

whereas heat energy requires yet a third factor, such as entropy. The equation for the kinetic energy content of gaseous molecules was given by Clerk Maxwell and is of the order

$$E = \frac{Nm}{\sigma^3} \sqrt{\frac{1}{2\pi}} \int_0^\infty x^4 \exp. - x^2/2\sigma^2 dx,$$

where  $x$  is the molecular velocity,  $N$  the number of molecules,  $m$  the mass of one molecule and  $\sigma$  the standard, or root mean square (R.M.S.), deviation of the distribution. This equation integrates to  $3/2 Nm\sigma^2$  and gives the work energy of the molecules. The heat energy can be determined from temperature  $\times$  mass of molecules  $\times$  entropy. The mean temperature (or velocity) is obtained by the integration of

$$U = \frac{2}{\sigma^3} \sqrt{\frac{1}{2\pi}} \int_0^\infty x^3 \exp. - x^2/2\sigma^2 dx,$$

which gives  $\frac{2\sqrt{2}}{\sqrt{\pi}}\sigma$ . Hence the heat energy is  $\frac{2\sqrt{2}}{\sqrt{\pi}}\sigma NmS$  and this is equal to the work energy, giving the entropy:

$$S = \frac{3\sqrt{\pi}}{4\sqrt{2}} \sigma \text{ or } S = 0.91 \sigma.$$

Entropy thus varies with the standard deviation, that is, high entropy corresponds to a flat probability curve. The probability of a velocity lying between the values of  $x$  and  $x + dx$  is proportional to  $\exp. - x^2/2\sigma^2$ . This indicates that the logarithm of the probability is inversely proportional to the standard deviation, or entropy.

The kinetic energy equation given above indicates that the most convenient temperature (or velocity, or  $x$ )-scale associated with the standard deviation (or entropy) should be logarithmic compared with the energy content. Lewis and Gibson<sup>3</sup> showed the connexion between the specific heat of solids and the log  $T$  (or  $D$ )-scale; and the use of the percentage deviation, or  $100 S/T$ , should form a measure of the accuracy of the values for entropy.

The question of the free energy release in a chemical reaction (omitting for the sake of simplicity, as before, all questions of constant pressure and constant column) can be summed up as follows. It has been shown experimentally that the driving force tending to make a reaction go in any one direction is the free energy, or work energy, which is released by the system. The release of heat energy, or the heat of the reaction  $\Delta H$ , is not a true guide. A method of determining the free energy change  $\Delta G$  is by the use of the equation

$$\Delta G = \Delta H - T\Delta S,$$

where  $\Delta S$  is the change in entropy.

If compounds  $A$  and  $B$  with entropies  $S_a$  and  $S_b$  are mixed, this is equivalent to adding two distribution curves; and since entropy is a function of the standard deviation, it is therefore permissible to add the entropies. At a given temperature when the reaction takes place the total change in entropy will be  $(S_a + S_b) - (S_c + S_d)$ . This is tantamount to saying that if the true measure of the potential of a chemical reaction is the free energy change (which for convenience is often expressed in heat units), then the final result from the heat change (heat of reaction) point of view can vary considerably from the work change value in either direction, depending upon whether the spread of the molecular velocities of the products is greater or less than those of the reacting molecules.

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<sup>1</sup> Dalton, John, "New System of Chemical Philosophy" (Part 1, 1808). Thomson, W., *Camb. Phil. Soc.* (1848); *Phil. Mag.*, **33**, 313 (1848); Collected "Papers", 1, 106 note (1882). Schreiber, K., *Ann. Physik.*, **64**, 163 (1898). Plank, R., *Forschungs.*, B, *Ver. deut. Ing.*, **4**, 282 (1933).

<sup>2</sup> Stern, O., *Z. Phys.*, **2**, 48 (1920). Zartman, I. F., *Phys. Rev.*, **37**, 383 (1931).

<sup>3</sup> Lewis, G. N., and Gibson, J. *Amer. Chem. Soc.*, **30**, 2554 (1917).

### Metastable Forms of Ice Produced by Super-cooled Water

In connexion with a recent letter<sup>1</sup> which describes these forms, it should be noted that the rule of successive states<sup>2</sup> would predict the preferential crystallization of the *least* stable solid state, in the absence of nuclei.

It may lead to confusion to refer to the ice separating at  $-70^\circ\text{C}$ . as a 'low-temperature form', since it frequently happens, owing to the operation of the above rule, that the metastable form which crystallizes most easily from melt or solution would in fact be the form which is stable at higher temperatures. For example, in the absence of nuclei, metastable  $\beta$  resorcinol (the 'high temperature form') separates from solution at low temperatures<sup>3</sup>.

A consideration of the rule of successive states may explain the high symmetry of the crystal form of ice which separates at  $-70^\circ\text{C}$ . in the absence of nuclei, as the production of this form from super-cooled water might be expected to involve a smaller negative entropy of activation than less symmetrical crystal forms.

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<sup>1</sup> Frank, F. C., *Nature*, **157**, 267 (1946). See also *Nature*, **157**, 449 (1946).

<sup>2</sup> Ubbelohde, A. R., *Trans. Faraday Soc.*, **33**, 1203 (1937).

<sup>3</sup> Robertson, J. M., and Ubbelohde, A. R., *Proc. Roy. Soc.*, A, **167**, 141 (1938).

### Geochemistry of Magmatic Iron Ore

CONSIDERING the percentage of certain constituents in olivine and clinopyroxene separated from rocks of the Skaergaard intrusion, Greenland, L. R. Wager and R. L. Mitchell<sup>1</sup> determined, for these minerals, data which show a lower concentration of vanadium, chromium, nickel, magnesium (plus titanium and phosphorus in the case of vanadium?, compare below), and a higher iron concentration the later the mineral was formed during the crystallization differentiation of the ancient Skaergaard magma. Comparing olivine and clinopyroxene containing similar relative concentrations of magnesium and iron, the former mineral is seen to be richer in chromium, cobalt and nickel than the latter, whereas the latter is seen to be richer in vanadium (plus titanium?, compare below) than the former.

The late, ultra-basic rock (extremely poor in chromium) of Eastern Uppland, Sweden, earlier mentioned in *Nature*<sup>2</sup> is characterized by the following mafic minerals (from earliest to latest, concentrations given in parts per million):

	Olivine (Fe <sub>2</sub> SiO <sub>4</sub> = 20%, Mg > Fe)	Clinopyroxene (FeSiO <sub>3</sub> = 30-35%, Mg > Fe)	Titano-magnetite (Fe <sub>2</sub> (Fe,Ti)O <sub>4</sub> = 99%, very little Mg present)
Ti	<100	<100	70,000
V	50	300	7,000
Cr	6	5	<0.5
Co	250	130	50
Ni	550	50	<0.5

Comparing olivine and clinopyroxene, we find a distribution of the actual trace elements which is roughly similar to that displayed by the Skaergaard rocks (apart from chromium in olivine). Moreover, it is interesting to get established the existence of magmatic iron oxide ore lacking chromium plus nickel and, contemporaneously, showing quite a low cobalt content. It is also interesting to trace once again the affinity of titanium and vanadium to iron oxide ore separated from gabbroic magma.

The most remarkable tendency displayed by these data is, however, the decrease in chromium, cobalt and nickel contemporaneously with the decrease of magnesium and the increase of iron. In the Skaergaard rocks and minerals<sup>1,2</sup>, as well as in several magmatic differentiates from Eastern Uppland<sup>3</sup>, we have already seen that vanadium, chromium, nickel and, finally, cobalt, vanish together with magnesium. According to crystallo-chemical experience, vanadium may be saved from such disappearance by the presence of titanium or (and) phosphorus (compare the above-mentioned titano-magnetite). The remaining elements just considered show no similar 'loop-hole', however. Thus, their existence or non-existence in a rock belonging to a normal suite of magmatic differentiates depends upon the contemporaneous existence or absence of magnesium.

The higher the magnesium (plus titanium or/and phosphorus in the case of vanadium) content, the lower is the iron and the higher the vanadium, chromium, cobalt and nickel. This seems to be a very important rule concerning any series of normal magmatic differentiates. The following sequence of magmatic rocks from the skerries south-east of Stockholm illustrates it very well (all concentrations are given in parts per million):

	Quartz-diorite	Porphyritic gneiss-granite rich in microcline	Gneiss-granite	Pyroxene-bearing gneiss-granite
SiO <sub>2</sub>	573,200	662,800	679,100	715,600
Mg	25,000	6,000	3,400	2,100
Fe	58,500	33,000	46,500	33,000
Ti	3,500	3,000	3,800	1,900
P	1,100	,500	,500	,200
V	,200	,35	<2.5	0
Cr	10	4	1.0	<0.3
Co	40	1.0	<0.5	0
Ni	25	2.0	1.0	<0.2
Mg : Fe	0.43	0.18	0.073	0.064

In order to test the rule just mentioned, I separated magnetite from two typical pegmatites of eastern Sweden, each of which belongs to a suite of differentiated magmatic rocks showing normal contents of titanium, phosphorus, vanadium, chromium, cobalt and nickel when magnesium is present in, at least, moderate quantities. The results are as follows: (a) magnetite, south-east part of the Stockholm skerries, titanium, 8,000 p.p.m.; vanadium, 150 p.p.m.; chromium, weak trace; cobalt, weak trace, nickel, 0; (b) magnetite, central Roslagen, eastern Uppland, titanium, 10,000 p.p.m.; vanadium, 100 p.p.m.; chromium, weak trace; cobalt, weak trace; nickel, weak trace. In both species, most phosphorus was removed during the separation. Thus it is evident that vanadium follows titanium here.

As a consequence of a rule concerning normal magmatic differentiates as well as by means of a few examples, I have now established in the crust the real existence of magmatic iron oxide ore very poor in, or lacking, chromium, cobalt and nickel and separated from basic as well as acid magma portions.

Turning to magmatic iron sulphide ore, similar results have been found for nickel (no data on vanadium, chromium and cobalt are at present available). A great many analyses on Swedish pyrrhotite (pyrite in a few cases) associated with medium and late stages of the basic part of magmatic differentiation (iron greater than magnesium, pyroxene-gabbros especially) never fail to show a deficiency of nickel. On the contrary, a few samples of pyrrhotite separated from early gabbros (magnesium greater than iron, olivine-gabbros) display high nickel contents.

A concrete example of this is (a) pyrrhotite separated from early gabbro from Boden, northern Sweden, Ni : S = 60 : 1,000, olivine present; (b) pyrrhotite separated from late gabbro belonging to the same suite of rocks as the early gabbro mentioned in (a) Ni : S = 7 : 1,000, no olivine present.