Int. J. Heat Mass Transfer. Vol. 14, pp. 565–571. Pergamon Press 1971. Printed in Great Britain

VAPOR PRESSURE AND PERIODICAL CLASSIFICATION OF CHEMICAL ELEMENTS

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(*Received* 27 *February* 1970)

Abstract—The periodical classification of the chemical elements has remarkable consequences also upon their thermodynamical properties. In particular it is shown in this paper that on (log p)/(1/T) diagram the lines of vapor pressure p of the equiatomical chemical elements, for each group or subgroup of the Mendeleev's classification, have a convergence point which is sufficiently determined. For each group or subgroup it is then sufficient a unique equation in which the single element is represented by the coordinates of a point only.

This new rule, even with some exceptions, and approximations, may be able to fill lacking informations, to sever discordant experimental results, to induce values of thermodynamical parameters which are dependent from the law of pressures, as heats of evaporation and specific heats.

Numerical examples are done on-rare-earth elements and rare gases of the atmosphere.

NOMENCLATURE

p, absolute pressure;
T, absolute temperature;
R, universal gas constant;
m, mole;
r, heat of evaporation;
v_s, v_i, orthobaric volumes of vapor and liquid (or solid);
c_s, c_i, orthobaric specific heat of vapor and liquid (or solid) on boundary lines.

THE PERIODICAL classification of chemical elements has important consequences in various fields of physical properties, and in particular, as it is demonstrated in this paper, for thermodynamical properties joined with the law of vapor pressure.

An ample critical work on this argument has been made in a recent treatise by Professor A. N. Nesmeyanov [1] for many elements and for pressures between 10^{-10} and 760 Torr, exception made for atmospherical gases, for hydrogen and helium and also for a certain number of lantanides, for which other sources have been utilized [2].

The above mentioned results have been represented in Figs. 1–10 on diagrams (log p)/(1/T) in which p is the pressure of saturated vapors (in Torr) and T is the absolute temperature (in °K).

In almost all cases and with good or sufficient approximation there is a systematical convergence of the curves in characteristical points or *poles P* for each group or subgroup of Mendeleev of equiatomical vapors.

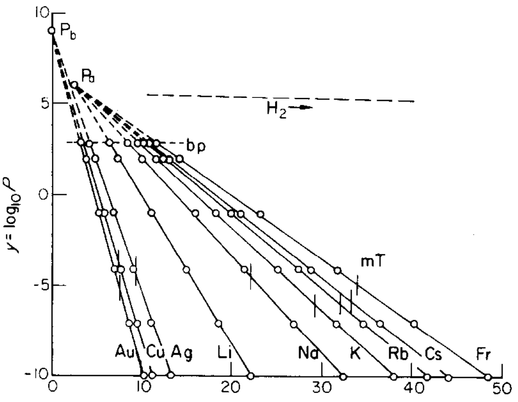

FIG. 1. Group I.

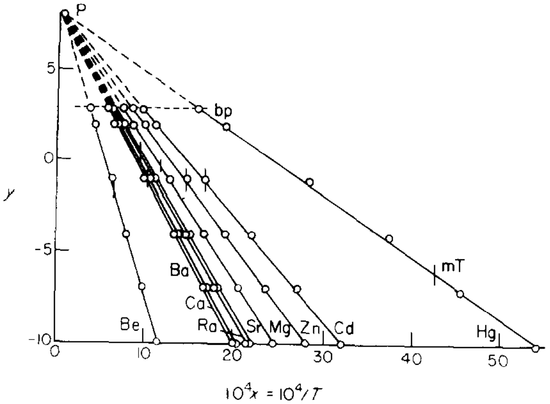

FIG. 2. Group II.

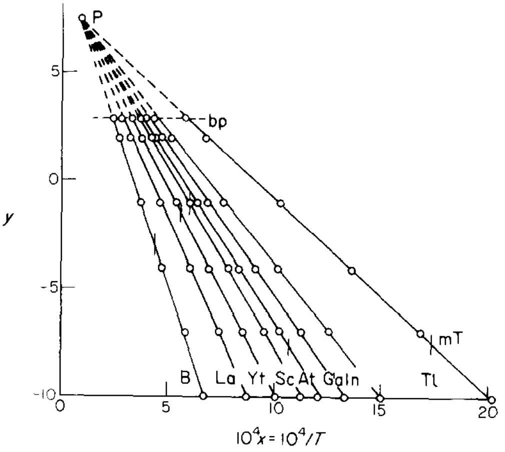

FIG. 3. Group III.

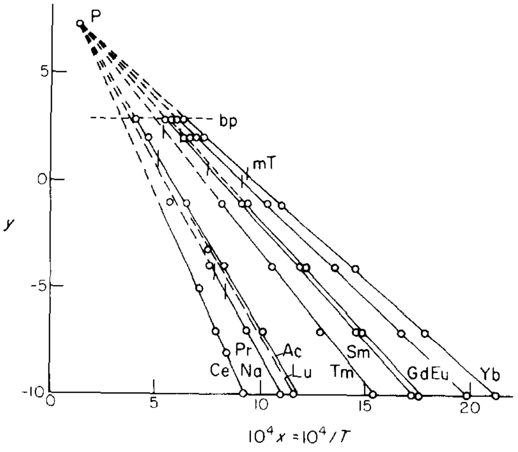

FIG. 4. Rare earths.

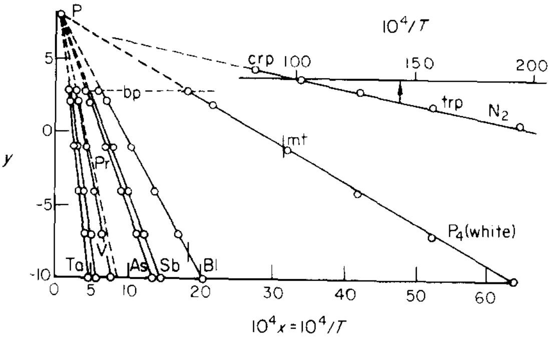

FIG. 5. Group V.

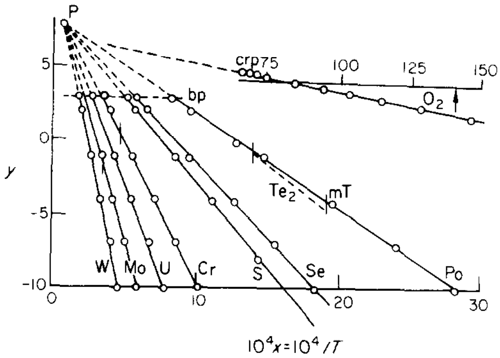

FIG. 6. Group VI.

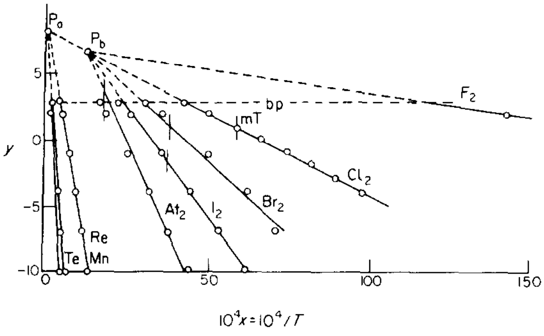

FIG. 7. Group VII.

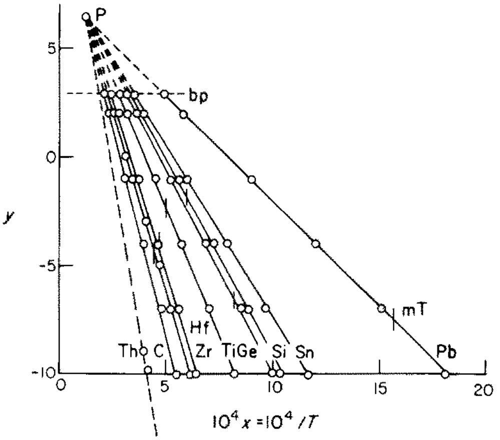

FIG. 8. Group IV.

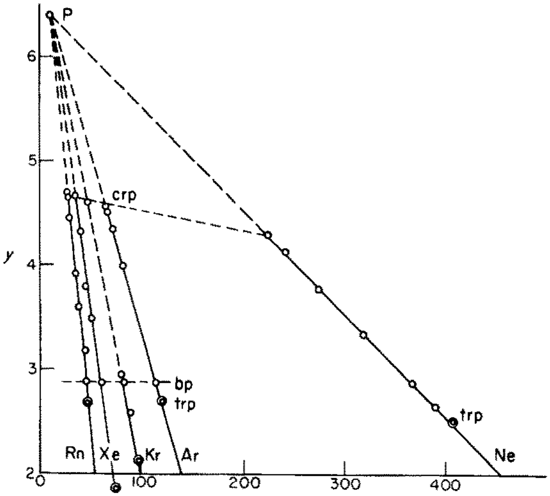

FIG. 9. Rare gases.

In fact groups I, III, VII and VIII are divided in subgroups.

In the IV Group values of C. Zwikker [3] for Hf and of A. J. Darnell [4] for Th are adopted.

In the group I, V, VI the convergence in their poles is not verified for biatomic gases, as respectively for normal hydrogen (75 per cent of ortho-hydrogen), N_2 and O_2.

Let us set:

$$y = \log p; \qquad x = \frac{1}{T} \tag{1}$$

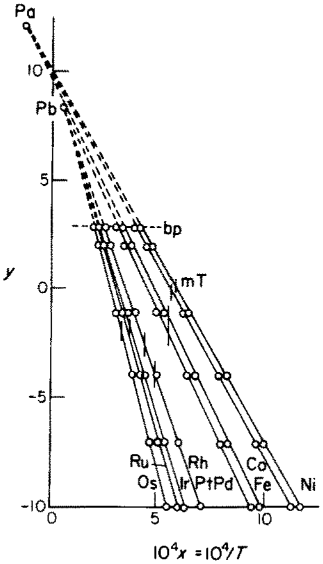

FIG. 10. Group VIII.

The Table 1 gives the values of y_p and x_p of poles P for various group and subgroups.

The numerical values of Table 1 are given with the approximation permitted by the graphical method, however for very large intervals of parameters y and x. This approximation is also, in many cases, about the same permitted by experimental methods.

The points cr p (critical point), b p (boiling point), tr p (triple point) and also little vertical lines for m T (melting temperature) are indicated on the curves.

In the figure of rare-earth elements the lines of Ce according to A. H. Daane [5], of Pr according to D. H. Ahmann [6] and also the unique experimental point, given by K. W. Foster [7] for Ac, are indicated.

The pressures for ly and Er have been calculated from the values of heats of evaporation, as it is shown in the following paragraph.

Other results are given in Fig. 11 for Ne, normal H_2 and He.

Table 1. *Coordinates of poles* P

	Group	y_p	x_p
I_a	—Li—Na—K—Rb—Cs—Fr	6	$2{\cdot}4 \times 10^{-4}$
I_b	—Cu—Ag—Au	9	$-0{\cdot}2 \times 10^{-4}$
II_a	—Be—Mg—Ca—Sr—Ba—Ra	8	$0{\cdot}6 \times 10^{-4}$
II_b	—Zn—Cd—Hg	8	$0{\cdot}6 \times 10^{-4}$
III_a	—B—Al—Sc—Y—La	7·4	$0{\cdot}9 \times 10^{-4}$
III_b	—Ga—In—Tl	7·4	$0{\cdot}9 \times 10^{-4}$
III_c	—Ce—Sm—Eu—Gd—Tm—Yb—Lu —Ac	7·2	$1{\cdot}2 \times 10^{-4}$
IV_a	—Ti—Zr—Hf—Th	6·5	$1{\cdot}3 \times 10^{-4}$
IV_b	—C_1—Si—Ge—Sn—Pb	6·5	$1{\cdot}3 \times 10^{-4}$
V_a	—V—Nb—Ta—Pa	8	$0{\cdot}6 \times 10^{-4}$
V_b	—P—As—Sb—Bi	8	$0{\cdot}6 \times 10^{-4}$
VI_a	—Cr—Mo—W—V	7·8	$0{\cdot}7 \times 10^{-4}$
VI_b	—S—Se—Te—Po	7·8	$0{\cdot}7 \times 10^{-4}$
VII_a	—Mn—Ma—Re	8·2	$0{\cdot}5 \times 10^{-4}$
VII_b	—F_2—Cl_2—Br_2—J_2—At_2	6·7	12×10^{-4}
VIII_a	—Fe—Co—Ni	12	$-1{\cdot}3 \times 10^{-4}$
VIII_b	—Ru—Rh—Pd—Os—Ir—Pt	8·3	$0{\cdot}6 \times 10^{-4}$
0)	—Ne—Ar—Kr—Xe—Rn	6·4	10×10^{-4}

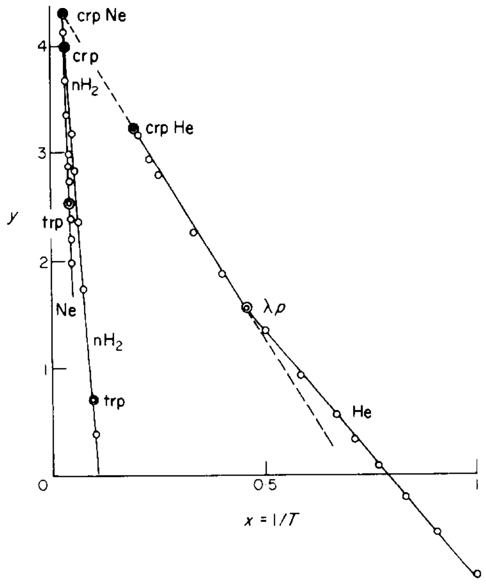

FIG. 11.

The polar property of vapor pressures although not rigorous, is certainly useful to fill lacking informations*, to sever discordant experimental data, to induce value of thermodynamical parameters which are dependent from the law of pressures as heats of evaporation and specific heats.

So, from known relations, neglecting little terms:

$$\log_{10} p = A - \frac{B}{T} \tag{2}$$

(A, B constants)

$$\frac{r}{T} = (v_s - v_l)\frac{\mathrm{d}p}{\mathrm{d}T} \tag{3}$$

(r heat of evaporation, v_s, v_l orthobaric volumes of vapor and liquid, or solid)

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* Perhaps also for transuranium elements.

and when:

$$v_s \gg v_i \tag{4}$$

$$v_s = \frac{RT}{mp} \tag{5}$$

(R universal constant of gases, m mole) we have:

$$\frac{\mathrm{d}p}{p} = \frac{mr}{R}\frac{\mathrm{d}T}{T^2} \tag{6}$$

and from the equation (2):

$$B = \frac{mr}{2{,}302\,R}. \tag{7}$$

For the points P and M (chosen distant from P) we have:

$$y_P = A - Bx_P; \qquad y_M = A - Bx_M \tag{8}$$

and therefore:

$$B = \frac{y_P - y_M}{x_M - x_P}; \qquad A = y_P + Bx_P. \tag{9}$$

For instance, for the rare gases of the atmosphere and putting $y_M = +2$ we obtain the results given by Table 2.

Table 2. *Values of* A *and* B *for rare gases*

Element	x_M	A	B
Ne	456×10^{-4}	6·5	98
Ar	140×10^{-4}	6·7	338
Kr	100×10^{-4}	6·9	490
Xe	73×10^{-4}	7·1	700
Rn	55×10^{-4}	6·5	980

In the Table 3 values of r for the same rare gases, deduced from the equation (7), are compared with those indicated by F. Henning [2] for the corresponding boiling points.

The difference $(c_s - c_i)$ is given by:

$$c_s - c_i = \frac{\mathrm{d}r}{\mathrm{d}T} - \frac{r}{T}. \tag{10}$$

Table 3. *Values of* r *for rare gases*

Element	m	(cal /g)	r (Henning)
Ne	39·94	22·2	25
Ar	20·18	38·7	37·6
Kr	83·7	26·7	28
Xe	131·3	24·3	23
Rn	222	20·6	—

Neglecting, for boiling points, the term $(\mathrm{d}r/\mathrm{d}T)$, we obtain:

	Ne	Ar	Kr	Xe	Rn	
$c_s - c_i =$	0·50	0·25	0·13	0·09	(0·07)	cal/(g°K)

The Table 4 give values of x_M, A, B for rare-earth elements, excepting for Pm, Te, Ho for which no experimental data are given.

For Pr, Dy, Er the above mentioned constants have been derived from experimental values of heats of evaporation (respectively 79–69–63 cal/g atom) given by Professor Nesmeyanov.

Table 4. *Values of* A *and* B *for rare-earth elements*

Element	x_M	A	B
Ce	$9{\cdot}3 \times 10^{-4}$	9·7	$2{\cdot}12 \times 10^4$
Pr	$11{\cdot}2 \times 10^{-4}$	9·3	$1{\cdot}72 \times 10^4$
Nd	$11{\cdot}2 \times 10^{-4}$	9·2	$1{\cdot}72 \times 10^4$
Sm	$17{\cdot}3 \times 10^{-4}$	8·5	$1{\cdot}07 \times 10^4$
Eu	$19{\cdot}9 \times 10^{-4}$	8·3	$0{\cdot}92 \times 10^4$
Gd	$17{\cdot}5 \times 10^{-4}$	8·5	$2{\cdot}05 \times 10^4$
Dy	$12{\cdot}7 \times 10^{-4}$	9·0	$1{\cdot}50 \times 10^4$
Er	$12{\cdot}1 \times 10^{-4}$	9·1	$1{\cdot}58 \times 10^4$
Tm	$15{\cdot}5 \times 10^{-4}$	8·6	$1{\cdot}20 \times 10^4$
Yb	$21{\cdot}3 \times 10^{-4}$	8·2	$0{\cdot}86 \times 10^4$
Lu	$11{\cdot}9 \times 10^{-4}$	9·1	$1{\cdot}61 \times 10^4$
Ac	$11{\cdot}8 \times 10^{-4}$	9·1	$1{\cdot}62 \times 10^4$

Another example of regularity of values of constants is given, for alkali-metals, in the Table 5.

To permit calculations of constant A and B in all cases, together with Table 1, the Table 6 gives values of x_M corresponding (with some exceptions) to the value -10 for y_M.

Table 5. Values of A *and* B *for alkali-metals*

Element	x_M	A	B
Li	22·2 × 10^{-4}	7·94	8·07 × 10^{3}
Na	32·4 × 10^{-4}	7·28	5·33 × 10^{3}
K	38·1 × 10^{-4}	7·07	4·48 × 10^{3}
Rb	41·8 × 10^{-4}	6·98	4·06 × 10^{3}
Cs	44·0 × 10^{-4}	6·92	3·85 × 10^{3}
Fr	48·6 × 10^{-4}	6·83	3·46 × 10^{3}

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Table 6. Values of x_M *for* $y_M = -10$

Group I		Group II		Group III		Group IV		Group V		Group VI		Group VII		Group VIII	
Li	22·2 × 10^{-4}	Be	11·5 × 10^{-4}	B	6·8 × 10^{-4}	C_1	5·6 × 10^{-4}	P_4	64·0 × 10^{-4}	S	16·1 × 10^{-4}	F_2	(198 × 10^{-4} a 1 Torr)	Fe	9·8 × 10^{-4}
Na	32·4 × 10^{-4}	Mg	24·6 × 10^{-4}	Al	12·1 × 10^{-4}	Si	10·5 × 10^{-4}	As	13·4 × 10^{-4}	Se	18·3 × 10^{-4}	Cl_2	(97 × 10^{-4} a 10^{-4} Torr)	Co	11·3 × 10^{-4}
K	38·1 × 10^{-4}	Ca	20·4 × 10^{-4}	Ga	13·3 × 10^{-4}	Ge	10·2 × 10^{-4}	Sb	14·4 × 10^{-4}	Po	28·2 × 10^{-4}	Br_2	(61·3 × 10^{-4} a 10^{-4} Torr)	Ni	11·7 × 10^{-4}
Rb	41·8 × 10^{-4}	Sr	21·9 × 10^{-4}	In	15·1 × 10^{-4}	Sn	11·7 × 10^{-4}	Bi	20·4 × 10^{-4}	Cr	10·3 × 10^{-4}	I_2	62 × 10^{-4}	Ru	6·0 × 10^{-4}
Cs	44·0 × 10^{-4}	Ba	20·1 × 10^{-4}	Tl	20·2 × 10^{-4}	Pb	18·1 × 10^{-4}	V	7·7 × 10^{-4}	Mo	5·9 × 10^{-4}	At_2	42·5 × 10^{-4}	Rh	7·1 × 10^{-4}
Fr	48·6 × 10^{-4}	Ra	21·6 × 10^{-4}	Sc	11·3 × 10^{-4}	Ti	8·3 × 10^{-4}	Nb	5·5 × 10^{-4}	W	4·6 × 10^{-4}	Mn	13·5 × 10^{-4}	Pd	9·4 × 10^{-4}
Cu	11·1 × 10^{-4}	Zn	28·0 × 10^{-4}	Yt	10·1 × 10^{-4}	Zr	6·4 × 10^{-4}	Ta	5·0 × 10^{-4}	V	7·9 × 10^{-4}	Te	6·0 × 10^{-4}	Os	5·5 × 10^{-4}
Ag	13·2 × 10^{-4}	Cd	32·2 × 10^{-4}	La	8·8 × 10^{-4}	Hf	6·3 × 10^{-4}	Pa	8·8 × 10^{-4}			Re	5·0 × 10^{-4}	Ir	6·4 × 10^{-4}
Au	10·3 × 10^{-4}	Hg	54·5 × 10^{-4}	(v. Tab. n. 4)		Th	4·2 × 10^{-4}							Pt	7·1 × 10^{-4}

PRESSION DE VAPEUR ET CLASSIFICATION PÉRIODIQUE DES ÉLÉMENTS CHIMIQUES

Résumé—La classification périodique des éléments chimiques a de remarquables conséquences sur leurs propriétés thermodynamiques. On montre en particulier sur le diagramme (log p), ($1/T$) que pour chaque groupe ou sous-groupe de la classification de Mendeleev, les lignes de pression de vapeur p des éléments chimiques équiatomiques ont un point de convergence bien déterminé. Pour chaque groupe ou sous-groupe il existe une équation unique, dans laquelle l'élément simple est représenté par les coordonnées d'un point. Cette règle nouvelle, même avec quelques exceptions et approximations, peut combler certaines lacunes dans les informations pour séparer les résultats expérimentaux discordants et pour induire les valeurs des paramètres d'évaporation et leschaleurs spécifiques.

On donne des exemples numériques concernant les terres rares et les gaz rares dans l'atmosphère.

DAMPFDRUCK UND PERIODISCHE ORDNUNG DER ELEMENTE

Zusammenfassung—Die periodische Ordnung der chemischen Elemente hat bemerkenswerte Konsequenzen auch bezüglich der thermodynamischen Eigenschaften. In diesem Bericht wird im besonderen gezeigt, dass in Diagrammen für (log p), ($1/T$) die Linien des Dampfdruckes p der gleichatomigen chemischen Elemente, für jede Gruppe oder Untergruppe der Mendeleevchen Einteilung, einen Konvergenzpunkt haben der hinreichend bestimmt ist. Für jede Gruppe oder Untergruppe ist dann eine einzige Gleichung ausreichend, in der das einzelne Element durch die Koordinaten nur eines Punktes wiedergegeben wird.

Diese neue Regel könnte in der Lage sein, mit einigen Ausnahmen und Näherungen, fehlende Informationen zu geben, widersprechende experimentelle Ergebnisse auszusondern und Werte thermodynamischer Parameter anzuführen, die abhängig sind vom Druckgesetz, wie die Verdampfungswärme und die spezifische Wärme.

Numerische Beispiele werden durchgeführt an Elementen der seltenen Erden und den Spurengasen der Atmosphäre.

ДАВЛЕНИЕ ПАРА И ПЕРИОДИЧЕСКАЯ КЛАССИФИКАЦИЯ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ

Аннотация—Периодическая классификация химических элементов оказывает заметное влияние на их термодинамические свойства. В частности, в этой статье показано, что на диаграмме (*log* P), ($1/T$) линии давления пара химических элементов одинаковой атомности (для каждой группы или подгруппы таблицы Менделеева) сходятся в одной вполне определенной точке. Тогда, для каждой группы или подгруппы имеется единственное уравнение, в котором отдельный элемент представлен координатами только одной точки.

Даже при некоторых исключениях и приближениях это новое правило позволит восполнить недостаток информации, исключить несогласующиеся экспериментальные данные, определить значения термодинамических параметров, зависящих от закона давления, как например, теплота испарения и удельная теплоемкость.

Даются численные примеры для редкоземельных элементов и благородных газов атмосферы.