The Richard Stockton College of New Jersey
Chemistry Program, School of Natural Sciences and Mathematics
PO Box 195, Pomoma, NJ

CHEM 3410: Physical Chemistry I — Fall 2008

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Lecture 11: Entropy changes with P, V and T and equilibrium

References

1. Levine, *Physical Chemistry*, Sections 4.1–4.3

Key Concepts

- It is often important to express changes in a state function, like S, as a function of variables of interest, like (T, V), or (T, P), depending on the conditions of the actual process. This is accomplished by using the differential form of a state function. For example, $S(T, V)$ can be written as:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

- The trick the becomes expressing the partial derivatives in terms of quantities that are either measurable or tabulated somewhere. In this case, the first partial is related to the constant volume heat capacity:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$$

  The second partial is a bit more of a challenge. If we use a Maxwell relation (Eqn 6.27) along with Equation 3.7 we can show that:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha}{\kappa}$$

  Putting this together we get:

$$dS = \frac{C_v}{T}dT + \frac{\beta}{\kappa}dV$$

- To get the total change in entropy, we could integrate from state 1 at V_1 and T_1 to state 2 at V_2 and T_2:

$$\int_1^2 dS = \Delta S = \int_{T_1}^{T_2} \frac{C_v}{T}dT + \int_{V_1}^{V_2} \frac{\alpha}{\kappa}dV$$

- This is a useful method for writing changes in state functions, such as internal energy or entropy, in terms of (1) the variables we are interested in and (2) quantities that are measurable or tabulated, like thermal expansion, heat capacities, etc.

- We can now try to understand how to develop criteria for equilibrium in simple systems and then try to move onto more complex and real systems.

- We can apply the combined first and second law to an isolated systems to determine conditions for equilibrium. For this type of system, **entropy** is maximized at equilibrium.

- For thermal equilibrium between two isolated bodies at different temperatures, our physical intuition tells us that equilibrium is reached when the temperatures are equal. This can be shown formally by employing our expression of dU in terms of dS and dV and making some simplifications due to the isolated nature of the system.

Related Exercises in Levine

Exercise 4.4,4.5