

ON THE COMPLETE KELVIN EQUATION

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The Kelvin equation quantifies the deviation in equilibrium vapor pressure above a curved surface from that which would exist above a plane surface at the same temperature. As the importance of surfaces and colloids is being recognized more often in chemical engineering applications, the Kelvin equation is being used by an increasing number of chemical engineers. In addition, as surfaces and colloids are being introduced to more chemical engineering students—either as separate graduate or upper-year undergraduate courses, or as a part of a physical chemistry course—the Kelvin equation is being presented to an increasing number of students.

Although Lord Kelvin was the first to introduce the idea that the equations of capillarity would lead to a different vapor pressure at a curved surface,^[1] he presented only a rough derivation and arrived at the original approximate form of the equation, which was not thermodynamically correct. Since that time, the correct equation^[2] and its derivation^[3,4] have been presented in the literature and can even be found in a minority of textbooks.^[5-7] Unfortunately, the majority of textbooks have this equation^[8-11] and its derivation^[12-17] incorrect. Researchers and educators who make use of the Kelvin equation should be aware of these errors.

I believe the reason that the “complete” Kelvin equation and its correct derivation have not been adopted more often in literature is that there does not exist in the literature a complete discussion that points out where the errors are in often-published and incorrect derivations of the Kelvin equation. This paper is an attempt to address that deficiency.

DERIVATION OF THE KELVIN EQUATION

To understand the correct derivation of the Kelvin equation, it is necessary to begin at the conditions for thermodynamic equilibrium at a curved interface. Although one can choose a variety of thermodynamic systems from which to derive these conditions for equilibrium, the most general derivations require varying amounts of differential geometry

to arrive at exactly the same answer. Thus, for purposes of illustration, consider the relatively simple capillary system shown in Figure 1. A single component fluid is enclosed in a cylindrical, diathermal, piston-cylinder device surrounded by a constant-temperature, constant-pressure reservoir. The cylinder has a single cylindrical capillary in which an equilibrium liquid-vapor interface will exist. External fields, such as gravity, will be neglected in this derivation. (For a complete treatment, including gravity, see Ward and Sasges.^[18]) For geometrical simplicity we will assume that the contact angle (as measured through the liquid) is zero.

The conditions for equilibrium can be found by requiring that variations in the entropy of the isolated system about the equilibrium state vanish subject to the constraints of the system. Mathematically, we may write

$$dS^L + dS^V + dS^S + dS^{LV} + dS^{SV} + dS^{SL} + dS^R = 0 \quad (1)$$

where S^L , S^V , and S^S are the entropies of the liquid, the vapor, and the solid phases, respectively, and S^{LV} , S^{SV} , S^{SL} , and S^R are the entropies of the liquid-vapor, the solid-vapor, and the solid-liquid interphases, and the reservoir, respectively. Each of the entropy differentials may be written using the fundamental relation and the definitions of the intensive properties.^[19] For the liquid phase, denoted by the superscript L,

$$dS^L = \frac{1}{T^L} dU^L + \frac{P^L}{T^L} dV^L - \frac{\mu^L}{T^L} dN^L \quad (2)$$



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where T , U , P , V , μ , and N denote temperature, internal energy, pressure, volume, chemical potential, and number of moles, respectively. For the vapor phase, denoted by the superscript V ,

$$dS^V = \frac{1}{T^V} dU^V + \frac{P^V}{T^V} dV^V - \frac{\mu^V}{T^V} dN^V \quad (3)$$

Assuming that the system imposes no stress components on the solid other than the pressure,^[19] we may write for the solid phase (denoted by the superscript S)

$$dS^S = \frac{1}{T^S} dU^S + \frac{P^S}{T^S} dV^S - \frac{\mu^S}{T^S} dN^S \quad (4)$$

where μ^S and N^S are the chemical potential and the number of moles of solid molecules.

For the liquid-vapor interphase, denoted by the superscript LV ,

$$dS^{LV} = \frac{1}{T^{LV}} dU^{LV} - \frac{\gamma^{LV}}{T^{LV}} dA^{LV} - \frac{\mu^{LV}}{T^{LV}} dN^{LV} \quad (5)$$

where γ denotes interfacial tension and A denotes area of the interface. For the solid-vapor interphase, denoted by the superscript SV

$$dS^{SV} = \frac{1}{T^{SV}} dU^{SV} - \frac{\gamma^{SV}}{T^{SV}} dA^{SV} - \frac{\mu^{SV}}{T^{SV}} dN^{SV} - \frac{\mu_s^{SV}}{T^{SV}} dN_s^{SV} \quad (6)$$

where μ^{SV} and N^{SV} are the chemical potential and number of moles of fluid molecules located in the solid-vapor interphase and μ_s^{SV} and N_s^{SV} are the chemical potential and number of moles of solid molecules located in the solid-

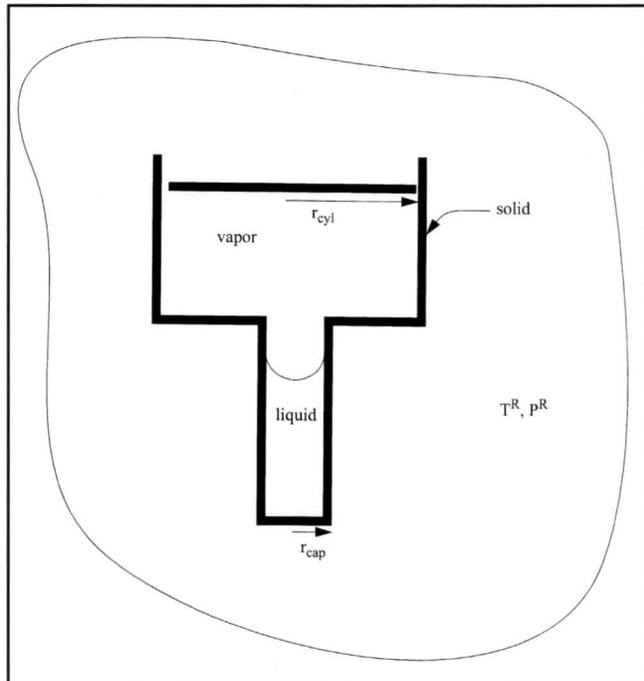


Figure 1. Schematic diagram of a capillary system.

vapor interphase. For the solid-liquid interphase, denoted by the superscript SL

$$dS^{SL} = \frac{1}{T^{SL}} dU^{SL} - \frac{\gamma^{SL}}{T^{SL}} dA^{SL} - \frac{\mu_s^{SL}}{T^{SL}} dN_s^{SL} - \frac{\mu^{SL}}{T^{SL}} dN^{SL} \quad (7)$$

In Eqs. 5-7, it is assumed

- That curved interfaces are placed so that the interfacial tension does not depend on curvature (Gibbs surface of tension)
- That flat interfaces are placed so that there are no solid molecules in the interfaces (Gibbs dividing surface).

For the reservoir, denoted by the superscript R

$$dS^R = \frac{1}{T^R} dU^R + \frac{P^R}{T^R} dV^R - \frac{\mu^R}{T^R} dN^R \quad (8)$$

where μ^R and N^R are the chemical potential and number of moles of the molecules making up the reservoir.

The constraints on the system shown in Figure 1 must now be enumerated. The total internal energy of the isolated system is constant so that

$$dU^R = -dU^L - dU^V - dU^S - dU^{LV} - dU^{SV} - dU^{SL} \quad (9)$$

The total number of molecules in the reservoir, the total number of fluid molecules, and the total number of solid molecules must remain constant so that

$$dN^R = 0 \quad (10)$$

$$dN^L = -dN^V - dN^{LV} - dN^{SV} - dN^{SL} \quad (11)$$

$$dN^S = -dN_s^{SV} - dN_s^{SL} \quad (12)$$

The total volume of the isolated system remains constant so that

$$dV^R = -dV^L - dV^V \quad (13)$$

It is assumed that the volume of the solid is constant so that

$$dV^S = 0 \quad (14)$$

Since we have assumed *a priori* that the liquid-vapor interface is spherical (no gravitational effects) and that the contact angle is zero, the liquid-vapor interface will be hemispherical with a radius of curvature equal to the radius of the cylindrical capillary, r_{cap} . Thus

$$dA^{LV} = 0 \quad (15)$$

From geometry,

$$dA^{SL} = \frac{2}{r_{cap}} dV^L \quad (16)$$

Also from geometry,

$$dA^{SV} = -dA^{SL} + \frac{2}{r_{cyl}} (dV^V + dV^L) \quad (17)$$

where r_{cyl} is the radius of the large cylindrical vessel which contains the capillary (see Figure 1).

Substituting Eqs. 2-17 into Eq. 1 and collecting like terms yields

$$\begin{aligned} & \left(\frac{1}{T^L} - \frac{1}{T^R} \right) dU^L + \left(\frac{1}{T^V} - \frac{1}{T^R} \right) dU^V + \left(\frac{1}{T^S} - \frac{1}{T^R} \right) dU^S \\ & + \left(\frac{1}{T^{LV}} - \frac{1}{T^R} \right) dU^{LV} + \left(\frac{1}{T^{SV}} - \frac{1}{T^R} \right) dU^{SV} + \left(\frac{1}{T^{SL}} - \frac{1}{T^R} \right) dU^{SL} \\ & + \left(\frac{\mu_S^L}{T^S} - \frac{\mu_S^{SV}}{T^{SV}} \right) dN_S^{SV} + \left(\frac{\mu_S^L}{T^S} - \frac{\mu_S^{SL}}{T^{SL}} \right) dN_S^{SL} + \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} \right) dN^V \\ & + \left(\frac{\mu^L}{T^L} - \frac{\mu^{LV}}{T^{LV}} \right) dN^{LV} + \left(\frac{\mu^L}{T^L} - \frac{\mu^{SV}}{T^{SV}} \right) dN^{SV} + \left(\frac{\mu^L}{T^L} - \frac{\mu^{SL}}{T^{SL}} \right) dN^{SL} \\ & + \left(\frac{P^L}{T^L} + \frac{\gamma^{SV}}{T^{SV}} \frac{2}{r_{\text{cap}}} - \frac{\gamma^{SV}}{T^{SV}} \frac{2}{r_{\text{cyl}}} - \frac{\gamma^{SL}}{T^{SL}} \frac{2}{r_{\text{cap}}} - \frac{P^R}{T^R} \right) dV^L \\ & + \left(\frac{P^V}{T^L} - \frac{\gamma^{SV}}{T^{SV}} \frac{2}{r_{\text{cyl}}} - \frac{P^R}{T^R} \right) dV^V = 0 \quad (18) \end{aligned}$$

Since the equality in Eq. 18 must be satisfied for arbitrary variations about the equilibrium state, each set of parentheses may be set equal to zero. Taking the limit as r_{cyl} goes to infinity (*i.e.* neglecting interfacial effects at the system-reservoir boundary) yields the following conditions for equilibrium:

$$T^L = T^V = T^S = T^{LV} = T^{SV} = T^{SL} = T^R \quad (19)$$

$$\mu_S^L = \mu_S^{SV} = \mu_S^{SL} \quad (20)$$

$$\mu^L = \mu^V = \mu^{LV} = \mu^{SV} = \mu^{SL} \quad (21)$$

$$P^V = P^R \quad (22)$$

$$P^V - P^L = \frac{2\gamma^{LV}}{r_{\text{cap}}} \quad (23)$$

In order to find Eq. 23, the Young equation for a contact angle of zero was used

$$\gamma^{SV} - \gamma^{SL} = \gamma^{LV} \quad (24)$$

Eq. 23 is the Laplace equation for the geometry shown in Figure 1.

Eqs. 19-23 are the conditions that must be satisfied in order for thermodynamic equilibrium to exist in the system shown in Figure 1. If, for example, a more general derivation were performed in which the contact angle was not assumed to be zero, Eqs. 19-22 would remain unchanged and the Laplace equation would become

$$P^V - P^L = \frac{2\gamma^{LV}}{r_{\text{cap}}} \cos\theta \quad (25)$$

where θ is the contact angle, and the Young equation would come out of the derivation as an additional condition for equilibrium

$$\gamma^{SV} - \gamma^{SL} = \gamma^{LV} \cos\theta \quad (26)$$

The format of the above derivation of the conditions for equilibrium was chosen carefully. Effects of adsorption on solid surfaces are often neglected^[3] when the conditions for equilibrium are derived for systems such as the one shown in Figure 1. Including these effects, however, ensures that the chemical potentials of the solid-vapor and solid-liquid interfaces appear in Eq. 21. That such an equilibrium exists, leads to interesting phenomena such as the dependence of contact angle on adsorption in the same way that fluid-fluid interfacial tension is known to depend on adsorption.^[18,20]

The Kelvin equation may be found by combining the Laplace equation, Eq. 23, with the chemical potential equality

$$\mu^L = \mu^V \quad (27)$$

from Eq. 21. It is clear from the above extremization of entropy that for thermodynamic equilibrium to exist, the Laplace equation (Eq. 23) and the equality of chemical potentials (Eq. 27) must be satisfied simultaneously and since the pressures are different in the liquid and vapor phases at equilibrium, we may write Eq. 27 as

$$\mu^L(T, P^L) = \mu^V(T, P^V) \quad (28)$$

If one had exact forms of the chemical potential (and gravity and contact angle could truly be neglected) then the Kelvin equation found in this way would be exact. For the purposes of illustration, assume the vapor may be treated as an ideal gas so that

$$\mu^V(T, P^V) = \mu^V(T, P_\infty) + RT \ln \left(\frac{P^V}{P_\infty} \right) \quad (29)$$

where P_∞ could be any reference pressure but it is taken here to be the saturation pressure at a plane interface. Assuming the liquid is incompressible

$$\mu^L(T, P^L) = \mu^L(T, P_\infty) + v^L (P^L - P_\infty) \quad (30)$$

where v^L is the molar volume of the liquid. Substituting Eqs. 29 and 30 in Eq. 28 yields

$$RT \ln \left(\frac{P^V}{P_\infty} \right) = v^L (P^L - P_\infty) \quad (31)$$

Substituting Eq. 23 in Eq. 31 yields the "complete" Kelvin

equation,

$$RT \ln \left(\frac{P^V}{P_\infty} \right) = -\frac{2 \nabla^L \gamma^{LV}}{r_{\text{cap}}} + \nabla^L (P^V - P_\infty) \quad (32)$$

For a generalization of the Kelvin equation to systems in which the contact angle is not zero, Eq. 25 should be used instead of Eq. 23. For a generalization of the thermodynamic treatment of curved interfaces to systems in which gravity cannot be neglected, see Ward and Sasges.^[18] For treatments with nonideal vapors and liquids, there are a number of sources.^[3,21-23]

An approximate form of the Kelvin equation in which the second term on the right-hand side is missing is widely published in textbooks.^[8-17]

$$RT \ln \left(\frac{P^V}{P_\infty} \right) = -\frac{2 \nabla^L \gamma^{LV}}{r_{\text{cap}}} \quad (33)$$

The above equation is not thermodynamically correct since it cannot satisfy the two requirements for equilibrium (Eqs. 23 and 27) at the same time.

MAGNITUDE OF THE DISCREPANCY

In many cases, the neglected term is negligible and the approximate Kelvin equation will yield adequate results.^[2] In a very widely referenced experimental validation of the Kelvin equation* cyclohexane at room temperature was used,^[2] for which the second term on the right-hand side of the complete Kelvin equation is equal to approximately 0.05% of the first term on the right-hand side for the range of radii considered (4 to 20 nm). One may find circumstances, however, for which the missing term should not be neglected. Looking at Eq. 32, it is clear that the significance of the second term on the right-hand side increases as pressure increases. High-pressure systems are often important for chemical engineers.

For example, if one considered a fluid, the vapor of which behaved like an ideal gas, but which had the same thermodynamic properties of water at 360°C, for the same range of radii as in Fisher and Israelachvili,^[2] *i.e.* 4 to 20 nm, then the second term on the right-hand side of the complete Kelvin equation would be 14% of the first term. (Note that for this calculation, the surface tension of water was extrapolated linearly from data between -8° and 100°C.) Of course, to make accurate calculations for a substance such as water, the vapor of which cannot be treated as an ideal gas, the com-

* Using a slightly different geometry than the one presented here—the complete Kelvin equation would be

$$RT \ln \left(\frac{P^V}{P_\infty} \right) = -\frac{\nabla^L \gamma^{LV}}{r_{\text{cap}}} + \nabla^L (P^V - P_\infty) \quad (34)$$

plete Kelvin equation would need to be derived using non-ideal chemical potential equations.^[21-23]

COMMENTS ON DERIVATIONS IN THE LITERATURE

Several derivations of the approximate Kelvin equation are presented in textbooks which give readers the illusion that one can arrive at Eq. 33 without neglecting a term.

Incorrect Derivation No. 1

In one such derivation, the change in the Gibbs free energy, ΔG , in the formation of an interface is set to zero.^[15,17] In other words, the authors assert that the Gibbs free energy will be an extremum when the system is in equilibrium. This thought comes from applying the thermodynamics of simple, single-phase systems to multiphase systems.

From thermodynamics, we find the free energy of a particular system by requiring that the free energy be that energy which is minimized when entropy is maximized subject to the constraints of the problem. For a simple, single-phase system kept at fixed temperature and pressure, the free energy of the system will indeed turn out to be the Gibbs free energy, G . For the multiphase system shown in Figure 1, however, extremization of the entropy subject to the constraints of the system yields a different free energy.

Derivation of the Free Energy

Consider the system shown in Figure 1. The difference form of the fundamental relation for the reservoir is

$$\Delta U^R = T^R \Delta S^R - P^R \Delta V^R + \mu_R^R \Delta N_R^R \quad (35)$$

The constraints may be written

$$\Delta U^R = -\Delta U^L - \Delta U^V - \Delta U^S - \Delta U^{LV} - \Delta U^{SV} - \Delta U^{SL} \quad (36)$$

$$\Delta N_R^R = 0 \quad (37)$$

$$\Delta V^R = -\Delta V^L - \Delta V^V \quad (38)$$

$$T^R = T \quad (39)$$

$$P^R = P^V \quad (40)$$

Substituting Eqs. 36-40 in Eq. 35 yields

$$0 = \Delta U^L + \Delta U^V + \Delta U^S + \Delta U^{LV} + \Delta U^{SV} + \Delta U^{SL} + T \Delta S^R + P^V \Delta V^V + P^V \Delta V^L \quad (41)$$

For spontaneous changes

$$\Delta S^R \geq -\Delta S^L - \Delta S^V - \Delta S^S - \Delta S^{LV} - \Delta S^{SV} - \Delta S^{SL} \quad (42)$$

Substituting Eq. 41 in Eq. 42 and rearranging gives, for

spontaneous changes

$$\Delta \left[(U^L - TS^L) + (U^V - TS^V + P^V V^V) + (U^S - TS^S) + (U^{LV} - TS^{LV}) + (U^{SV} - TS^{SV}) + (U^{SL} - TS^{SL}) + P^V V^L \right] \leq 0 \quad (43)$$

In other words, the free energy that is minimized when the entropy of the system plus its surroundings is maximized is

$$B = F^L + G^V + F^S + F^{LV} + F^{SV} + F^{SL} + P^V V^L \quad (44)$$

where F represents a Helmholtz free energy. An extremum in the above free energy will correspond to the conditions for equilibrium given in Eqs. 19-23.

Incorrect Derivation No. 2

In another often-published derivation,^[12,14,16] it is asserted that "for liquid-vapor equilibrium at a spherical surface, both the liquid and vapor must be brought to the same pressure," $P_\infty + \Delta P$.^[16] The change in free energy of the liquid is written

$$\Delta G = \int_{P_\infty}^{P_\infty + \Delta P} \nabla^L dP = \nabla^L \Delta P \quad (45)$$

The free energy change of the vapor is written

$$\Delta G = RT \ln \left(\frac{P_\infty + \Delta P}{P_\infty} \right) \quad (46)$$

Eqs. 45 and 46 are then equated to give Eq. 33. The only way that equating Eqs. 45 and 46 can give Eq. 33, is if ΔP has the meaning of $P^V - P^L$ in Eq. 45 and the meaning of $P^V - P_\infty$ in Eq. 46, which does not make sense.

CONCLUSION

Correct derivations of the "complete" Kelvin equation presented in the literature have not been incorporated in many mainstream textbooks. In this paper a simple, yet thorough, thermodynamic derivation of the "complete" Kelvin equation has been presented. Although the "complete" equation presented here and the "approximate" Kelvin equation, given most often in textbooks, do not differ significantly for many experimental circumstances, in other experimental circumstances, the difference may be important. In particular, the complete Kelvin equation and the approximate Kelvin equation differ at high pressures. Since chemical engineers may encounter high pressures, it is important that they be aware of the complete Kelvin equation along with its correct derivation. Incorrect derivations of the approximate Kelvin equation, published in textbooks, have been discussed in light of the proper thermodynamic treatment.

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