2.6 Supporting Information
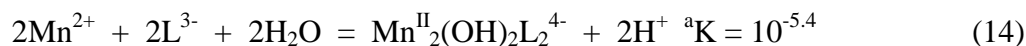
Thermodynamic Information Reported in the Literature

The thermodynamic database CRITICAL *(1)* provides equilibrium constants at fixed ionic strength, which can be converted to infinite dilution scale equilibrium constants using the Davies Equation *(2)*. Following the convention used by Martell et al. *(1)*, the fully protonated form of citric acid is denoted as H_3L^0(aq) in the equations provided below.

Equilibria Solely Among Inorganic Species:

$$H_2O = OH^- + H^+ \qquad\qquad {}^aK = 10^{-13.997} \qquad (1)$$

$$Mn^{2+} + H_2O = Mn^{II}OH^+ + H^+ \qquad\qquad {}^aK = 10^{-10.597} \qquad (2)$$

$$Mn^{2+} + 3H_2O = Mn^{II}(OH)_3^- + 3H^+ \qquad\qquad {}^aK = 10^{-34.20} \qquad (3)$$

$$Mn^{2+} + 4H_2O = Mn^{II}(OH)_4^+ + 4H^+ \qquad\qquad {}^aK = 10^{-48.288} \qquad (4)$$

$$2Mn^{2+} + H_2O = Mn^{II}{}_2OH^{3+} + H^+ \qquad\qquad {}^aK = 10^{-7.197} \qquad (5)$$

$$2Mn^{2+} + 3H_2O = Mn^{II}{}_2(OH)_3^+ + 3H^+ \qquad\qquad {}^aK = 10^{-23.891} \qquad (6)$$

$$Mn^{2+} + 2H_2O = Mn^{II}(OH)_2(s) + 2H^+ \qquad\qquad {}^aK = 10^{-15.194} \qquad (7)$$

Equilibria Involving Citric Acid:

$$L^{3-} + H^+ = HL^{2-} \qquad\qquad {}^aK = 10^{6.396} \qquad (9)$$

$$L^{3-} + 2H^+ = H_2L^- \qquad\qquad {}^aK = 10^{11.157} \qquad (10)$$

$$L^{3-} + 3H^+ = H_3L^0 \qquad\qquad {}^aK = 10^{14.285} \qquad (11)$$

$$Mn^{2+} + L^{3-} = Mn^{II}L^- \qquad\qquad {}^aK = 10^{5.08} \qquad (12)$$

$$Mn^{2+} + H^+ + L^{3-} = Mn^{II}HL^0 \qquad\qquad {}^aK = 10^{9.58} \qquad (13)$$

$$2Mn^{2+} + 2L^{3-} + 2H_2O = Mn^{II}{}_2(OH)_2L_2^{4-} + 2H^+ \quad {}^aK = 10^{-5.4} \qquad (14)$$

The chemical potential of -557.7 kJ/mole for MnOOH(manganite) reported by Bricker *(3)*, in combination with chemical potentials for solute species reported by Robie et al. *(4)* allow us to calculate an E^o for the $MnOOH(s)/Mn^{2+}(aq)$ half reaction:
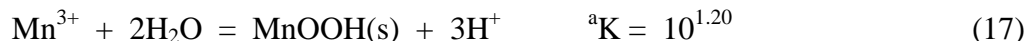
$$MnOOH(s) + 3H^+ + e^- = Mn^{2+} + 2H_2O \quad \Delta G^o = -144.66 \text{ kJ/mole} \quad (15)$$

$$E^o = 1.50 \text{ volts}$$

A reduction potential for the $Mn^{3+}(aq)/Mn^{2+}(aq)$ half-reaction can only be measured in highly concentrated acid. Owing to nonideal effects in such solutions, extrapolation to infinite dilution conditions are provisional in nature. According to James J. Morgan (pers. commun.) along with the references *(5, 6)*, an E^o value of 1.57 volts is reasonable:

$$Mn^{3+}(aq) + e^- = Mn^{2+}(aq) \quad\quad E^o = 1.57 \text{ volts} \quad (16)$$

Subtracting Reaction 15 from Reaction 16 yields:

$$Mn^{3+} + 2H_2O = MnOOH(s) + 3H^+ \quad\quad {}^aK = 10^{1.20} \quad (17)$$

Finally, Patel et al. *(7)* provide the following standard reduction potential, based upon experiments performed in solutions containing 0.10 M citrate:

$$Mn^{III}(L)_2(aq)^{3-} + e^- = Mn^{II}(L)_2(aq)^{4-} \quad\quad E^o = 0.58 \text{ volts} \quad (18)$$
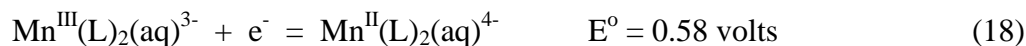
The ionic strength was not indicated. Hence, following Clark's convention *(8)* we report the reduction potential as an E_o, rather than as an infinite dilution scale value, E^o.
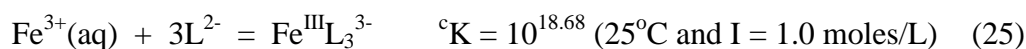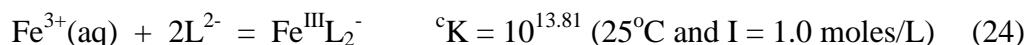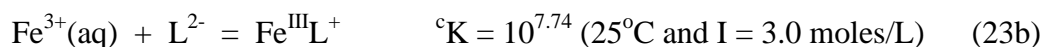
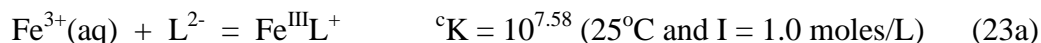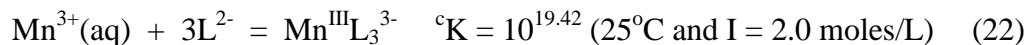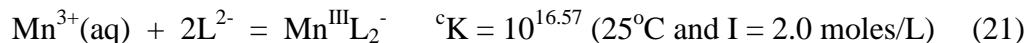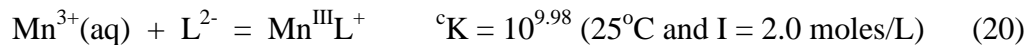## Estimates of Thermodynamic Data

Mn^{III}-citrate complex formation constants are not available in the literature. Harris *(9)* developed a linear free energy relationship (LFER) for calculating logK values for Mn^{III}-aminocarboxylate complexes from corresponding values for Fe^{III}-aminocarboxylate complexes:
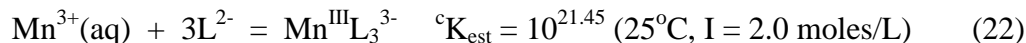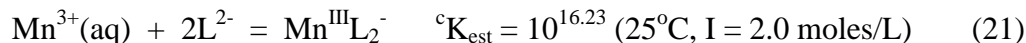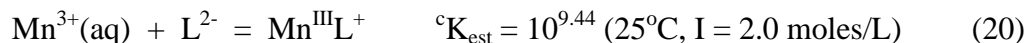
$$logK_{Mn} = 1.09(logK_{Fe}) + 1.09 \quad (19)$$

Can an equation developed for $RCOOH/R_3N$ Lewis Base groups be applied to chelating agents with $RCOOH/ROH$ groups? logK values for both Mn^{III} and for Fe^{III} are available in the CRITICAL *(1)* database:

$$Mn^{3+}(aq) + L^{2-} = Mn^{III}L^+ \qquad {}^cK = 10^{9.98} \text{ (25}^oC \text{ and I = 2.0 moles/L)} \qquad (20)$$

$$Mn^{3+}(aq) + 2L^{2-} = Mn^{III}L_2^- \qquad {}^cK = 10^{16.57} \text{ (25}^oC \text{ and I = 2.0 moles/L)} \qquad (21)$$

$$Mn^{3+}(aq) + 3L^{2-} = Mn^{III}L_3^{3-} \qquad {}^cK = 10^{19.42} \text{ (25}^oC \text{ and I = 2.0 moles/L)} \qquad (22)$$

$$Fe^{3+}(aq) + L^{2-} = Fe^{III}L^+ \qquad {}^cK = 10^{7.58} \text{ (25}^oC \text{ and I = 1.0 moles/L)} \qquad (23a)$$

$$Fe^{3+}(aq) + L^{2-} = Fe^{III}L^+ \qquad {}^cK = 10^{7.74} \text{ (25}^oC \text{ and I = 3.0 moles/L)} \qquad (23b)$$

$$Fe^{3+}(aq) + 2L^{2-} = Fe^{III}L_2^- \qquad {}^cK = 10^{13.81} \text{ (25}^oC \text{ and I = 1.0 moles/L)} \qquad (24)$$

$$Fe^{3+}(aq) + 3L^{2-} = Fe^{III}L_3^{3-} \qquad {}^cK = 10^{18.68} \text{ (25}^oC \text{ and I = 1.0 moles/L)} \qquad (25)$$
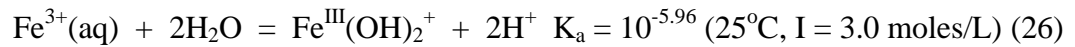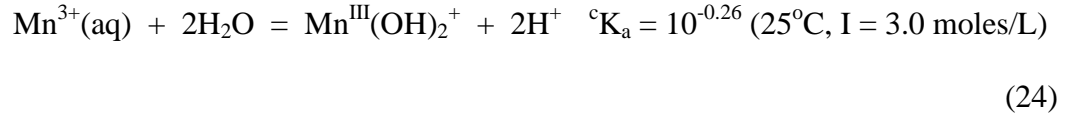
Fe^{III}-oxalate thermodynamic data is not available for an ionic strength of 2.0 moles/L. We will estimate logK values at I = 2.0 moles/L by assuming that the logK is midway between values obtained at 1.0 moles/L and 3.0 moles/L ionic strength. In addition, we will assume that the magnitude of this correction is the same for 1:1, 1:2, and 1:3 complexes. Hence, logK values for Reactions 23, 24, and 25 become 7.66, 13.89, and 18.68. Using the Harris LFER, we obtain the following logK values for Mn^{III}:

$$Mn^{3+}(aq) + L^{2-} = Mn^{III}L^+ \qquad {}^cK_{est} = 10^{9.44} \text{ (25}^oC, \text{ I = 2.0 moles/L)} \qquad (20)$$

$$Mn^{3+}(aq) + 2L^{2-} = Mn^{III}L_2^- \qquad {}^cK_{est} = 10^{16.23} \text{ (25}^oC, \text{ I = 2.0 moles/L)} \qquad (21)$$

$$Mn^{3+}(aq) + 3L^{2-} = Mn^{III}L_3^{3-} \qquad {}^cK_{est} = 10^{21.45} \text{ (25}^oC, \text{ I = 2.0 moles/L)} \qquad (22)$$
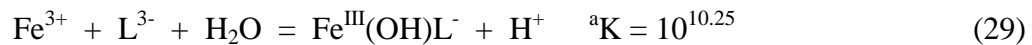
Hence, the Harris LFER underestimated logK for the 1:1 and 1:2 complexes by 0.54 and 0.34 log units, respectively. The logK for the 1:3 complex is overestimated by 2.03 log units.

The alcohol group of citric acid requires special consideration, since it is considerably more basic than either RCOOH or R_3N groups. logK values for coordination of hydroxide ion is perhaps the best available analogy. The following constants are available in CRITICAL *(1)*:

$$Mn^{3+}(aq) \ + \ H_2O \ = \ Mn^{III}OH^{2+} \ + \ H^+ \quad {}^cK_a = 10^{+0.27} \ (25^oC, \ I = 3.0 \ moles/L) \ (23)$$

$$Mn^{3+}(aq) \ + \ 2H_2O \ = \ Mn^{III}(OH)_2{}^+ \ + \ 2H^+ \quad {}^cK_a = 10^{-0.26} \ (25^oC, \ I = 3.0 \ moles/L)$$

$$(24)$$

$$Fe^{3+}(aq) \ + \ H_2O \ = \ Fe^{III}OH^{2+} \ + \ H^+ \quad {}^cK_a = 10^{-3.09} \ (25^oC, \ I = 3.0 \ moles/L) \quad (25)$$

$$Fe^{3+}(aq) \ + \ 2H_2O \ = \ Fe^{III}(OH)_2{}^+ \ + \ 2H^+ \quad K_a = 10^{-5.96} \ (25^oC, \ I = 3.0 \ moles/L) \ (26)$$

logK for formation of $Mn^{III}OH^{2+}$ is 3.36 log units higher than the corresponding logK for $Fe^{III}OH^{2+}$. With $Mn^{III}(OH)_2{}^+$, the logK is 5.70 log units higher than for $Fe^{III}(OH)_2{}^+$.

The following equilibrium constants for monomeric Fe^{III}-citrate complexes are available in CRITICAL *(1)* (owing to the relatively low concentrations of $Mn^{III/II}$ and citric acid in our system, we will ignore multimeric species):

$$Fe^{3+} \ + \ L^{3-} \ = \ Fe^{III}L^0 \qquad\qquad {}^aK = 10^{13.17} \qquad\qquad (27)$$

$$Fe^{3+} \ + \ H^+ \ + \ L^{3-} \ = \ Fe^{III}HL^+ \qquad\qquad {}^aK = 10^{14.42} \qquad\qquad (28)$$

$$Fe^{3+} \ + \ L^{3-} \ + \ H_2O \ = \ Fe^{III}(OH)L^- \ + \ H^+ \qquad {}^aK = 10^{10.25} \qquad\qquad (29)$$

As noted earlier, the fully protonated form of citric acid is denoted as $H_3L^0(aq)$. If the alcohol deprotonates and coordinates the central metal ion, the reaction is stoichiometrically accounted for by equating proton loss with hydroxide ion gain, in the manner of Reaction 29. Subtracting Reaction 27 from Reaction 29 reveals a pK_a for this reaction:

$$Fe^{III}L^0 \ + \ H_2O \ = \ Fe^{III}(OH)L^- \ + \ H^+ \qquad\qquad {}^aK = 10^{-2.92} \qquad\qquad (30)$$

Reaction 30 is an indication of the Lewis Acidity of Fe^{III}. Note that the pK_a for

$Fe^{III}L^0/Fe^{III}(OH)L^-$ (Reaction 30) and the pK_a for $Fe^{3+}(aq)/Fe^{III}OH^{2+}$ (Reaction 25) are

only 0.17 log units different.

If we assume that the Harris LFER applies to Mn^{III}-citrate complexes, we obtain:

$$Mn^{3+} + L^{3-} = Mn^{III}L^0 \qquad\qquad {}^aK = 10^{15.45} \qquad (31)$$

$$Mn^{3+} + H^+ + L^{3-} = Mn^{III}HL^+ \qquad\qquad {}^aK = 10^{16.81} \qquad (32)$$

$$Mn^{3+} + L^{3-} + H_2O = Mn^{III}(OH)L^- + H^+ \qquad {}^aK = 10^{12.26} \qquad (33)$$

Subtracting Reaction 31 from Reaction 33 yields a Reaction for $Mn^{III}L^0/Mn^{III}(OH)L^-$ that

is analogous to Reaction 30:

$$Mn^{III}L^0 + H_2O = Mn^{III}(OH)L^- + H^+ \qquad\qquad {}^aK = 10^{-3.19} \qquad (34)$$

If our expectation that coordination of the alcoholate group is analogous to coordination

of hydroxide ions, then the pK_a for Reaction 34 is too high (stating this differently, the ${}^aK$

for Reaction 33 is too low).

Calculation #1

In Figure 2.3, $Mn^{III}(aq)$ values are reported for an experiment employing 200 μM

citric acid, 200 μM MnO_2, and 10 mM MOPS (pH 7.1). The MnO_2 employed in this

experiment contains 22 % Mn^{III}, which corresponds to 44 μM $TOTMn^{III}$. For our first

calculation, we will (i) use the Harris logK values "as is", (ii) employ

MnOOH(manganite) as the solubility-limiting phase, and (iii) arbitrarily set the ionic

strength equal to 1.0×10^{-2} M. The following concentrations are obtained:

$$1.84 \times 10^{-12} \text{ M } Mn^{III}L^0(aq)$$

$$4.27 \times 10^{-18} \text{ M } Mn^{III}HL^+$$

$$\underline{1.91 \times 10^{-8} \text{ M } Mn^{III}(OH)L^-}$$

Sum: 5.68×10^{-8} M $Mn^{III}(aq)$

The calculated value of $Mn^{III}(aq)$ is far short of the 4.8 μM maximum value reported in Figure 2.3. $Mn^{III}L^0(aq)$ and $Mn^{III}HL^+$ do not appear to be prospects for explaining the reported maximum value of $Mn^{III}(aq)$. In order for $Mn^{III}L^0(aq)$ to account for the experimental observations, logK for Reaction 31 would have to be increased by more than six orders-of-magnitude; the logK for $Mn^{III}HL^+$ (Reaction 32) would have to be increased by an even greater amount.

A New Estimate of ^aK for Reaction 33

Let us assume that we are correct in our appraisal that ^aK for Reaction 33 is too low. Increasing ^aK for Reaction 33 by 2.41 log units (from $^aK = 10^{12.26}$ to $^aK = 10^{14.67}$) yields the following concentrations:

1.79×10^{-12} M $Mn^{III}L^0(aq)$

4.17×10^{-18} M $Mn^{III}HL^+$

$\underline{4.79 \times 10^{-6} \text{ M } Mn^{III}(OH)L^-}$

Sum: 4.79×10^{-6} M $Mn^{III}(aq)$

Using this new value for the ^aK of Reaction 33 to calculate the ^aK for Reaction 34 yields a value of $10^{-0.78}$. The pK_a for Reaction 34 is now only 1.05 log units away from the pK_a for Reaction 23.
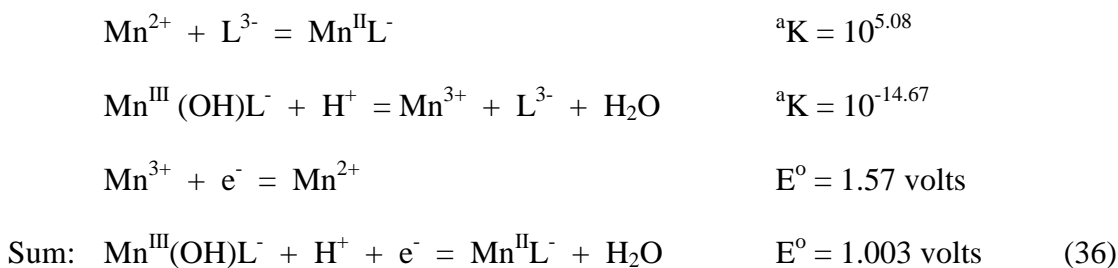
The maximum value of $Mn^{III}(aq)$ reported in Figure 2.3 reflects a balance between source and sink terms for dissolved Mn^{III}. Hence, $^aK = 10^{14.67}$ for Reaction 33 is a lower estimate.

Additional Useful Half-Reactions

Bricker *(3)* report a chemical potential of -453.1 kJ/mole for MnO_2(birnessite), from which the following half-reaction and corresponding standard reduction potential can be derived:

$$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad E^0 = 1.292 \text{ volts} \tag{35}$$
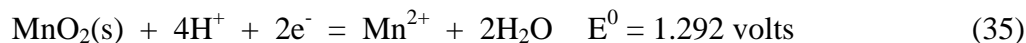
Reactions 12, 16, and 33 can be combined to obtain a standard reduction potential for the $Mn^{III}(OH)L^-/Mn^{II}L^-$ half reaction:

$$Mn^{2+} + L^{3-} = Mn^{II}L^- \qquad\qquad\qquad {}^aK = 10^{5.08}$$

$$Mn^{III}(OH)L^- + H^+ = Mn^{3+} + L^{3-} + H_2O \qquad {}^aK = 10^{-14.67}$$

$$Mn^{3+} + e^- = Mn^{2+} \qquad\qquad\qquad\qquad E^o = 1.57 \text{ volts}$$

Sum: $\quad Mn^{III}(OH)L^- + H^+ + e^- = Mn^{II}L^- + H_2O \qquad E^o = 1.003 \text{ volts} \tag{36}$

Structure-Reactivity Relationships among Citrate Analogs

See Tables S2.1 and S2.2

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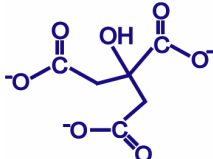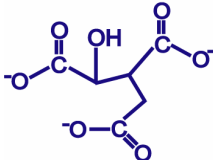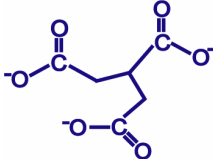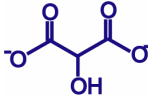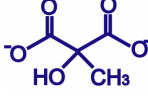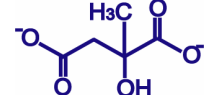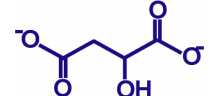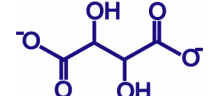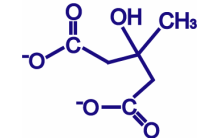
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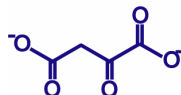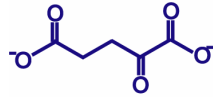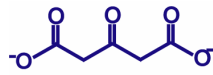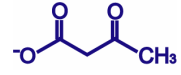
Table S2.1. CE Analytical Methods Developed for Separating Ionic Components from Reactions of Organic Substrate with MnO_2 or MnOOH

Analytes		Electrolyte	Detection
Parent compound	**Degradation Products**		**Wavelength (nm)**
		Direct UV Photometric Method	
citrate	3- ketoglutarate, acetoacetate	pH 9.5 20 mM pyrophosphate / 2 mM phosphate 0.4 mM TTAB	190
isocitrate	malate, malonate, oxalate, pyruvate, glycolate	pH 9.5 20 mM pyrophosphate / 2 mM phosphate 0.4 mM TTAB	190
citramalate	acetoacetate	pH 6.0 20 mM pyrophosphate 0.4 mM TTAB	190
oxaloacetate	malonate, pyruvate, oxalate	pH 5.4 20 mM pyrophosphate 0.4 mM TTAB	190
2-ketoglutarate	Succinate	pH 6.0 20 mM pyrophosphate 0.4 mM TTAB	190
3- ketoglutarate	malonate, oxalate, acetoacetate	pH 8.0 20 mM pyrophosphate 0.4 mM TTAB	190
		Indirect UV Photometric Method	
tartronate	Oxalate, glyoxylate, formate	pH 7.8 5 mM phthalate, 12.5 mM Tris 0.25 mM TTAB	200

Table S2.2. Compounds Included in This Study: Names, pK$_a$s, Structures, Maximum Rates (r$_{max}$) for Reaction 5.0 mM Subtrate with 200 mM MnO$_2$ and MnOOH at pH 5.0 (10 mM Butyrate)

I.D.	Name (Abbreviation)	pK$_a$s[1]	Structure	Induction Observed?	r$_{max}$[2] (mM/h)	
					MnO$_2$	**MnOOH**
I	Citrate	3.13 4.76 6.40		Yes	2.78×10^2	2.31×10^1
II	DL-isocitrate	3.28 4.73 6.45		No	1.9×10^1	5.2×10^0
III	Tricarballylate (TCA)	3.67 4.90 6.44		No	6.0×10^{-2}	$<5.0 \times 10^{-2}$
IV	Tartronate	2.24[3] 4.68[3]		No	$> 3 \times 10^3$	1.01×10^2
V	Methyltartronate (MTA)			No	$> 3 \times 10^3$	
VI	DL-citramalate	3.55 5.46		Slight	3.4×10^1	1.04×10^1
VII	DL-malate	3.46 5.10		No	1.67×10^1	3.6×10^0
VIII	DL-tartrate	3.04 4.37		No	8.1×10^0	6.7×10^0
IX	3-Hydroxy-3-methylglutarate (3-HMG)			No	2.0×10^{-2}	$< 2.0 \times 10^{-2}$

X	Oxaloacetate (OAA)	2.56 4.37		Yes	2.02×10^2	8.2×10^0
XI	2-Ketoglutarate (2-KGA)			No	4.5×10^1	2.2×10^1
XII	3-Ketoglutarate (3-KGA)			Yes	3.15×10^1	7.1×10^0
XIII	Acetoacetate (AAA)	3.79		No	4.4×10^0	5.0×10^{-1}

[1] Obtained from (1) for 25°C and ionic strength of 0.0. [2] Induction period observation and rates (r_{max}) obtained from Mn^{II}(aq) production. [3] Temperature = 20 °C