

CHEMICAL POTENTIALS - SUMMARY FOR READING MCQUARRIE

PHYSICAL CHEMISTRY 1 – PROF. DAVID M. ROGERS

The following summary of chemical potentials is helpful for organizing your reading of McQuarrie chapters 22–26.

| Phase | Reference State | μ_α | definitions |
|---------|--------------------------|---|---|
| Solid | Pure solid | $\mu_\alpha^0(P, T)$ | |
| Gas | $P \rightarrow 0$ | $\mu_\alpha^0(T) + RT \ln f_\alpha$ | $f_\alpha = \gamma_\alpha P_\alpha / 1 \text{ bar}$ |
| Solvent | $x_\alpha \rightarrow 1$ | $\mu_\alpha^*(P, T) + RT \ln(\gamma_\alpha x_\alpha)$ | $x_\alpha = n_\alpha / N$ |
| Solute | $[\alpha] \rightarrow 0$ | $\mu_\alpha^\infty(P, T) + q_\alpha \phi + RT \ln a_\alpha$ | $a_\alpha = \gamma_\alpha [\alpha] / 1 \text{ M}$ |

The table above uses x_α as the mol fraction (number of moles of α divided by total number of moles). The partial pressure of a gas is defined as the mol fraction times the total pressure,

$$(1) \quad P_\alpha = x_\alpha P.$$

To interpret the table, think of the free energy of every substance as a sum of three contributions:

- The free energy of the pure substance in its reference state, $\Delta_f G^0(\alpha)$.
- The entropy change due to dilution if the substance is ‘ideal’, $RT \ln(P_\alpha/1 \text{ bar})$.
- The free energy due to interaction with other components of the mixture, $RT \ln \gamma_\alpha$.

Note that n_α moles of a pure solid, gas, or liquid, α , in its reference state has the Gibbs free energy,

$$(2) \quad G_\alpha^0(P, T) = n_\alpha \mu_\alpha^0(P, T).$$

For a pure liquid μ^* is used instead of μ^0 because it reminds us that the reference state is the pure liquid. The table of standard free energies of formation (Tbl. 26.1 on p. 1057) provides several examples.

For a solute, the reference state is infinite dilution. Very dilute solutes have a lot in common with ideal gasses. Of course, μ_α^∞ depends on the solute and the solvent, but not on other solutes present. The $q_\alpha \phi$ term is the charge of the solute (q_α) times the electrical voltage of the solution (ϕ). This last part cancels for neutral solutions, but is important for electrochemistry. There, areas of the solvent separated by a membrane can have different potentials, ϕ . Anions move toward the anode, so the anode of a 1.5 volt battery will have $\phi = +1.5 \text{ V}$ if the cathode has $\phi = 0$.

The ‘fudge factors,’ $\gamma_\alpha(P, T, \{x\})$ are full functions of the thermodynamic state (pressure, temperature, and mol fraction). They are always 1 when the mol fractions, $\{x\}$, go to the reference state. They also stay close to 1 near the reference state. In almost every

application case, you should do the calculation with $\gamma = 1$ first, and then re-do it (consulting a physical or analytical chemistry textbook) if non-ideal behavior is important.

For example, a real, single-component gas has (Eq. 22.64)

$$(3) \quad \mu(T, P) = G^0(T) + \int_{P^0}^P \left(\left(\frac{\partial \mu(T, P)}{\partial P} \right)_T - \frac{RT}{P} + \frac{RT}{P} \right) dP.$$

Since $\left(\frac{\partial \mu(T, P)}{\partial P} \right)_T = \bar{V}$ and $\int \frac{RT}{P} dP = RT \ln P/P^0$, the fudge factor is,

$$(4) \quad \ln \gamma(P, T) = \int_{1 \text{ bar } P^0}^P \frac{Z(P, T) - 1}{P} dP.$$

This equation can be integrated even starting from $P^0 = 0$, and so the reference free energy $G^0(T)$ is appropriate for an infinitely dilute ideal gas.

1. APPLICATIONS

Most of the applications in Chapters 22-26 follow the pattern:

- Consider the equilibrium between 2 sides of a reaction
- Set the free energy change of the reaction equal to 0 and find $K_{\text{eq}} = e^{-\Delta G^0/RT}$.
- Use the limiting forms of γ to find a simpler expression, $K_{\text{eq}}(\text{ideal})$ under ideal conditions.
- Use that answer to replace $\Delta G^0/RT$, so that no free energies appear in the resulting expression.

Try and work this out for the Henderson-Hasselbalch equation, noting

$$(5) \quad \text{pH} \equiv -\log_{10}(a_{H^+})$$

and

$$(6) \quad \log_{10} x = \frac{\ln x}{\ln 10} = \frac{\ln x}{2.3026}.$$

Next, try a liquid-vapor equilibrium for 1-propanol with some solute, where the vapor is always ideal ($f = P / 1 \text{ bar}$). You should derive Raoult's law. Doing the same for the partial pressure of the solute gives Henry's law.