The Triple Point

A. Thermodynamics

1. *Phase Equilibria*: $X(\ell) \leftrightarrow X(g)$ and $X(s) \leftrightarrow X(g)$
(vaporization and sublimation)

2. *Clapeyron Eqn*: $dP/dT = \Delta S/\Delta V$
Since these are *equilibrium* processes at fixed T,
$\Delta S = \Delta H/T$, where $\Delta H = \Delta H_{vap}$ or ΔH_{sub}.

3. *Clausius-Clapeyron*: When one phase is g and P is not high,

$\Delta V \approx V_{gas} \approx nRT/P$, giving
$$\frac{d\ln P}{dT} = \frac{\Delta H_m}{RT^2}$$

or, using $d(1/T) = -\,dT/T^2$,
$$\frac{d\ln P}{d(1/T)} = -\frac{\Delta H_m}{R}$$

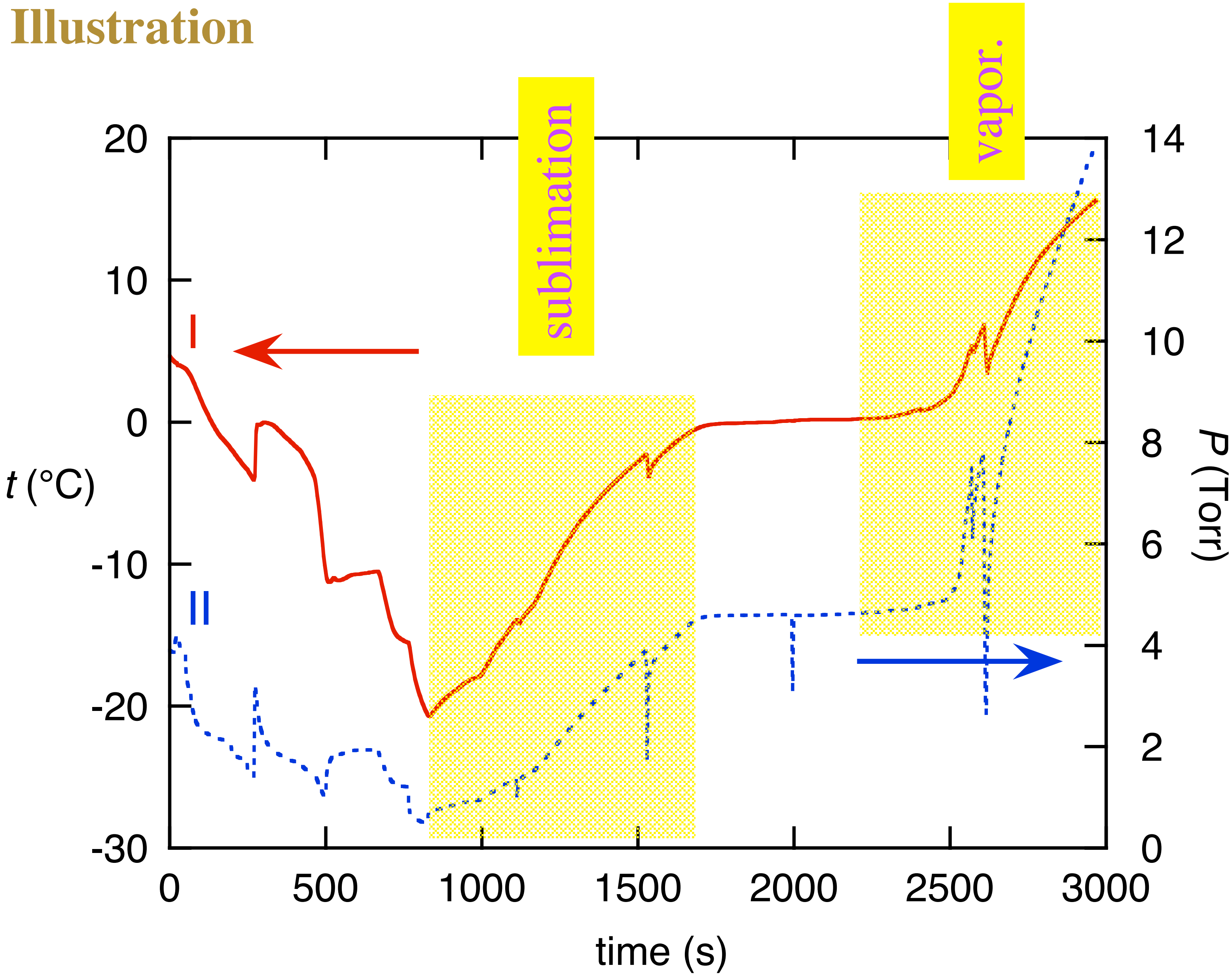
4. *Integration*: $\ln P = const - \Delta H_m/RT$ (ΔH_m assumed const.)
Substituting P_0 at T_0 (any reference point),

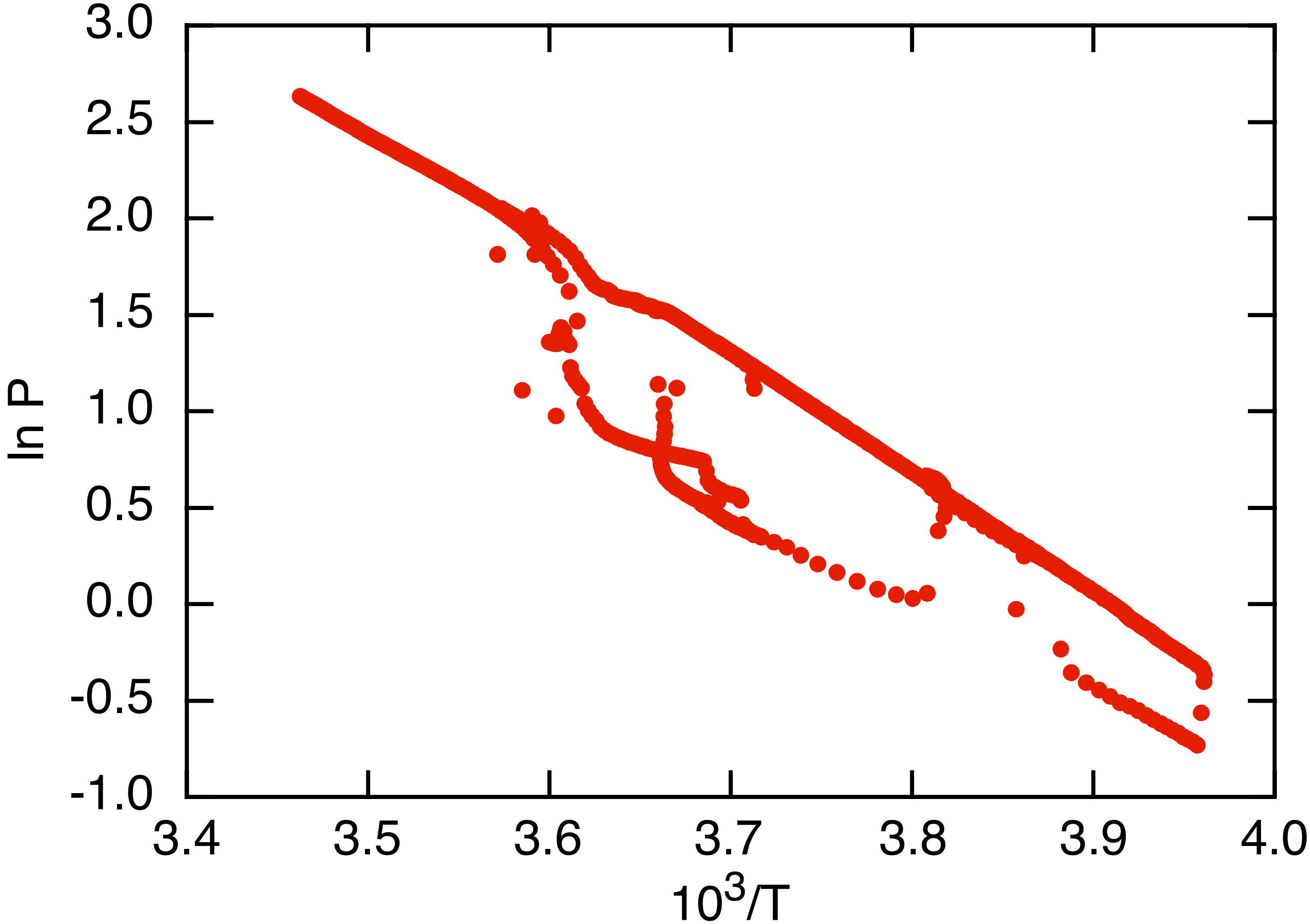
4th time! ⇒
$$\ln\frac{P}{P_0} = \frac{\Delta H_m}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

B. Experiment

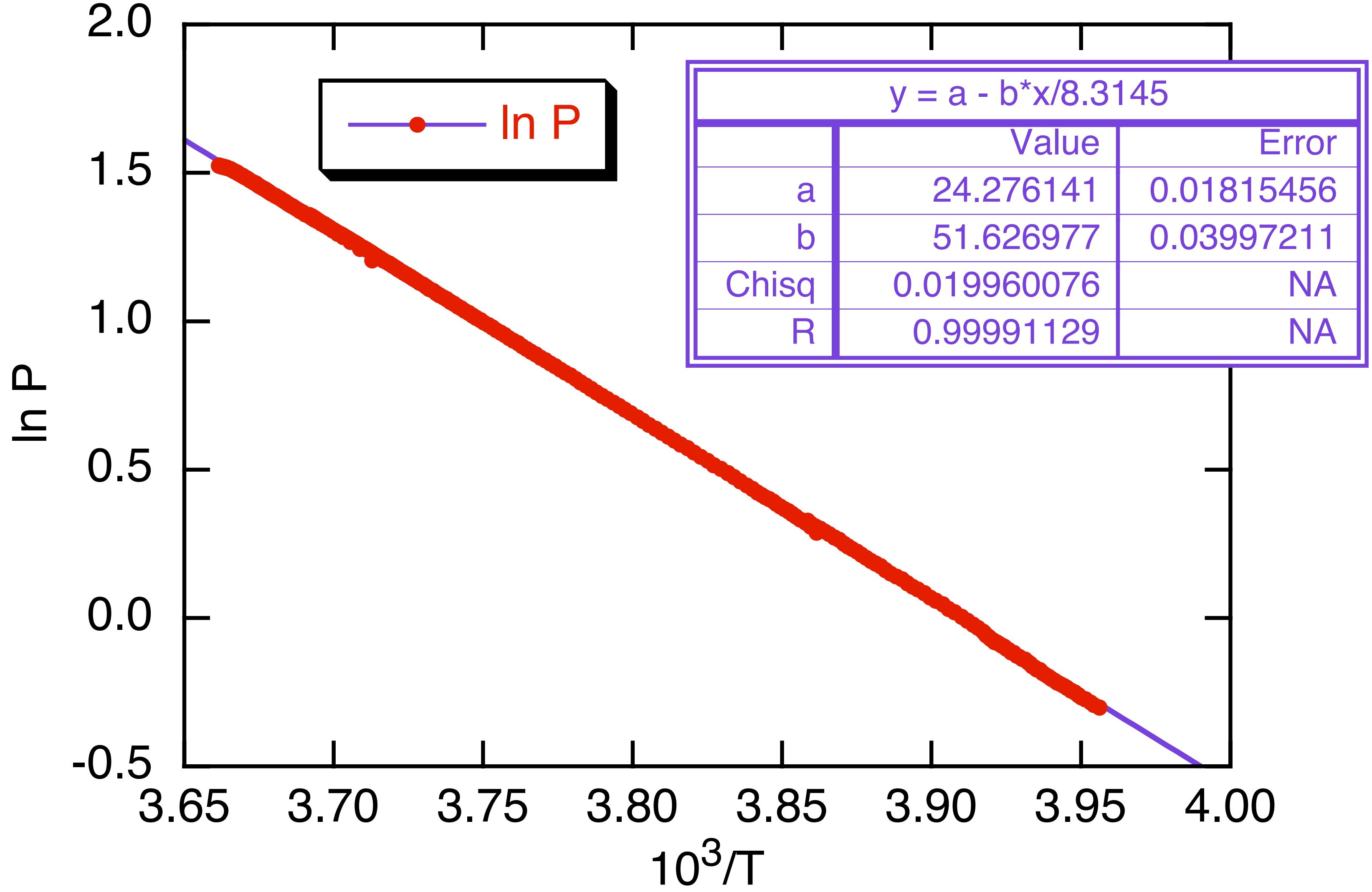
1. "Freeze-dry" sample; then record P and T on warmup.
2. Edit data to remove non-equilibrium pts (if necessary).
3. Plot ln P vs. $1/T$, for sublimation *and* vaporization regions.
4. Fit to obtain ΔH_{sub} and ΔH_{vap}. and their uncertainties.
5. Calculate $\Delta H_{fus} = \Delta H_{sub} - \Delta H_{vap}$ and its uncertainty.

C. Illustration

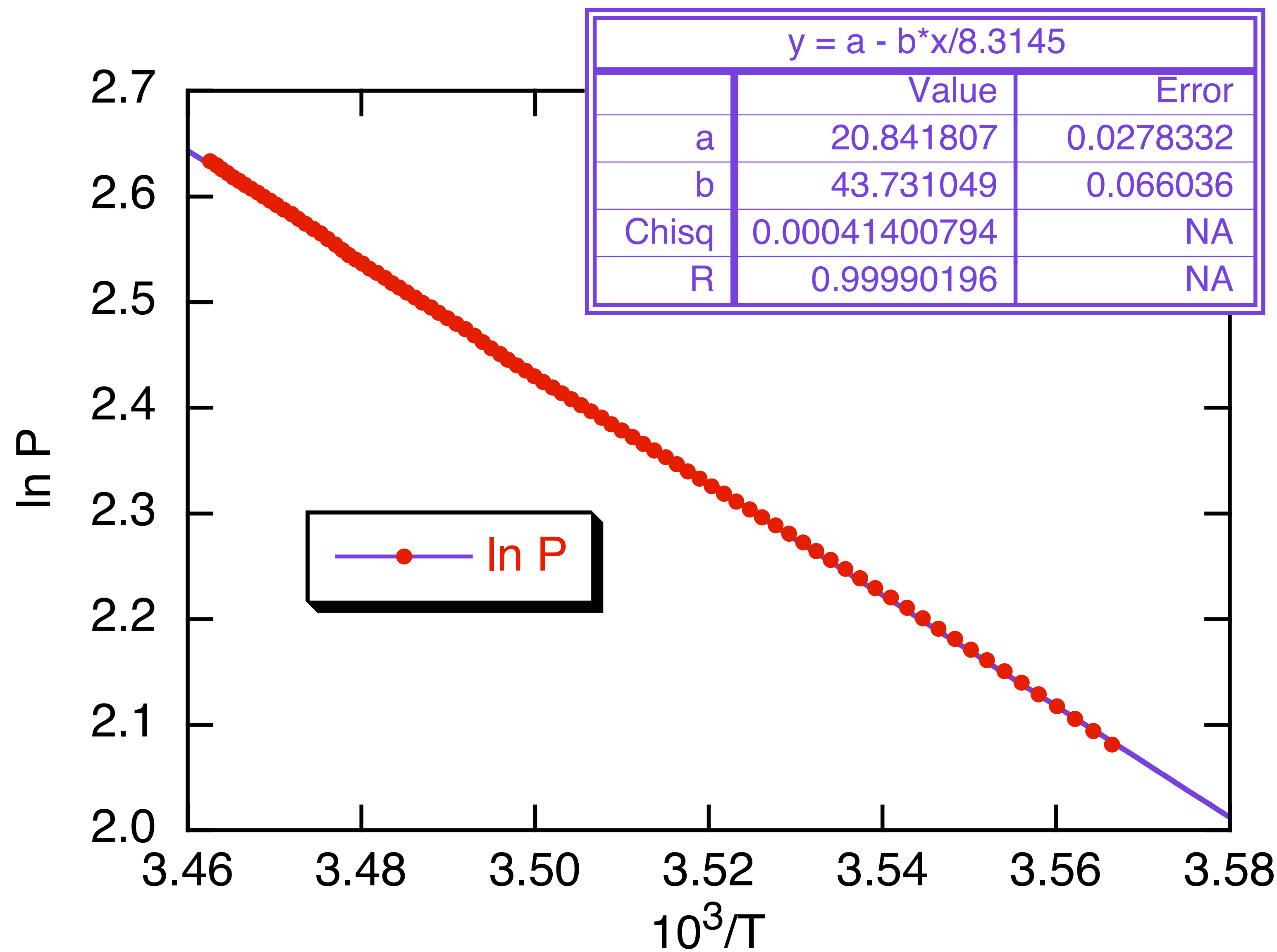


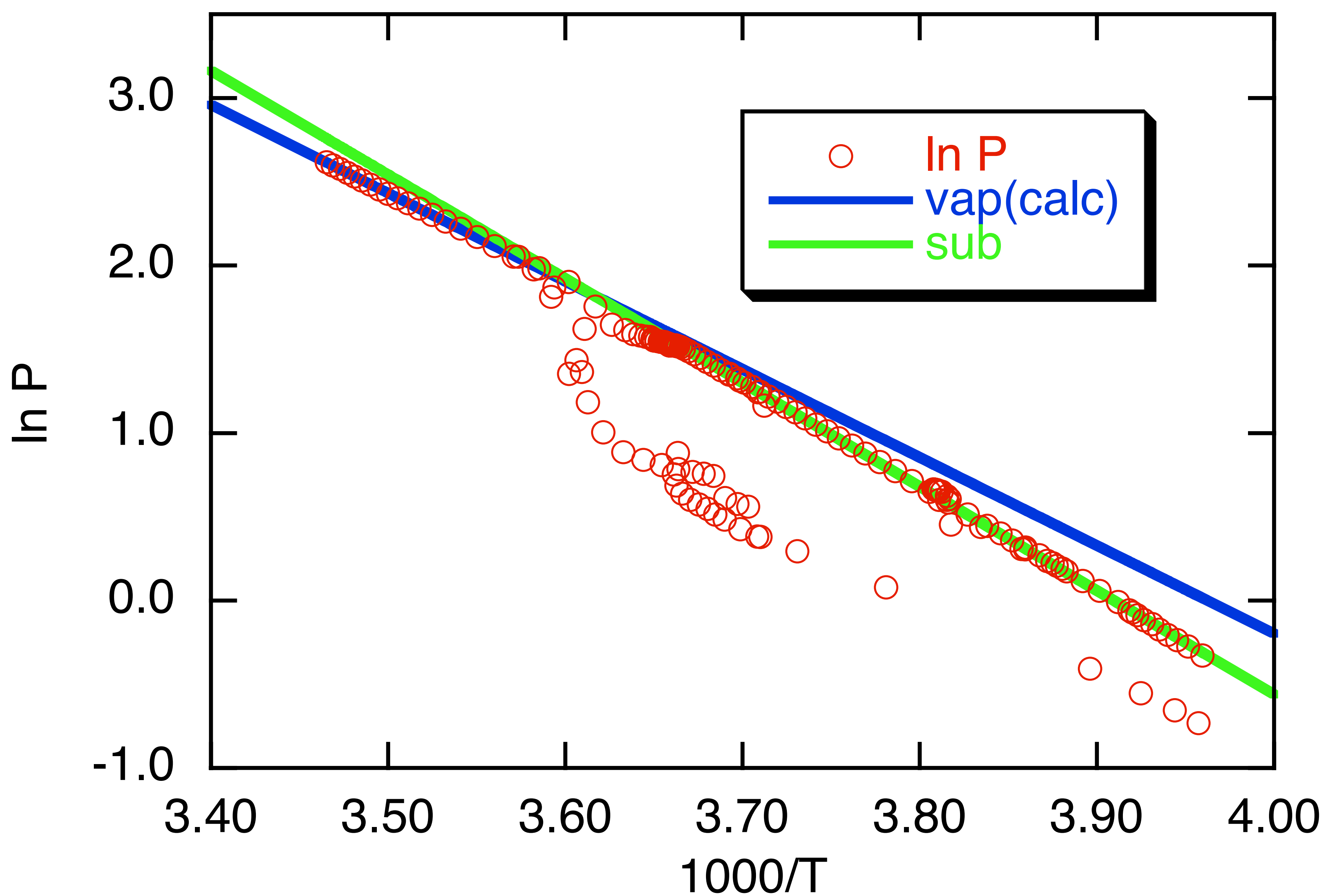


3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ln P
3.4
3.5
3.6
3.7
3.8
3.9
4.0
10^3/T



ln P
y = a - b*x/8.3145
Value
Error
a
24.276141
0.01815456
b
51.626977
0.03997211
Chisq
0.019960076
NA
R
0.99991129
NA
2.0
1.5
1.0
0.5
0.0
-0.5
ln P
3.65
3.70
3.75
3.80
3.85
3.90
3.95
4.00
10^3/T


y = a - b*x/8.3145
Value
Error
a
20.841807
0.0278332
b
43.731049
0.066036
Chisq
0.00041400794
NA
R
0.99990196
NA
ln P
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
3.46
3.48
3.50
3.52
3.54
3.56
3.58
10^3/T
ln P



ln P
vap(calc)
sub
3.0
2.0
1.0
0.0
-1.0
3.40
3.50
3.60
3.70
3.80
3.90
4.00
1000/T