

FCh cheatsheet

A handy guide containing the most important formulae of physical chemistry (thermodynamics) that a chemical engineer will need in practical life. The derivation steps are important to give you a sense of purpose, but for brevity they are only outlined in *very* brief points.

Definitions are marked with \equiv

Statements valid only for ideal gas (resp. ideal mixture) are marked *

Czech names are in violet

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Equations of state

(EOS, *stavové rovnice*)

For liquids, there is usually only thermal expansion coeff (*koef izobarické roztažnosti*) α , and isothermal compressibility (*stlačitelnost*) κ :

$$\alpha \equiv \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T} \right)_p \quad (1)$$

$$\kappa \equiv -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial p} \right)_T \quad (2)$$

$$\frac{\alpha}{-\kappa} = \left(\frac{\partial p}{\partial T} \right)_{V_m} \quad (3)$$

For gases, generally $pV = znRT$, where z is the compressibility factor; for * $z = 1$.

Common non-ideal EOS are: virial 1st order (4), van der Waals (5), Redlich-Kwong (6):

$$p = \frac{RT}{V_m} \left(1 + \frac{Bp}{RT} \right) \quad (4)$$

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (5)$$

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m - b)} \quad (6)$$

By the way, the Boyle temp can be calculated from critical: $T_B \doteq 3.3 T_c$

A real gas is closest to ideal at T_B , meaning $z \doteq 1$

Core Thermodynamics

Volume work (*basic physics*):

$$dW = -pdV \quad (7)$$

First TD law defines internal energy U (*vnitřní energie*):

$$dU = dQ + dW \quad (8)$$

Isobaric process [p] leads us to define enthalpy H (but H is valid under any conditions):

$$dU = dQ - pdV \quad (9)$$

$$dQ = dU + pdV = d(U + pV) = dH \quad (10)$$

$$H \equiv U + pV \quad (11)$$

Heat capacity: at isochoric conditions we may substitute from 8, at isobaric from 10. Heat capacity is usually used in intensive form $C_m \equiv C/n$.

$$C_V \equiv \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (12)$$

$$C_p \equiv \left(\frac{\partial Q}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (13)$$

Mayer's * formula can be proven: $\frac{\partial H}{\partial T} - \frac{\partial U}{\partial T} = \frac{\partial(U+pV)}{\partial T} - \frac{\partial U}{\partial T} = \frac{\partial(pV)}{\partial T} = nR$

$$* C_{pm} - C_{Vm} = R \quad (14)$$

Second TD law (equal for a reversible process, greater for irreversible)

$$dS \geq \frac{dQ}{T} \quad (15)$$

TD1 + TD2 (just substitute eqs 15, 11 into 8) gets us the total differentials of U, H :

$$dU = TdS - pdV \quad (16)$$

$$dH = TdS + Vdp \quad (17)$$

Gibbs energy

When we consider *other* W than volume W (total reversible work $dW_{rev} = -pdV + dW_{other}$), then eq 16 becomes:

$$dU = TdS - pdV + dW_{other} = dQ_{rev} + dW_{rev} \quad (18)$$

And at [T] it leads us to define the Helmholtz free energy F :

$$d(U - TS) = dW_{rev} \quad (19)$$

$$F \equiv U - TS \quad (20)$$

At [T] $dF = dW_{rev}$ while at [T, V] $dF = dW_{other}$

At $[T]$:

$$dF = -pdV + dW_{other} \quad (21)$$

And at $[p]$ it leads us to define the Gibbs free energy G :

$$d(F + pV) = dW_{other} \quad (22)$$

$$G \equiv F + pV = H - TS \quad (23)$$

By combining eqs 20+16, resp. 23+17, we get the total differentials of F, G :

$$dF = -SdT - pdV \quad (24)$$

$$dG = -SdT + Vdp \quad (25)$$

Entropy differential

By applying the *Schwarz's theorem*, we can quantify various state function derivations:

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (26)$$

$$\frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T} \quad \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad (27)$$

Combining TD2 with C_p or C_V (eqs 15 + 12, 13), we get:

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \quad (28)$$

$$\left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \quad (29)$$

Combining 28+26, resp. 29+27, we get two forms of S total differential:

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV \quad (30)$$

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_p dp \quad (31)$$

Adiabatic compression work

When all these are fulfilled: adiabatic, *, $C_V = const$, only volume work and no other work, then we apply TD1, $dQ = 0$, C_V and Mayer (eqs 8+12+14):

$$dU = dW \quad (32)$$

$$nC_V dT = -pdV \quad (33)$$

$$\frac{C_V}{T} dT = -\frac{R}{V} dV \quad (34)$$

Definite integral from V_1, T_1 to V_2, T_2 , let $\kappa \equiv \frac{C_{pm}}{C_{Vm}} - 1$:

$$\ln \frac{T_2}{T_1} = \left(\frac{C_{pm}}{C_{Vm}} - 1 \right) \ln \frac{V_2}{V_1} = \kappa \ln \frac{V_2}{V_1} \quad (35)$$

Alternatively, we may use *indefinite* integral on eq 34, to get:

$$TV^{(\kappa-1)} = \text{const} \quad pV^\kappa = \text{const} \quad (36)$$

Reversible work: a common problem is to integrate $dW = -pdV$ from p_1, V_1 to p_2, V_2 . Using eq 36 we can express $p = p_1 \left(\frac{V_1}{V} \right)^\kappa$, and let $K \equiv p_1 V_1^\kappa = p_2 V_2^\kappa$:

$$\begin{aligned} W &\geq \int_{V_1}^{V_2} p_1 V_1^\kappa \frac{dV}{V^\kappa} = K \left[\frac{1}{1-\kappa} V^{1-\kappa} \right]_{V_1}^{V_2} = \frac{1}{1-\kappa} \left(\frac{K}{V_2^{\kappa-1}} - \frac{K}{V_1^{\kappa-1}} \right) \\ W &\geq \frac{1}{1-\kappa} (p_2 V_2 - p_1 V_1) \end{aligned} \quad (37)$$

Gibbs phase rule

Let there be f phases (for example 1, 2, 3...) and k components ($A, B, C...$)

The variables needed to fully describe the system are T, p , and molar fracs x :

$$\begin{array}{ccc} x_{1A} & x_{1B} & x_{1C} \\ x_{2A} & x_{2B} & x_{2C} \\ x_{3A} & x_{3B} & x_{3C} \end{array} \quad (38)$$

The number of molar fracs = $f(k-1)$; the $k-1$ is because $\sum_i^f x_i = 1$ for each phase.

That means total variables = $f(k-1) + 2$

Note: T, p is common for system, not per phase; thermal & mechanical equilibrium is assumed.

These equations are left to describe the *phase equilibrium*:

$$\mu_1^A = \mu_1^B = \mu_1^C \quad (39)$$

$$\mu_2^A = \mu_2^B = \mu_2^C \quad (40)$$

$$\mu_3^A = \mu_3^B = \mu_3^C \quad (41)$$

That's $k(f-1)$ equations (see eq 52 for μ definition).

When we add c arbitrary bounds (equations), the degrees of freedom (*stupně volnosti*) are:

$$v = f(k-1) + 2 - k(f-1) - c = k - f + 2 - c \quad (42)$$

Clapeyron equation

Describes the relation $p(T)$ of a single-component phase transition from phase 1 \rightarrow 2.

Equilibrium is when $dG_m^1 = dG_m^2$, and we substitute G differential from eq 25:

$$-S_{m1}dT + V_{m1}dp = -S_{m2}dT + V_{m2}dp \quad (43)$$

$$\frac{dp}{dT} = \frac{S_{m2} - S_{m1}}{V_{m2} - V_{m1}} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \Delta V_m} \quad (44)$$

The last equality comes from applying TD2 and TD1 with H (eqs 15+10), because a *single-component* phase transition is at $[T, p]$

When phase 2 is * gas, then $V_{m2} \gg V_{m1}$, and so $\Delta V_m \doteq V_{m2} \doteq \frac{RT}{p}$
 p then means vapor pressure p° (tlak sytých par). This is the Clausius-Clapeyron equation:

$$\frac{d \ln p^\circ}{dT} = \frac{\Delta H_m}{RT^2} \quad (45)$$

We could assume $\Delta H_m = \text{const}$ and use *indefinite* integral to get $p^\circ(T)$, but it's very inaccurate, instead the empirical Antoine equation is used universally:

$$\ln p^\circ = A - \frac{B}{T + C} \quad (46)$$

Definite integral, however, may be used as a good estimate for small intervals:

$$\ln \frac{p_2^\circ}{p_1^\circ} = \frac{-\Delta H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (47)$$

Mixing

For **ideal mixtures** Dalton $p = \sum p_i$, Amagat $V = \sum V_i$,
also $\Delta H^{\text{mix}} = 0$, **but** $\Delta S^{\text{mix}} \neq 0$, therefore $\Delta G^{\text{mix}} \neq 0$ either. Why is that?

Imagine two ideal gases A, B , both at p , each in a compartment of V_A, V_B and let $V \equiv V_A + V_B$.
Connecting the compartments means A expands $V_A, p \rightarrow V, p_A$, where p_A is partial pressure
of A in whole V . Analogically B expands $V_B, p \rightarrow V, p_B$, and the process happens at $[T]$.
Using eqs *either* 30+26 *or* 31+27 (let's go with the latter), we get:

$$\Delta S^{\text{mix}} = \Delta S_A + \Delta S_B = \int_p^{p_A} \left(\frac{\partial S}{\partial p} \right)_T dp + \int_p^{p_B} \left(\frac{\partial S}{\partial p} \right)_T dp = -n_A R \ln \frac{p_A}{p} - n_B R \ln \frac{p_B}{p} \quad (48)$$

$$\Delta S_m^{\text{mix}} = -x_A R \ln x_A - x_B R \ln x_B \dots = -R \sum_i x_i \ln x_i \quad (49)$$

Let $\dot{G}_{m,i}$ be G_m for pure component i , then:

$$\Delta G^{\text{mix}} = \Delta H^{\text{mix}} - T \Delta S^{\text{mix}} = RT \sum_i x_i \ln x_i \quad (50)$$

$$G_m^{\text{mix}} = x_1 \dot{G}_{m1} + x_2 \dot{G}_{m2} \dots + \Delta G^{\text{mix}} = \sum_i x_i \dot{G}_{m,i} + RT \sum_i x_i \ln x_i \quad (51)$$

Now let's d/dn_i and add excess G^E which quantifies the **non-ideal** mixture deviation,
and let's define chemical potential μ_i of component i in a mixture, and μ_i° for pure std i :

$$\mu_i \equiv \bar{G}_{m,i} \equiv \frac{\partial G}{\partial n_i} \quad (52)$$

$$\left(\frac{\partial G}{\partial n_i} \right)_{T,p} = \dot{G}_{m,i} + RT \ln x_i + G^E \quad (53)$$

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (54)$$

We have thus defined **activity** a_i as such number, that it includes the non-ideality from G^E .

By the way, $\bar{G}_{m,i}$ is called the partial G_m for i in a mixture.

Non-ideal mixing behavior can be expressed *either* with partial, *or* excess quantities.

Following applies for *any* partial quantity: $V_m^{\text{mix}} = \sum_i x_i \bar{V}_i$ (especially useful for V).

Note that there can be an ideal mixture of non-ideally behaving components, as well as a non-ideal mixture of ideally behaving components...

Reaction thermodynamics

$\Delta_{\text{R}}H^\circ$ at std temp T° , where $\Delta_{\text{F}}H_i^\circ$ is the std formation enthalpy of compound i :

$$\Delta_{\text{R}}H^\circ = \sum_i \nu_i \Delta_{\text{F}}H_i^\circ \quad (55)$$

Kirchhoff's law to get $\Delta_{\text{R}}H$ at a given temp T :

$$\Delta_{\text{R}}H = \Delta_{\text{R}}H^\circ + \int_{T^\circ}^T \Delta C_p dT \quad (56)$$

$$\Delta C_p = \sum_i \nu_i C_{pi} \quad (57)$$

Note: $\Delta C_p = \frac{\partial(\Delta H)}{\partial T}$ as per eq 13

Chemical equilibrium: we extend G differential (eq 25) with dependence on components n_i :

$$\partial G = -SdT + Vdp + \sum_i \frac{\partial G}{\partial n_i} dn_i \quad (58)$$

We assume thermal & mechanical equilibrium, so $[T, p]$, and use μ_i definition from eq 52. Also, we use reaction extent (**reakční rozsah**) $\xi \equiv \frac{n_i - n_i^0}{\nu_i}$, so $dn_i = \nu_i d\xi$:

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_i \nu_i \mu_i \equiv \Delta_{\text{R}}G \quad (59)$$

Using a_i from eq 54 leads us to define $\Delta_{\text{R}}G^\circ \equiv \sum_i \nu_i \mu_i^\circ$, and let's define the reaction quotient $Q \equiv \prod_i a_i^{\nu_i}$:

$$\Delta_{\text{R}}G = \sum_i \nu_i \mu_i^\circ + \sum_i \nu_i RT \ln a_i \quad (60)$$

$$\Delta_{\text{R}}G = \Delta_{\text{R}}G^\circ + RT \ln \prod_i a_i^{\nu_i} = \Delta_{\text{R}}G^\circ + RT \ln Q \quad (61)$$

Note that Q can be calculated anytime, not just in equilibrium, and can therefore have any value. In equilibrium $\Delta_{\text{R}}G = 0$, and **only then** $K \equiv Q$, the equilibrium constant:

$$\Delta_{\text{R}}G^\circ = -RT \ln K \quad (62)$$

Usually we approx. $a_i \doteq \frac{c_i}{c^\circ}$ or $a_i \doteq \frac{p_i}{p^\circ}$ (when std state = pure component), and we express $c_i(\xi), p_i(\xi)$, so that $K = K(\xi_{\text{eq}}) \rightarrow$ eq 62 can be solved for ξ_{eq}

Temp. dependence: as per eq 23, $\Delta_{\text{R}}G^\circ = \Delta_{\text{R}}H - T\Delta_{\text{R}}S$, therefore $\frac{\Delta_{\text{R}}G^\circ}{T} = \frac{\Delta_{\text{R}}H}{T} - \Delta_{\text{R}}S$.

At first glance, we could naively think that d/dT is very easily done in one step:

$$\frac{\partial \frac{\Delta_{\text{R}}G^\circ}{T}}{\partial T} = \frac{-\Delta_{\text{R}}H}{T^2} \quad (63)$$

This equation is indeed true, but doing the derivation is actually way more difficult... Though the naive approach serves as a great mnemotechnic!

Vapor-liquid equilibrium

Raoult+Dalton's law relates partial pressure p_i , molar. fracs in vapor phase y_i , in liquid x_i , and pure i vapor pressure (see Antoine eq 46). In this form valid only for * vapor phase (*often reasonable assumption*), but considers non-ideal liquid mixing, then $a_i = \gamma_i x_i$.

$$p_i = y_i p = \gamma_i x_i p_i^\circ \quad (64)$$

γ_i is the activity coeff, for * liquid mixture $\gamma = 1$, otherwise quantified as function $\vec{\gamma} = \vec{\gamma}(T, \vec{x})$, for example using the [NRTL](#) model.

Boiling point is defined as such temperature, that these add up to system pressure p . Summing up eq 64 draws the **isothermal boiling point curve**, a function $p = p(\vec{x})$:

$$p = \sum_i \gamma_i x_i p_i^\circ \quad (65)$$

Dew point (*rosný bod*) curve is the same eq rewritten as function $p = p(\vec{y})$.

Here shown for binary, but the same can be done for any number of components:

$$\begin{aligned} p &= x_1 \gamma_1 p_1^\circ + (1 - x_1) \gamma_2 p_2^\circ \\ p &= \frac{y_1 p}{\gamma_1 p_1^\circ} \gamma_1 p_1^\circ + \left(1 - \frac{y_1 p}{\gamma_1 p_1^\circ}\right) \gamma_2 p_2^\circ \end{aligned}$$

Move all terms with p to left-hand side, then substitute $y_2 = 1 - y_1$ and divide by $(p \gamma_2 p_2^\circ)$:

$$\begin{aligned} p \left(1 - y_1 + y_1 \frac{\gamma_2 p_2^\circ}{\gamma_1 p_1^\circ}\right) &= \gamma_2 p_2^\circ \\ \left(\frac{y_2}{\gamma_2 p_2^\circ} + \frac{y_1}{\gamma_1 p_1^\circ}\right) &= \frac{1}{p} \\ \sum_i \frac{y_i}{\gamma_i p_i^\circ} &= \frac{1}{p} \end{aligned} \quad (66)$$

Eq 66 in reciprocal form draws the **isothermal dew point curve**.

The two isothermal curves (forming pxy diagram) have very limited practical application...

The **isobaric boiling + dew point functions** (Txy diagram) as $T = T(\vec{x}), T = T(\vec{y})$ are much more useful, but unfortunately cannot be expressed analytically.

Set p as constant, substitute Antoine into p_i° to get these as *implicit* functions.

Another often used form of VLE is the **isobaric xy diagram** as a function $\vec{y} = \vec{y}(\vec{x})$.

It combines boiling & dew curves into one, while information on boiling T is separate. It is again implicit for T , this time a set of *two* eqs: 1) 65 with p as const, 2) substitute 65 into 66.

Note: isobaric form of VLE is implicit because T cannot be isolated from Antoine eq.

And when liquid mixture is non-ideal, T is also in the γ model.