# 11

# THE NERNST POSTULATE

## 11-1 NERNST'S POSTULATE, AND THE PRINCIPLE OF THOMSEN AND BERTHELOT

One aspect of classical thermodynamics remains. That is the exploration of the consequences of postulate IV, to the effect that the entropy vanishes at zero temperature.

The postulate as first formulated by Walther Nernst in 1907 was somewhat weaker than our postulate IV, stating only that the entropy *change* in any isothermal process approaches zero as the temperature approaches zero. The statement that we have adopted emerged several decades later through the work of Francis Simon and the formulation of Max Planck; it is nevertheless referred to as the Nernst postulate. It is also frequently called the "third law" of thermodynamics.

Unlike the other postulates of the formalism, the Nernst postulate is not integral to the overall structure of thermodynamic theory. Having developed the theory almost in its entirety, we can now simply append the Nernst postulate. Its implications refer entirely to the low-temperature region, near $T = 0$.

The historical origins of the Nernst theorem are informative; they lie in the "principle of Thomsen and Berthelot"—an empirical (but nonrigorous) rule by which chemists had long predicted the equilibrium state of chemically reactive systems.

Consider a system maintained at constant temperature and pressure (as by contact with the ambient atmosphere), and released from constraints (as by mixture of two previously separated chemical reactants). According to the empirical rule of Thomsen and Berthelot, the equilibrium state to which the system proceeds is such that the accompanying process evolves the greatest efflux of heat, or, in the more usual language, "the process is realized that is most exothermic."

The formal statement of this empirical rule is most conveniently put in terms of the enthalpy. We recall that in isobaric processes the enthalpy acts as a potential for heat, so that the total heat efflux is

$$\text{heat efflux} = H_{\text{initial}} - H_{\text{final}} \tag{11.1}$$

The statement of Thomsen and Berthelot therefore is equivalent to the statement that the equilibrium state is the one that maximizes $H_{\text{initial}} - H_{\text{final}}$, or minimizes $H_{\text{final}}$.

The *proper* criterion of equilibrium at constant temperature and pressure is, of course, the minimization of the Gibbs potential. Why then should these two differing criteria provide similar predictions at low temperatures (and, in fact, sometimes even at or near room temperature)?

In an isothermal process

$$\Delta G = \Delta H - T\Delta S \tag{11.2}$$

so that *at* $T = 0$ the changes in the Gibbs potential and in the enthalpy are equal ($\Delta S$ certainly being bounded). But that is not sufficient to explain why they remain approximately equal over some nonnegligible temperature range. However, dividing by $T$

$$\frac{\Delta H - \Delta G}{T} = \Delta S \tag{11.3}$$

We have seen from equation 11.2 that $\Delta H = \Delta G$ at $T = 0$; hence the left-hand side of equation 11.3 is an indeterminate form as $T \to 0$. The limiting value is obtained by differentiating numerator and denominator separately (L'Hospital's rule), whence

$$\left(\frac{d\Delta H}{dT}\right)_{T=0} - \left(\frac{d\Delta G}{dT}\right)_{T=0} = \lim_{T\to 0} \Delta S \tag{11.4}$$

By *assuming* that

$$\lim_{T\to 0} \Delta S = 0 \tag{11.5}$$

it was ensured by Nernst that $\Delta H$ and $\Delta G$ have the same initial slope (Fig. 11.1), and that therefore the change in enthalpy is very nearly equal to the change in Gibbs potential over a considerable temperature range.

The Nernst statement, that the *change* in entropy $\Delta S$ vanishes in any reversible isothermal process at zero temperature, can be restated: *The* $T = 0$ *isotherm is also an isentrope* (or "adiabat"). This coincidence of isotherm and isentrope is illustrated in Fig. 11.2.

The Planck restatement assigns a particular value to the entropy: *The* $T = 0$ *isotherm coincides with the* $S = 0$ *adiabat.*

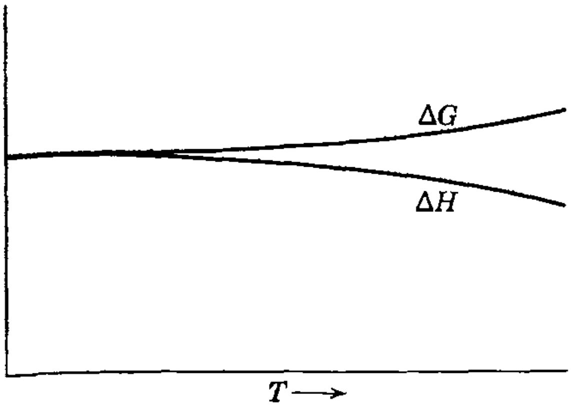

FIGURE 11.1
Illustrating the principle of Thomsen and Berthelot.

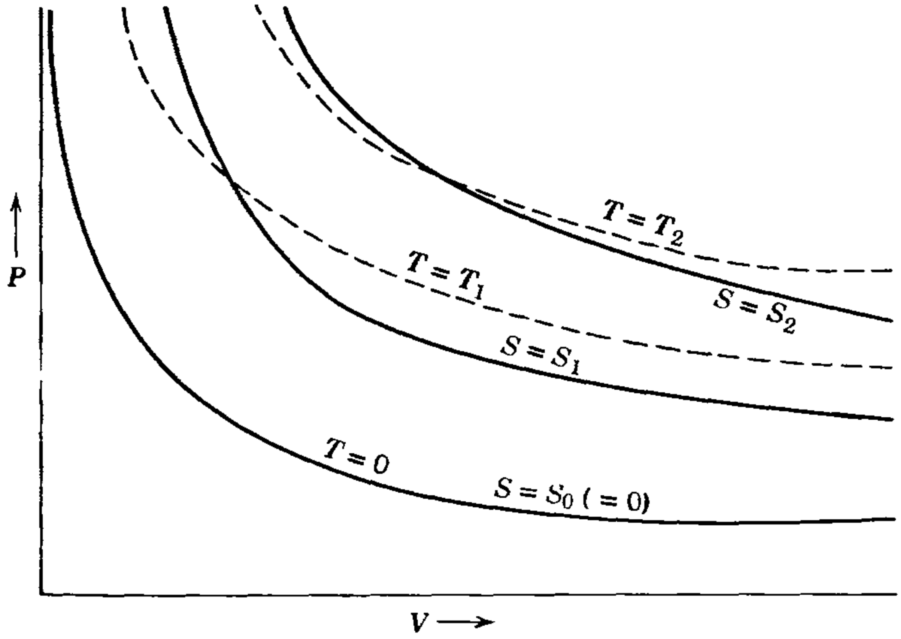

FIGURE 11 2
Isotherms and isentropes ("adiabats") near $T = 0$.

In the thermodynamic context there is no a priori meaning to the absolute value of the entropy. The Planck restatement has significance only in its statistical mechanical interpretation, to which we shall turn in Part II. We have, in fact, chosen the Planck form of the postulate rather than the Nernst form largely because of the pithiness of its statement rather than because of any additional thermodynamic content.

The "absolute entropies" tabulated for various gases and other systems in the reference literature fix the scale of entropy by invoking the Planck form of the Nernst postulate.

## PROBLEMS

**11.1-1. Does the two-level system of Problem 5.3-8 satisfy the Nernst postulate? Prove your assertion.**

## 11-2 HEAT CAPACITIES AND OTHER DERIVATIVES AT LOW TEMPERATURE

A number of derivatives vanish at zero temperature, for reasons closely associated with the Nernst postulate.

Consider first a change in pressure at $T = 0$. The change in entropy must vanish as $T \to 0$. The immediate consequence is

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \to 0 \qquad (\text{as } T \to 0) \tag{11.6}$$

where we have invoked a familiar Maxwell relation. It follows that the coefficient of thermal expansion $\alpha$ vanishes at zero temperature.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \to 0 \qquad (\text{as } T \to 0) \tag{11.7}$$

Replacing the pressure by the volume in equation 11.6, the vanishing of $(\partial S/\partial V)_T$ implies (again by a Maxwell relation)

$$\left(\frac{\partial P}{\partial T}\right)_v \to 0 \qquad (\text{as } T \to 0) \tag{11.8}$$

The heat capacities are more delicate. If the entropy does not only approach zero at zero temperature, but *if it approaches zero with a bounded derivative* (i.e., if $(\partial s/\partial T)_v$ is not infinite) then

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v \to 0 \qquad (\text{as } T \to 0) \tag{11.9}$$

and, similarly, *if* $(\partial s/\partial T)_P$ is bounded

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_P \to 0 \qquad (\text{as } T \to 0) \tag{11.10}$$

Referring back to Fig. 11.1 it will be noted that both $\Delta G$ and $\Delta H$ were drawn with zero slope; whereas equations 11.4 and 11.5 required only that $\Delta G$ and $\Delta H$ have the *same* slope. The fact that they have zero slope is a consequence of equation 11.10 and of the fact that the temperature derivative of $\Delta H$ is just $N\,\Delta c_p$.

The vanishing of $c_v$ and $c_p$ (and the zero slope of $\Delta G$ or $\Delta H$) appears generally to be true. However, whereas the vanishing of $\alpha$ and $\kappa_T$ are direct consequences of the Nernst postulate, the vanishing of $c_v$ and $c_p$ are observational facts which are suggested by, but not absolutely required by, the Nernst postulate.

Finally, we note that the pressure in equation 11.6 can be replaced by other intensive parameters (such as $B_e$ for the magnetic case) leading to general analogues of equation 11.7, and similarly for equation 11.8.

## 11-3 THE "UNATTAINABILITY" OF ZERO TEMPERATURE

It is frequently stated that, as a consequence of the Nernst postulate, the absolute zero of temperature can never be reached by any physically realizable process. Temperatures of $10^{-3}$ K are reasonably standard in cryogenic laboratories; $10^{-7}$ K has been achieved; and there is no reason to believe that temperatures of $10^{-10}$ K or less are fundamentally inaccessible. The question of whether the state of *precisely* zero temperature can be realized by any process yet undiscovered may well be an unphysical question, raising profound problems of absolute thermal isolation and of infinitely precise temperature measurability. The theorem that does follow from the Nernst postulate is more modest. It states that *no reversible adiabatic process starting at nonzero temperature can possibly bring a system to zero temperature.* This is, in fact, no more than a simple restatement of the Nernst postulate that the $T = 0$ isotherm is coincident with the $S = 0$ adiabat. As such, the $T = 0$ isotherm cannot be intersected by any *other* adiabat (recall Fig. 11.2).