CHAPTER 9

GRAVITATIONAL FIELD

§9.01 *Nature of gravitational field*

The formulae of chapter 1 are easily extended so as to take account of the presence of a gravitational field. Such a field is characterized by a gravitational potential Φ with a definite value at each place. The modification of the gravitational field by the presence of matter in amounts dealt with in ordinary chemical and physical processes is completely negligible compared with the earth's field or any other field of comparable importance. We may therefore regard the gravitational field as completely independent of the state of the thermodynamic system considered. In this sense, we call the gravitational field an *external field*, and regard the gravitational potential at each point as independent of the presence or state of any matter there. It is owing to this fact that, although the abstract theories of gravitational potential and electrostatic potential are in some ways parallel, yet their significance for thermodynamic systems is different.

§9.02 *Phases in gravitational field*

Since a phase was defined as completely homogeneous in its properties and *state*, two portions of matter of identical temperature and composition will be considered as different phases if they are differently situated with respect to a gravitational field. It follows that the mere presence of a gravitational field excludes the possibility of a phase of finite depth in the direction of the field. In the presence of a gravitational field even the simplest possible kind of system must be considered as composed of a continuous sequence of phases each differing infinitesimally from its neighbours.

§9.03 *Thermodynamic functions in gravitational field*

The characteristic property of the gravitational potential is that the work w required to bring a quantity of matter of mass m from a place where the potential is Φ^{α} to a place where it is Φ^{β} is given by

$$w=m(\Phi^{\beta}-\Phi^{\alpha}) \qquad 9.03.1$$

thus depending on the mass but not on the chemical nature of the matter. In transferring an amount $\mathrm{d}n_i$ of the species i from the phase α to the phase β, the gravitational work is

$$(\Phi^{\beta}-\Phi^{\alpha})M_i\mathrm{d}n_i \qquad 9.03.2$$

where M_i is the proper mass of the species i. Thus formula (1.27.2) for $\mathrm{d}U^{\alpha}$ must for each phase α contain the extra terms $\Sigma_i\Phi^{\alpha}M_i\mathrm{d}n_i^{\alpha}$. That is to say

$$\mathrm{d}U^{\alpha}=T^{\alpha}\mathrm{d}S^{\alpha}-P^{\alpha}\mathrm{d}V^{\alpha}+\sum_i(\mu_i^{\alpha}+M_i\Phi^{\alpha})\mathrm{d}n_i^{\alpha} \qquad 9.03.3$$

whence follows directly

$$\mathrm{d}G^{\alpha}=-S^{\alpha}\mathrm{d}T^{\alpha}+V^{\alpha}\mathrm{d}P^{\alpha}+\sum_i(\mu_i^{\alpha}+M_i\Phi^{\alpha})\mathrm{d}n_i^{\alpha}. \qquad 9.03.4$$

It follows that to take account of the effect of a gravitational field one has merely to replace μ_i^{α} throughout by $\mu_i^{\alpha}+M_i\Phi^{\alpha}$.

Although in all thermodynamic formulae the quantity Φ^{α} occurs only in combinations of the form $\mu_i^{\alpha}+M_i\Phi^{\alpha}$, yet the gravitational potential difference $\Phi^{\beta}-\Phi^{\alpha}$ between two phases α and β, in contrast to the electric potential difference $\psi^{\beta}-\psi^{\alpha}$, is thermodynamically determinate owing to the fact that its value is independent of the presence and nature of the phase there. The phase may therefore be removed without altering Φ and then $\Phi^{\beta}-\Phi^{\alpha}$ can be determined in empty space by direct mechanical measurements.

§9.04 *Equilibrium in gravitational field*

For the equilibrium as regards the species i between two phases α and β defined not merely by their temperature, pressure, and composition, but also by their gravitational potentials, we have in analogy with (1.39.5) the general condition

$$\mu_i^{\alpha}+M_i\Phi^{\alpha}=\mu_i^{\beta}+M_i\Phi^{\beta} \qquad \text{(equilibrium).} \qquad 9.04.1$$

§9.05 *Dependence of μ_i on T and P*

Observing that M_i and Φ^{α} are independent of T^{α} and P^{α}, we obtain, dropping the superscript $^{\alpha}$ throughout,

$$\partial\mu_i/\partial T = \partial^2 G/\partial n_i \partial T = -\partial S/\partial n_i = -S_i \qquad 9.05.1$$

$$\partial\mu_i/\partial P = \partial^2 G/\partial n_i \partial P = \partial V/\partial n_i = V_i \qquad 9.05.2$$

precisely the same as in the absence of a gravitational field.

§9.06 *Single component in gravitational field*

For the equilibrium of a single component i in a gravitational field we have according to (9.04.1)

$$\mathrm{d}\mu_i + M_i \mathrm{d}\Phi = 0 \qquad 9.06.1$$

or at constant temperature using (9.05.2)

$$V_i \mathrm{d}P + M_i \mathrm{d}\Phi = 0 \qquad (T \text{ const.}). \qquad 9.06.2$$

If ϱ denotes the density, then

$$\varrho_i = M_i / V_i. \qquad 9.06.3$$

Substituting (3) into (2) we obtain

$$\mathrm{d}P = -\varrho_i \mathrm{d}\Phi \qquad 9.06.4$$

in agreement with the general condition of hydrostatic equilibrium.

In the case of a single perfect gas we have

$$V_i = RT/P. \qquad 9.06.5$$

Substituting (5) into (2) we obtain

$$RT \mathrm{d} \ln P + M_i \mathrm{d}\Phi = 0 \qquad 9.06.6$$

and by integration

$$RT \ln(P^\beta / P^\alpha) = M_i(\Phi^\alpha - \Phi^\beta) \qquad 9.06.7$$

or

$$P^\beta / P^\alpha = \exp\{-M_i(\Phi^\beta - \Phi^\alpha)/RT\}. \qquad 9.06.8$$

For a liquid, on the other hand, neglecting compressibility and so treating V_i as independent of P, we can integrate (2) immediately obtaining

$$V_i(P^\beta - P^\alpha) = M_i(\Phi^\alpha - \Phi^\beta). \qquad 9.06.9$$

Alternatively integrating (4) we obtain

$$P^\beta - P^\alpha = \varrho_i(\Phi^\alpha - \Phi^\beta). \qquad 9.06.10$$

§9.07 *Mixture in gravitational field*

For the equilibrium of each species i of a mixture in a gravitational field we have according to (9.04.1)

$$\mathrm{d}\mu_i + M_i \mathrm{d}\Phi = 0. \qquad 9.07.1$$

Using (9.05.2) we obtain at constant temperature

$$\mathrm{D}\mu_i + V_i \mathrm{d}P + M_i \mathrm{d}\Phi = 0 \qquad (T \text{ const.}) \qquad 9.07.2$$

where D denotes $\Sigma_i \mathrm{d}x_i(\partial/\partial x_i)_{T,P}$. But according to the Gibbs–Duhem relation we have

$$\sum_i x_i \mathrm{D}\mu_i = 0. \qquad 9.07.3$$

Multiplying (2) by x_i, summing over all species i, and using (3) we obtain

$$\sum_i x_i V_i \mathrm{d}P + \sum_i x_i M_i \mathrm{d}\Phi = 0. \qquad 9.07.4$$

Introducing the proper volume V_m and the proper mass M_m given respectively by

$$V_\mathrm{m} = \sum_i x_i V_i \qquad 9.07.5$$

$$M_\mathrm{m} = \sum_i x_i M_i \qquad 9.07.6$$

we can write (4) as

$$V_\mathrm{m} \mathrm{d}P + M_\mathrm{m} \mathrm{d}\Phi = 0. \qquad 9.07.7$$

But the density ϱ is related to V_m, M_m, by

$$\varrho = M_\mathrm{m}/V_\mathrm{m}. \qquad 9.07.8$$

Substituting (8) into (7), we recover the usual condition of hydrostatic equilibrium

$$\mathrm{d}P = -\varrho \mathrm{d}\Phi. \qquad 9.07.9$$

If we substitute for dP from (7) into (2), we obtain

$$\mathrm{D}\mu_i + (M_i - V_i M_\mathrm{m}/V_\mathrm{m})\mathrm{d}\Phi \qquad 9.07.10$$

or, according to (8),

$$\mathrm{D}\mu_i + (M_i - \varrho V_i)\mathrm{d}\Phi = 0. \qquad 9.07.11$$

The differential equations of this section can be integrated only in certain exceptionally simple cases which we shall consider in turn.

§9.08 *Mixture of gases*

For a mixture of perfect gases it is possible to integrate (9.07.2), but the same result can be obtained as follows. For any component i in two gaseous mixtures α, β at the same temperature T, we have

$$\mu_i^\beta - \mu_i^\alpha = RT \ln(p_i^\beta / p_i^\alpha) \qquad 9.08.1$$

where p_i^α and p_i^β are the fugacities in the two phases.

Substituting (1) into (9.04.1) we obtain as the equilibrium condition for the species i in a gravitational field

$$RT \ln(p_i^\beta / p_i^\alpha) = M_i(\Phi^\alpha - \Phi^\beta) \qquad 9.08.2$$

or

$$p_i^\beta / p_i^\alpha = \exp\{-M_i(\Phi^\beta - \Phi^\alpha)/RT\}. \qquad 9.08.3$$

If we differentiate (2) we obtain

$$\mathrm{d}p_i / p_i = -(M_i/RT)\mathrm{d}\Phi. \qquad 9.08.4$$

If the gas mixture is perfect then using

$$p_i = y_i RT / V_\mathrm{m} \qquad 9.08.5$$

we can rewrite (4) as

$$\mathrm{d}p_i = -(y_i M_i / V_\mathrm{m})\mathrm{d}\Phi. \qquad 9.08.6$$

Summing (6) over all species i, we obtain

$$\mathrm{d}P = -(M_\mathrm{m}/V_\mathrm{m})\mathrm{d}\Phi = -\varrho\, \mathrm{d}\Phi \qquad 9.08.7$$

thus verifying that (2) and (3) are consistent with hydrostatic equilibrium.

§9.09 *Ideal dilute solutions*

In the case of an ideal dilute solution we may replace (9.07.10) for each solute species s by

$$RT\mathrm{d} \ln m_s + (M_s - V_s M_\mathrm{m}/V_\mathrm{m})\mathrm{d}\Phi = 0. \qquad 9.09.1$$

In the limit of *extreme dilution* we may replace $M_\mathrm{m}/V_\mathrm{m}$ by M_1/V_1^0, where the superscript ^{0} relates to the pure solvent, and obtain

$$RT\mathrm{d} \ln m_s + (M_s - V_s M_1/V_1^0)\mathrm{d}\Phi = 0. \qquad 9.09.2$$

Neglecting compressibility, this can be integrated directly, giving

$$m_s^\beta / m_s^\alpha = \exp\{-(M_s - V_s M_1/V_1^0)(\Phi^\beta - \Phi^\alpha)/RT\}. \qquad 9.09.3$$

§9.10 *Chemical reaction in gravitational field*

For the chemical reaction

$$0=\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mathrm{B} \qquad 9.10.1$$

the most general form for the condition of equilibrium in the absence of a gravitational field is

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mu_{\mathrm{B}}=0. \qquad 9.10.2$$

In the presence of a gravitational field the corresponding equilibrium condition is evidently

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}}(\mu_{\mathrm{B}}+M_{\mathrm{B}}\Phi)=0. \qquad 9.10.3$$

But owing to the conservation of mass we have

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}}M_{\mathrm{B}}=0. \qquad 9.10.4$$

Multiplying (4) by Φ and subtracting from (3) we recover (2). It follows that any chemical equilibrium constant is independent of the gravitational potential or in other words is unaffected by the presence of a gravitational field.