that subsequent experiments on the Cd-Ga
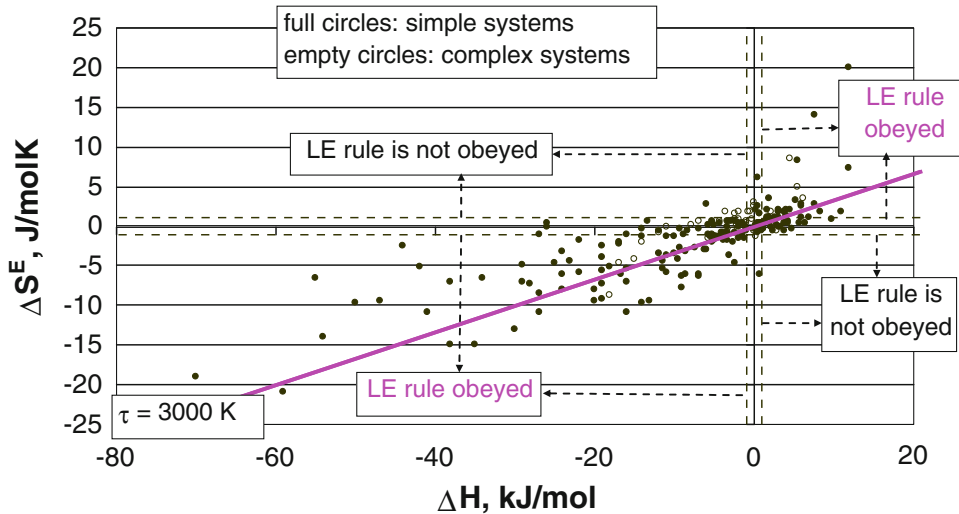
Fig. 2—The dependence of the excess entropy of mixing on the enthalpy of mixing in 209 equimolar systems with full thermodynamic description (data are taken from Ref. 34, each point corresponds to one binary system). The LE rule is obeyed when Eq. [11] is obeyed. The straight line shows the approximate rule of Lupis and Elliot[1,2]: $\tau \equiv \frac{\Delta H}{\Delta S^E} \cong 3000\,\mathrm{K}$.
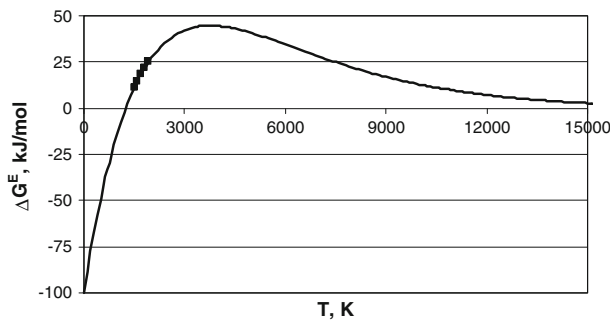

Fig. 3—Simulated data points (positioned along an imaginary linear line) and functional dependence (line) of an imaginary system in which both the heat of mixing and excess entropy of mixing have the same negative sign, but the term $-T \cdot \Delta S^E$ overwhelms the term ΔH. Thus, ΔG^E has a different sign. The graph shows schematically that even in this case, the LE rule can be obeyed.

system might change the conclusion about the only exception out of the rule.

From the comparison of experimental data with Eqs. [11] and [12], we can conclude that both the necessary and the sufficient practical conditions to obey the LE rule are fulfilled by most systems for which reliable experimental data are available.

VII. DISCUSSION

The thermodynamics of materials is based on "laws." Each law is a general statement based on an ever-increasing number of empirical observations. These laws have general validity for all types of materials and do not depend on the type of chemical bonding or specific physical interaction between the atoms and molecules. The laws cannot be proven in straightforward experiments. Rather, they are accepted through reasoning and by endless checking against empirical observations to

make sure that experimental facts do not contradict the laws.

The first two laws (the law of conservation of energy[43,44] and the law of dissipation of energy[45,46]) are absolute laws of thermodynamics. Thermodynamics was applied to describe equilibrium in heterogeneous substances by Gibbs,[47] and this subfield of thermodynamics is called today chemical (or materials) thermodynamics. After Gibbs, chemical (materials) thermodynamics was made more powerful when the heat theorem was introduced by Nernst, claiming that the free energy and heat of reaction curves are asymptotic at low temperatures.[48] Later, it became the 3rd law of thermodynamics and was reformulated by claiming that the entropy of perfect crystalline phases approach zero when the temperature approaches absolute zero[49,50] (more detailed discussion of the laws of thermodynamics can be found in References 29–31, 51, and 52).

So far, no law has been introduced concerning the behavior of materials at another extreme, at a high temperature limit. However, the LE rule discussed in this article has all the features (both for good and bad) characterizing the three existing laws of thermodynamics, i.e., (1) general validity, (2) impossibility to be proven with a 100 % certainty, (3) simple reasoning behind, and (4) usefulness in interpreting natural phenomena. The following provides more detail:

(a) The LE rule is probably generally valid for all materials, independent of their structure, chemical bonds, or physicochemical interactions between their entities (atoms, molecules, ions, etc.).
(b) The LE rule cannot be proven by any straightforward experiment as the infinite temperature is not achievable, although the tendency to obey the LE rule is proven by a large number of existing experimental data.
(c) The LE rule can be accepted through the simple reasoning given previously (temperature increase

Table III. On the T-Dependence of Heat of Mixing of Equimolar Liquid Binary Alloys[34]

#	System	State	$T \rightarrow T$ [K (°C)]	$\Delta H \rightarrow \Delta H$ (kJ/mol)	ΔC_p^{E}* (J/mol K)	Remark[†]
1	Au-In	L	800 (527) → 1210 (937)	−19.2 → −17.0	5.4	OK
2	Au-Sb	L	733 (460) → 1373 (1100)	−9.5 → −16	−10.8	NO
3	Au-Sn	L	755 (482) → 1369 (1096)	−12.1 → −11.4	1.1	OK
4	Cu-In	L	955 (682) → 1373 (1100)	−3.1 → −0.3	6.7	OK
5	Cu-Sb	L	929 (656) → 1375 (1102)	−3.7 → −3.0	1.6	OK
6	Ga-Te	L	1130 (857) → 1230 (957)	−32.1 → −30.7	14	OK
7	Hg-Tl	L	298 (25) → 583 (310)	−1.2 → −0.42	2.7	OK
8	In-Sb	L	957 (684) → 1184 (911)	−3.2 → −2.4	3.5	OK
9	In-Te	L	980 (707) → 1340 (1067)	−35 → −29	17	OK
10	Mg-Pb	L	943 (670) → 1223 (950)	−8.6 → −7.5	3.9	OK
11	Mg-Sn	L	1073 (800) → 1213 (940)	−13.4 → −12.4	7.1	OK
12	Mg-Zn	L	893 (620) → 1073 (800)	−6.0 → −3.1	16	OK
13	Ni-Sn	L	1580 (1307) → 1775 (1502)	−21 → −14	36	OK
14	Sb-Sn	L	783 (510) → 1108 (835)	−1.5 → −1.4	0.3	OK

*An average value of the excess heat capacity is found as the ratio of ΔH change and T change.
[†]Remark "OK": The system obeys Eq. [12]. Remark "NO": The system does not obey Eq. [12].

Table IV. On the Heat of Mixing and Excess Heat Capacity of Liquid Binary Alloys[11]

#	System A-B	T [K (°C)]	x_B	ΔH (kJ/mol)	ΔC_p^{E} (J/mol K)	Remark*
1	Al-Bi	1000 (727)	0.5	4.2	0	?
2	Al-Ga	952 (679)	0.5	0.7	0	?
3	Al-Li	879 (606)	0.5	−11	10	OK
4	Al-Ni	1923 (1650)	0.5	−50	15	OK
5	Au-Ga	750 (477)	0.67	−18.2	8.9	OK
6	Au-Ge	630 (357)	0.28	−6	4.5	OK
7	Au-In	850 (577)	0.67	−17.9	7.9	OK
8	Au-Sb	800 (527)	0.67	−3.3	5.5	OK
9	Au-Si	1000 (727)	0.5	−7.6	5.7	OK
10	Au-Sn	698 (425)	0.5	−12.3	7.5	OK
11	Au-Tl	823 (550)	0.45	−1.1	0	?
12	Ba-Mg	1000 (727)	0.7	−8.3	4.5	OK
13	Bi-Pb	680 (407)	0.5	−1.1	0	?
14	Ca-Mg	1080 (807)	0.65	−4.8	4	OK
15	Cd-Ga	610 (337)	0.4	2.3	3	NO
16	Cd-Pb	623 (350)	0.5	2.6	0	?
17	Cd-Sn	675 (402)	0.5	2.1	−1.5	OK
18	Ce-Cu	1850 (1577)	0.67	−17.5	4.3	OK
19	Ce-Mg	1050 (777)	0.8	−11.1	5.5	OK
20	Cu-Ga	1050 (777)	0.45	−12.6	6.3	OK
21	Cu-Si	1281 (1008)	0.25	−15	5.7	OK
22	Cu-Te	870 (597)	0.56	−15.3	16.5	OK
23	Cu-Ti	1500 (1227)	0.4	−3.5	3.5	OK
24	Cu-Zr	1500 (1227)	0.5	−16	8.5	OK
25	Ga-In	423 (150)	0.5	1.1	0	?
26	Ga-Mg	972 (699)	0.7	−11.5	3	OK
27	Ge-Te	990 (717)	0.5	−14.8	13.4	OK
28	Hg-Na	633 (360)	0.3	−17.5	12.9	OK
29	In-Sb	1158 (885)	0.5	−2.4	3.8	OK
30	Li-Mg	800 (527)	0.5	−3.3	8.4	OK
31	Li-Sn	1200 (927)	0.25	−34	4	OK
32	Mg-Pb	1100 (827)	0.45	−9.6	5	OK
33	Na-Sn	873 (600)	0.5	−20.7	21	OK
34	Na-Tl	673 (400)	0.5	−11.7	4.2	OK
35	Ni-Si	1575 (1302)	0.38	−67	48	OK
36	Ni-Zr	1261 (988)	0.74	−24	11.5	OK
37	Pb-Sn	623 (350)	0.5	1.4	0	?
38	Pd-Si	1600 (1327)	0.3	−70	45	OK
39	Sb-Sn	950 (677)	0.5	−1.3	0.5	OK
40	Se-Tl	700 (427)	0.6	−32.6	23.2	OK
41	Sn-Zn	750 (477)	0.5	3.4	−3	OK

*Remark "OK": The system obeys Eq. [12]. Remark "NO": The system does not obey Eq. [12]. "?": Data lead to a definite decision.

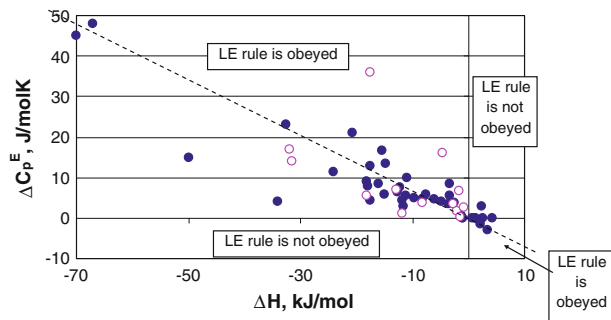Fig. 4—The dependence of the excess heat capacity of mixing on the enthalpy of mixing in 41 (full circles,[11] Table IV) + 14 (empty circles,[34] Table III) = 48 (7 overlapping) systems with available data (each point corresponds to one binary system). The LE rule is obeyed when Eq. [12] is obeyed. The equation of the straight line is $\tau_C \equiv \frac{\Delta H}{\Delta C_p^E} \cong -1500$ K.

leads to thermal expansion, *i.e.*, to increase in separation between the atoms, leading to the weakening the bonds between them, meaning the specific interaction, *i.e.*, nonideal behavior diminishes with temperature).

(d) The LE rule provides a useful limiting condition to be obeyed by any mathematical equation designed/selected to describe the temperature dependence of the excess thermodynamic functions in a wide *T*-range.

In conclusion, after 45 years since its first declaration, the LE rule can be considered as a potential fourth law of materials thermodynamics.

VIII.   CONCLUSIONS

1. The rule first formulated by Lupis and Elliott in 1966 is reformulated in this article as follows: "Real solid, liquid and gaseous solutions (and pure gases) gradually approach the state of an ideal solution (perfect gas) as temperature increases at any fixed pressure and composition."
2. This rule is rationalized through the heat expansion of phases and loss of any interaction with increased separation between the atoms.
3. It is shown that the rule is valid only if the standard state is properly selected. The standard state of the components and the solution should be selected identically, *i.e.*, the LE rule is valid only for the $A(\Phi) + B(\Phi) = A\text{-}B(\Phi)$ type of dissolution.
4. It is shown that the necessary and sufficient practical conditions to obey the LE rule can be described by Eqs. [11] and [12]. It is shown that these two conditions are fulfilled for most of the experimentally measured high-temperature solutions.
5. Additional confirmation of the validity of the LE rule is that for the 12 systems with full thermodynamic optimization, the exponential temperature dependence of the excess Gibbs energy (based on the LE rule) provides meaningful results, free of calculated artefacts. In contrary, when a linear temperature dependence for the excess Gibbs energy is used (contradicting the LE rule), artificial miscibility gaps appear in many of the calculated phase diagrams.
6. The LE rule is compared with the existing laws of thermodynamics. It is shown that the LE rule can be considered as a potential fourth law of materials thermodynamics, after 45 years since its first declaration.

APPENDIX: DEFINITIONS OF THERMODYNAMIC PROPERTIES OF SOLUTIONS AND GASES[29–31]

The definitions and equations given in this Appendix are widely known. Nevertheless, these equations are given here to avoid any possible misunderstanding with people, working in different fields and using different notation systems.

Let us consider a solution in state Φ, with Φ symbolizing gas, liquid, or solid with specific crystal structures (*i.e.*, the face-centered cubic crystal is a different state from the body-centered cubic crystal). Let us consider C components in this solution, numbered by $i = 1, 2, \ldots, C$. Then, the mole fraction of each component (x_i) is defined as

$$x_i \equiv \frac{n_i}{\sum_{i=1}^{C} n_i} \qquad [A1]$$

where n_i is the amount of component i (mol), dissolved in solution Φ. When the solution is gaseous, the mole fraction is usually defined through the partial pressures (p_i, bar)

$$x_i \equiv \frac{p_i}{\sum_{i=1}^{C} p_i} \qquad [A2]$$

The partial molar Gibbs energy of component i in the ideal solution is given by definition as:

$$G_i^{\Phi,id} \equiv G_i^{\Phi 0} + R \cdot T \cdot \ln x_i \qquad [A3]$$

where R is the universal gas constant (J/mol K), T is the absolute temperature (K), and $G_i^{\Phi 0}$ is the standard Gibbs energy of pure component i in the same state Φ (even if it is not stable) as that of the solution at given temperature and pressure (J/mol).

The partial molar Gibbs energy of component i in the real solution is defined by one of the following equations:

$$G_i^\Phi \equiv G_i^{\Phi,id} + \Delta G_i^E \equiv G_i^{\Phi 0} + R \cdot T \cdot \ln x_i + R \cdot T \cdot \ln \gamma_i$$
$$\equiv G_i^{\Phi 0} + R \cdot T \cdot \ln a_i \qquad [A4]$$

where ΔG_i^E is the partial excess Gibbs energy of component i (J/mol), γ_i is the activity coefficient of component i (called the fugacity coefficient for gases), and a_i is the activity (called fugacity for gases) of component i.

From Eq. [A4], Eqs. [A5] through [A8] follow:

$$a_i \equiv \gamma_i \cdot x_i \qquad [A5]$$

$$\Delta G_i^E \equiv R \cdot T \cdot \ln \gamma_i \qquad [A6]$$

The excess partial entropy of component i (ΔS_i^E, J/mol K) is defined as

$$\Delta S_i^E = -\left(\frac{d\Delta G_i^E}{dT}\right)_{p,x_i} \qquad [A7]$$

The partial enthalpy of mixing of component i (ΔH_i, J/mol) is defined as

$$\Delta H_i \equiv \Delta G_i^E + T \cdot \Delta S_i^E \qquad [A8]$$

The partial heat of mixing of the ideal solution equals zero by definition ($\Delta H_i^{id} \equiv 0$), which is why the term "excess" is not used in the name of the "partial enthalpy of mixing." The partial excess heat capacity of component i is defined as

$$\Delta C_{p,i}^E \equiv \left(\frac{d\Delta H_i}{dT}\right)_{p,x_i} \qquad [A9]$$

The excess partial molar volume of component i is defined as the difference between the partial molar volume of the component in the solution (V_i) and its molar volume in the pure reference state (V_i^0), having the same state as that of the solution. It is also defined as the derivative of the excess Gibbs energy by pressure

$$\Delta V_i^E \equiv V_i - V_i^0 = \left(\frac{\Delta G_i^E}{dp}\right)_{T,x_i} \qquad [A10]$$

The excess partial heat expansion coefficient of component i is defined as

$$\Delta \beta_i^E \equiv \left(\frac{d\Delta V_i^E}{dT}\right)_{p,x_i} \qquad [A11]$$

The excess partial compressibility of component i is defined as

$$\Delta \kappa_i^E \equiv -\left(\frac{d\Delta V_i^E}{dp}\right)_{T,x_i} \qquad [A12]$$

When the partial functions of all the components are known, the corresponding integral functions can be written as

$$\Delta Y^E = \sum_{i=1}^C x_i \cdot \Delta Y_i^E \qquad [A13]$$

with $Y = G, H, S, V, C_p, \beta$, and κ.

For perfect gases, the following law is valid:

$$p \cdot V_m = R \cdot T \qquad [A14]$$

where p is pressure (Pa) and V_m is the molar volume (m^3/mol). For real gases, the compression factor (Z) is introduced to show the difference between real and perfect gases

$$p \cdot V_m = Z \cdot R \cdot T \qquad [A15]$$

The compression factor can be described by a polynomial

$$Z \cong 1 + \sum_{j=1} \frac{C_j}{V_m^j} \qquad [A16]$$

where C_j is the jth virial coefficient. A less formal, widely known equation of state for gases is the van der Waals equation of state

$$p \cdot V_m \cong \frac{R \cdot T}{1 - \frac{b}{V_m}} - \frac{a}{V_m} \qquad [A17]$$

with semiempirical parameters a and b, having well-defined physical sense (see Reference 29). There are hundreds of other equations of state for gases, which are not considered here. Parameters Z, C_j, a, and b of Eqs. [A15] through [A17] have specific values for a given pure gas and are functions of gas composition for gaseous mixtures. Excess thermodynamic functions of gaseous mixtures can be expressed using parameters Z, C_j, a, and b and Eqs. [A15] through [A17]. At $Z = 1$, $C_j = a = b = 0$, all excess thermodynamic functions of gaseous mixtures become zero and the equation of state [A14] for perfect gases becomes valid.

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